THE CHEMISTRY AND TESTING OF CEMENT

THE
CHEMISTRY AND TESTING
OF CEMENT

BY

CECIL H. DESCH

D.Sc. (Lond.), Ph.D. (Würzb.)

GRAHAM YOUNG LECTURER IN METALLURGICAL CHEMISTRY
IN THE UNIVERSITY OF GLASGOW

LONDON
EDWARD ARNOLD
1911

PREFACE

From the earliest historical times, materials belonging to the class of calcareous cements have been used in the construction of buildings, the methods of preparing and applying them being the result of the experience of generations of builders, and undergoing little change in the course of centuries. The modern development of engineering practice, dating from the second half of the eighteenth century, gave a new importance to these materials, and brought about the invention of many new types of cement, some of which have in great measure superseded the older kinds. A large and important industry has thus come into existence, and has gradually spread from a few local centres until it has become established in most parts of the civilised world.

As the demand for cements on the part of the engineer and the builder has increased, so their requirements in respect of quality have become more exacting, and the manufacturer has not only been called on to increase his production, but also to improve the strength and stability of his product. This has been accomplished with a remarkable degree of success, partly as the result of improvements in mechanical processes and appliances, but also in no small degree through the co-operation of the chemist. This second factor assumes an increasing importance as the standard of quality is raised, and as efforts are made to extend the range of the raw materials employed in the industry.

If the chemical investigation of cement has been in the past less fruitful than might have been expected from the experience of other chemical industries, this is due to the complexity of the reactions occurring in its manufacture, and to certain experimental difficulties inherent in the investigation. It is only in recent years that this complexity has been fully realised, and that chemists have gained an insight into the nature of the complex and imperfectly characterised substances of which cements are composed.

The present work is written from the point of view of the chemist, and mechanical processes are only so far described as is necessary to render the account of the manufacture intelligible. References are given to larger works in which the engineering aspect of the industry may be studied. The attempt has here been made to explain the nature of the chemical compounds contained in cements, the reactions involved in their preparation from the raw materials, the changes which take place during setting and hardening, and the methods of controlling the quality of the product. The author has sought to present as fairly as possible the results of modern research, passing over the older loose and inaccurate views which are still frequently reproduced in many works of reference.

In considering the constitution of cement clinker and the reactions which occur in its production, special attention has been directed to the assistance afforded in such investigations by the microscope. The study of metallography, although of very recent origin, has rendered most important services to the manufacturer, worker, and user of metals and alloys, by furnishing a means of controlling the quality of the materials and the success of the technical operations. The application of similar microscopical methods to the study of cements has hitherto been neglected by all but a few investigators, and the author has sought to emphasise the value of this important aid to research. The photomicrographs illustrating this section of the work have been prepared in the Metallurgical Laboratory of the University of Glasgow.

The account given of the processes involved in the setting of lime and cement mortars is based on the view, which we owe to Dr. Michaëlis, that the principal products of the reaction are not crystalline but colloidal. The acceptance of this conclusion, whilst it necessitates a considerable change in the older explanations of the process of setting, places us in a position to conceive much more clearly than before the nature of the change, and the manner in which it is affected by variations in composition or in external conditions. The chemical details of work of this kind are naturally of a somewhat technical character, but it has also been sought to show the bearing of the chemical facts on the methods of using cement and concrete, and to give some practical hints as to the best means of utilising the valuable qualities of those materials under the conditions demanded by modern building and engineering work.

It will be observed that certain products are described which, although of considerable industrial importance on the Continent, are little used or known in the English cement industry. These products, granulated slag cement, sand-lime bricks, &c., have been included partly for the sake of their great scientific interest and their relationship to better known materials, and partly in order to show the nature of the materials and processes which are, or may become, able to compete with those in more general use under certain local conditions.

A word of explanation should be given as to the units employed. Temperatures, being mainly of interest to the chemist, are given throughout in degrees Centigrade, whilst the results of mechanical tests are given in British units and also in their approximate metric equivalents, the former being still generally employed in this country by the engineer, although abandoned by the chemist. In the chapter on analytical methods, metric units alone are employed, in accordance with the usual laboratory practice.

The author wishes to express his thanks to Mr. H. T. Desch, for much assistance in dealing with the practical aspects of cement, to Mr. H. K. G. Bamber, of the Associated Portland Cement Manufacturers, Mr. H. Earle, of Messrs. G. & T. Earle, Hull, and Mr. H. Bumby, of the Coltness Iron Co., Newmains, who have kindly supplied many specimens of material for examination and data referring to them, and lastly to Messrs. Baird and Tatlock, London, for the loan of blocks for Figures 11, 15, and 18.

C. H. D.

THE UNIVERSITY, GLASGOW,
December 1910.

CONTENTS

LIST OF PLATES

THE CHEMISTRY OF CEMENT

CHAPTER I

THE HISTORY OF CALCAREOUS CEMENTS

CEMENTS may be defined as adhesive substances capable of uniting fragments or masses of solid matter to a compact whole. Such a definition embraces a large number of very different substances having little in common with one another but their adhesiveness, and the very unequal technical and scientific importance of different members of the class has tended to bring about a restriction of the designation to one group of adhesive substances, namely, to the plastic materials employed to produce adhesion between stones, bricks, &c., in the construction of buildings and engineering works. Cements of this kind also bear a chemical relationship to each other, consisting, as they do, at least in modern technical practice, of mixtures which contain compounds of lime as their principal constituents. The term "cements" in this restricted sense then becomes equivalent to "calcareous cements." Such substances as animal glue, bitumen, and oleaginous preparations are relatively of less importance, and their chemical properties call for entirely separate treatment, and do not fall within the scope of the present work.

The use of cements in building is not met with below a relatively advanced stage of civilisation. The earlier structures are composed of earth, sometimes raised in the form of walls or domes by ramming successive layers, or of stone blocks, set one above another without the aid of any cementing material, as in prehistoric megalithic structures, and in the Cyclopean masonry of Greece. The stability of walls of the latter kind is derived entirely from the regular placing of heavy masses of stone without any assistance from adhesion. Although remarkable works have been accomplished by such a method of construction, notably in the domed chambers of Mycenæ, where small stone wedges are driven between the large blocks in order to tighten the joints, yet Cyclopean work has always given place in later times to masonry or brickwork, erected with the aid of some plastic material.

The simplest plan is that found in the brick walls of ancient Egyptian buildings. The bricks are dried in the sun without baking, and each course is covered with a moist layer of the loam used for making the bricks, with or without the addition of chopped straw. The drying of this layer makes the wall a solid mass of dry clay. Such a mode of construction is only possible in a rainless climate, as the unburnt material possesses no power of resistance to water. Burnt bricks and alabaster slabs were employed by the Babylonians and Assyrians, and were cemented together with bitumen. This method is very efficacious, but being necessarily confined to those regions in which natural deposits of the material occur, it was not copied elsewhere.

In the massive masonry constructions of the Egyptians we meet with our present-day system of uniting blocks and slabs of stone with a mortar, consisting of a mixture of sand with a calcareous adhesive material. There is some little uncertainty as to the character of this material. Whilst it is generally described by writers on Egypt as burnt lime, even where found in buildings as old as the Great Pyramid, the statement is definitely made[1] that the Egyptians never used lime, and that the cementing material was always obtained by burning gypsum. As the gypsum was quarried in a very impure state, it usually contained calcium carbonate, which might be partly decomposed in the process of burning, or even if found in an undecomposed state in the mortar would produce the impression that lime had been used. The gypsum was very roughly burnt, so that a mixture of the unchanged mineral with "dead-burnt" plaster was generally obtained. Such a mortar must have been irregular in setting, and troublesome to make use of successfully.

Whether the Egyptians were acquainted with the use of lime or not, the Greeks must have adopted this material at an early period, and the Romans must have borrowed it from them.[2] The mortar was prepared in the modern fashion, by slaking the lime and mixing with sand, and the examples of Roman brickwork which still exist are sufficient evidence of the perfection which the art attained in the ancient times. The remarkable hardness of the mortar in walls of Roman workmanship has sometimes led to the assumption that some secret was possessed by the workmen which is now lost, but a comparison of the analyses of the mortar with the descriptions of the method by ancient authors gives no ground for such a supposition. The good quality of the mortar is due simply to the thorough burning and fine grinding of the lime, and the very thorough mixing of the slaked or "tempered" lime with the sand. We know

---

[1] A. Choisy, *L'Art de Bâtir chez les Egyptiens*, Paris, 1904. L. J. Vicat, *Mortiers et Ciments Calcaires*, Paris, 1828, states that whilst the mortar of the Great Pyramid is composed of impure gypsum, true lime mortar is met with at Edfu and elsewhere. An analysis of mortar from the Great Pyramid by W. Wallace, *Chem. News*, 1865, **11**, 185, shows it to contain 81·5 per cent. of calcium sulphate, and only 9·5 per cent. of the carbonate.

[2] Analyses of early Greek and Phœnician mortars are given by W. Wallace, *loc. cit.*

that this, the essential operation of building with mortar, was not left to unskilled labourers, but was the special task of the master. The subsequent history of building abounds in examples of differences in the permanence of brickwork and masonry due to differences in the attention paid to this all-important point.

Both the Greeks and the Romans were aware of the fact that certain volcanic deposits, if finely ground and mixed with lime and sand, yielded a mortar which not only possessed superior strength, but was also capable of resisting the action of water, whether fresh or salt. The Greeks employed for this purpose the volcanic tuff from the island of Thera (now called Santorin), and this material, known as Santorin earth, still enjoys a high reputation on the Mediterranean. The mortar used at the present day by the peasants of Santorin—an island destitute of wood for building—is identical in its composition and preparation with that of ancient times.[1]

The corresponding material of the Roman builders was the red or purple volcanic tuff found at different points on and near the Bay of Naples. As the best variety of this earth was obtained from the neighbourhood of Pozzoli or Pozzuoli (in Latin *Puteoli*), the material acquired the name of Pozzolana,[2] and this designation has been extended to the whole class of mineral matters of which it is a type. Vitruvius says of it:[3] "There is a species of sand which, naturally, possesses extraordinary qualities. It is found under Baiæ and the territory in the neighbourhood of Mount Vesuvius; if mixed with lime and rubble, it hardens as well under water as in ordinary buildings."

If volcanic earth did not happen to be available, the

---

[1] M. Gary. *Mitt. k. Material-Prüf. Amt.*, 1907, **25**, 11.

[2] This spelling is to be preferred, as being the modern Italian form. It is adopted by the *New English Dictionary*, Oxford, and will be employed throughout the present work. Other forms, due mainly to French influence, are *pozzuólana* and *puzzuolana.*

[3] Bk. ii. chap. vi., English translation by Joseph Gwilt, London, 1826.

Romans made use of powdered tiles or pottery, which produced a similar effect. To quote Vitruvius[1] again, "If to river or sea sand, potsherds ground and passed through a sieve, in the proportion of one third part, be added, the mortar will be the better for use." It is remarkable that the word "cement" in its Late Latin and Old French forms was first employed to designate such materials, now classed as artificial pozzolanas; its meaning then changed to denote the mortar prepared by mixing the three ingredients, and it is only in recent times that it assumed its modern meaning.

The Romans carried their knowledge of the preparation of mortar with them to the remoter parts of their Empire, and the Roman brickwork found in England, for example, is equal to the best of that in Italy. Ground tiles were the most commonly used ingredient, but in a few districts deposits bearing some resemblance to the natural pozzolanas of the Bay of Naples were found. The use of the Rhenish volcanic tuffs known as Trass[2] was probably introduced at this time, and this material, like pozzolana, is still very largely employed at the present day.

A gradual decline in the quality of the mortar used in buildings set in after Roman times, and continued throughout the Middle Ages. Saxon and Norman buildings, for instance, constantly exhibit evidence of badly mixed mortars, often prepared from imperfectly burnt lime. The conclusion appears certain, from the examination of French buildings,[3] that during the ninth, tenth, and eleventh centuries the art of burning lime was almost completely lost, the lime being used in badly burnt lumps, without the addition of ground tiles. From the twelfth century onwards the quality improves, the lime being

---

[1] Bk. ii. chap. v.

[2] Formerly *Tarras*, a word of Dutch origin.

[3] E. E. Viollet-le-Duc, *Dict. raisonné de l'Architecture Française*, 1863, vol. vi. p. 402.

well burnt and well sifted. After the fourteenth century excellent mortar is found, and the precaution was evidently taken of washing the sand free from adhering dirt or clay.

The term "cement" was commonly applied at this time to the mortar, as for instance in the work, so much used as an authority in medieval and later times, the *De Proprietatibus Rerum* of Bartholomew Anglicus, in which we read: "Lyme . . . is a stone brent; by medlynge thereof with sonde and water sement is made."[1] The word "mortar" was, however, also employed as early as 1290.[2]

The Roman mixture of lime and natural or artificial pozzolana long retained its position as the only suitable material for work under or exposed to water. Thus Belidor, for a long time the principal authority on hydraulic construction, recommends an intimate mixture of tiles, stone chips, and scales from a blacksmith's forge, carefully ground, washed free from coal and dirt, dried and sifted, and then mixed with freshly slaked lime.[3] The same author mentions the use of pozzolana or trass where such materials are available. It is remarkable that works on building, even as late as 1838,[4] quote Vitruvius as almost the sole authority on the mixing of mortar, whilst St. Augustine[5] is cited for details of the slaking of lime!

When we come to more recent times, the most important advance in the knowledge of cements, the forerunner of all modern inventions and discoveries in this connection, is undoubtedly the investigation carried out by John Smeaton. On being called upon in 1756 to erect a new

---

[1] English translation by John Trevisa, 1397.

[2] Date of the first quotation of the word in the *New English Dictionary*.

[3] Belidor, *Architecture Hydraulique*, vol. ii. bk. i. chap. ix., Paris, 1788.

[4] J. Rondelet, *L'Art de Bâtir*, Paris, 1838.

[5] *City of God*, bk. xxi.

lighthouse on the Eddystone Rock after the destruction of the previously existing building by fire, he proceeded to make inquiries as to the best building materials for work under such severe conditions.[1] He found that the usual mortar for work under water was composed of "two measures of quenched or slaked lime, in the dry powder, mixed with one measure of *Dutch Tarras*,[2] and both very well beat together to the consistence of a paste, using as little water as possible." The results with this mixture not being always satisfactory, he attempted to discover the effect of using limes of different origin, comparing the mixtures by a cold-water test (immersing a stiffly-worked ball of mortar in water immediately after setting). Finding that lime from the Aberthaw limestone, in Glamorgan, gave better results than ordinary lime, he compared the chemical behaviour of different limestones, and discovered that those which gave the best results as mortars agreed in containing a considerable proportion of clayey matter. This was the first occasion on which the properties of hydraulic lime were recognised. He also compared together several varieties of natural and artificial pozzolana as substitutes for trass, including burnt ironstone and forge scales. Ultimately, mortar prepared with blue Lias hydraulic lime, and pozzolana from Civita Vecchia, in equal quantities, very thoroughly mixed, was used for the work.

In spite of the success of Smeaton's experiments, the use of hydraulic lime made little progress, and the old mixture of lime and pozzolana retained its supremacy for a long period. The discovery that a hydraulic cement could be made by calcining nodules of argillaceous lime-

---

[1] *A Narrative of the Building . . . of the Eddystone Lighthouse*, J. Smeaton, 2nd edn., folio, London, 1793. The experiments in question form chap. iv. of bk. iii.

[2] So called from being shipped from Holland. Smeaton found in 1755 that the material really came from Andernach, on the Rhine.

stone, known as septaria, found in certain Tertiary strata, was made in 1796.[1] The product thus obtained was given the inappropriate and misleading name of Roman cement, from its hydraulic properties, although it in no way resembles the Roman mortar. Being a quick-setting cement, it was found useful in work in contact with water. About the same time, a similar natural cement was prepared in France from similar concretions found near Boulogne, and deposits of "cement rock," capable of yielding a hydraulic cement on calcination, were found at Rosendale and at Louisville, in the United States. It was not long before the American natural cement industry attained great importance.

The investigations of L. J. Vicat[2] on hydraulic lime led him to prepare an artificial hydraulic lime by calcining an intimate mixture of limestone (chalk) and clay, ground together in a wet mill. This process may be regarded as the principal forerunner of the manufacture of Portland cement.

It was in 1827 that the original patent for Portland cement was taken out by Joseph Aspdin, a Yorkshire bricklayer. Aspdin's proposal was to mix lime with clay or argillaceous earth with water "to a state approaching impalpability," to dry the mixture in a slip pan, and to calcine it in a kiln "till the carbonic acid is entirely expelled." The name Portland cement was given to the product from a fancied resemblance of the colour of the cement after setting to Portland stone.[3]

The process thus described is incapable of yielding a cement of the kind now known as Portland cement, the temperature of calcination being too low for the chemical

---

[1] Patent by James Parker, of Northfleet.

[2] *Recherches expérimentales*, Paris, 1818, and the later work already cited on page 3.

[3] The patent is reproduced, with notes on the history of the industry in England, in *Concrete and Constr. Eng.*, 1908, **2**, 456.

reactions to proceed to completion. This defect soon became obvious, and it was not long before the practice was adopted of calcining at a higher temperature. The Portland cement industry, which has spread from the original works at Wakefield and on the Thames, has now become world-wide, and has assumed enormous importance, particularly in England, France, Germany, and the United States.

All the varieties of artificial hydraulic cement were at first employed solely for work exposed to the action of water, common lime mortar being used for brickwork and masonry above ground. Gradually, however, Portland cement has succeeded, in spite of its greater cost of production, in largely superseding lime mortars and natural cements, even for such purposes as these. The homogeneity of the product, owing to the high temperature to which it is heated, and the possibility of maintaining a constant composition by controlling the proportions of the two ingredients of the artificial mixture, are advantages which have enabled Portland cement to obtain precedence over all its rivals. Its production therefore increases relatively to other cements as well as absolutely. In a few regions, the abundance of local deposits capable of yielding a satisfactory natural cement gives rise to an industry of considerable importance, but even here the tendency is for cements of the Portland type to gain ground.

Within recent years the improvements in the kilns and mechanical appliances of the industry, and the improved knowledge of the limits of composition within which a satisfactory product can be obtained, have led to the production of cement which is as far superior to the Portland cement of a few years ago as the latter was to the early natural cements. There is no reason to suppose that the limit of improvement has been reached, or that great further advances, both in appliances and methods, may not yet be made. A few of the directions in which such advances may possibly take place are indicated later. A chronological table of the most important discoveries and inventions in connection with cement is given in the Appendix.

The use of concrete, an artificial conglomerate of gravel or broken stone with sand and lime or cement, is also of great antiquity. Vitruvius describes it, and Pliny[1] thus refers to the construction of cisterns:—"Cisterns should be made of five parts of pure gravelly sand, two of the very strongest quicklime, and fragments of silex[2] not exceeding a pound each in weight; when thus incorporated, the bottom and sides should be well beaten with iron rammers." A form of concrete made with broken tiles was much employed for pavements, and cement mixed with oil or other organic matter was often applied as a surface coat for waterproofing purposes. Much of the best concrete was made from broken brick, lime, and pozzolana, whilst in large works volcanic tuff generally took the place of brick. The great vaults of the Thermæ and of the Basilica of Constantine are cast in concrete.[3]

The most famous of Roman buildings erected in concrete is the Pantheon, the walls of which, 20 feet thick, are of tuff and pozzolana concrete thinly faced with brick, whilst the dome, 142 feet 6 inches in span, is cast solid in concrete containing pumice and pozzolana. Wooden boards were used as moulds, and the concrete was filled in in a semi-fluid condition. The present condition of many Roman buildings of this class is a sufficient testimony to the excellence of the material.

Concrete was also employed in building walls through-

---

[1] *Hist. Nat.*, bk. xxxvi. chap. 52.

[2] Not true silex, or flint, but a hard lava from the Alban Hills.

[3] J. H. Middleton, *Encyc. Brit.*, 9th edn., vol. xx. p. 809.

out the Middle Ages, but less systematically, and with less knowledge of the material, than under the Romans. The early Christian Churches of Rome have concrete walls, whilst examples of the same mode of construction in England are Kendal Castle[1] and Corfe Castle, a Saxon structure, from which Smeaton derived the idea of using concrete in engineering works. Much of the concrete in medieval buildings is of very inferior quality. It is not until quite modern times that it again assumes importance, being largely utilised for the foundations of bridges, and for embankments and other marine or river works. A great impetus was given to its use by the introduction of Portland cement, and in recent years concrete made with cement, or in exceptional cases with hydraulic lime, has occupied a very important place among building, and still more among engineering, materials. The invention of reinforced concrete, a material in which the resistance to compression of well-mixed and hardened concrete is combined with the tensile strength of steel, has increased the production of the material, and has had a far-reaching effect in bringing about a steady improvement in the quality of cement.

As the demand for Portland cement, especially as an ingredient of concrete, increased, and the requirements of engineers called for a more perfect material, it became increasingly desirable that standards of quality should be set up, by which any consignment could be judged after the performance of certain agreed tests. In this way standard specifications have arisen in most countries, sometimes under official auspices, but more often as the work of voluntary organisations of engineers and consumers, or of associations of cement manufacturers. That in use in Great Britain, and known as the British Standard Specification, was drawn up in 1904 by the Engineering Standards Committee, and revised in 1907 and 1910. The German

---

[1] Schaffhäutl, *Dingl. polyt. Journ.*, 1851, **122**, 186.

Standard Specification was drawn up by the Association of German Portland Cement Manufacturers. All such specifications are liable to revision from time to time, the alterations made being almost invariably in the direction of increasing the stringency of the requirements. At the same time, the best qualities of commercial cement very commonly more than fulfil the conditions of the official specifications, and it is not uncommon for engineers and contractors, especially those engaged in reinforced concrete construction, to make use of private specifications of greater stringency, and to obtain from manufacturers cement of the improved quality desired.[1]

The scientific study of cements is of quite recent date. Even the earliest authors dealt with the theory of setting, but their explanations were naturally of an extremely hypothetical character. Thus Vitruvius, who probably only recorded the current opinion of his time, and did not make any original contribution to the subject, is only able to suggest, in explanation of the properties of mortar, that: "stones . . . having passed through the kiln, and having lost the property of their former tenacity by the action of intense heat, their adhesiveness being exhausted, the pores are left open and inactive. The moisture and air which were in the body of the stone having, therefore, been extracted and exhausted, the heat being partially retained, when the substance is immersed in water before the heat can be dissipated, it acquires strength by the water rushing into all its pores, effervesces, and at last all the heat is excluded. . . . The pores of limestone, being thus opened, it more easily takes up the sand mixed with it, and adheres thereto, and hence, in drying, binds the stones together, by which sound work is obtained."[2]

---

[1] See B. Hannen, *J. Roy. Inst. Brit. Architects*, 1905, 491; C. H. Desch, *Eng. Times*, Feb. 28, 1907.

[2] Bk. ii. chap. v.

Smeaton's remarkable experiments, in which he showed that the hydraulic limes owed their special properties to the clayey constituents of the limestone, were of fundamental importance for the understanding of the nature of cements, but they received little attention from chemists. The hypothesis of Bergmann,[1] assigning the hydraulic properties of cements to the presence of manganese salts, although based on the accidental finding of some manganese in a hydraulic lime, was generally accepted, and was only overthrown by the work of Collet-Descotils,[2] who proved that the burning converted the silica into a soluble form, and especially by the very thorough theoretical and practical investigations of Vicat.[3] The great range of materials studied by this author renders his work particularly valuable. His principal theoretical conclusion was that the silica of the clay was the essential agent in the hardening process. On the other hand, Frémy,[4] who failed to prepare a calcium silicate with hydraulic properties, but succeeded in obtaining artificially a hydraulic calcium aluminate, assigned the principal share to the alumina. Frémy's work also contains an interesting anticipation of the thesis maintained to-day by Michaëlis, that the hardening of Portland cement and the reaction between lime and pozzolana are processes of the same chemical nature. The proof by J. N. Fuchs[5] that quartz and other forms of crystalline silica are inactive, whilst the amorphous and hydrated forms behave as pozzolanas, marked a further step in advance. The view that basic silicates are formed in burning, and are then hydrolysed by water, yielding lime and hydrated lower silicates, was propounded by A. Winkler[6] and has since fully established itself.

It is unnecessary, in such a brief survey of the history

---

[1] *Opusc. chim. phys.*, ii. 229.

[2] *Journ. des Mines*, 1813, **34**, 308.

[3] *Op. cit.*

[4] *Compt. rend.*, 1865, **60**, 993.

[5] *Dingl. polyt. Journ.*, 1883, **49**, 271.

[6] *J. prakt. Chem.*, 1856, **67**, 444.

of cement investigations, to mention the hypotheses and modifications of hypotheses that have seen the light since the publication of Vicat's work. The two authors who have most contributed to the solution of the problems involved are W. Michaëlis and H. Le Chatelier, of whom Michaëlis is the earlier in point of date, his first paper on the subject of cements having appeared in 1867,[1] whilst the French chemist's first publication dates from 1883 only.[2] Both investigators have since continued to devote attention to the subject, and the account of the constitution of cement and of the process of setting contained in the following pages is mainly based on their researches and on the work of others who have developed their ideas in other directions. Some further historical notes will be found below, in connection with microscopical and other methods of investigation.

The following works and memoirs may be referred to for the history of the manufacture and investigation of calcareous cements:—

Raucourt de Charleville, *Traité sur l'Art de faire de bons Mortiers*, 2nd edn. Paris, 1828.
Sir C. W. Pasley, *Observations on Lime, Calcareous Cements, &c.* London, 1838.
L. J. Vicat, *Treatise on Calcareous Mortars and Cements*, translated with additions by J. T. Smith. London, 1837.
Q. A. Gillmore, *Practical Treatise on Limes, Hydraulic Cements and Mortars.* New York, 1874 (for American cements).
W. Michaëlis, *Die hydraulischen Mörtel.* Leipzig, 1869.
Schaffhäutl, *Dingl. polyt. Journ.*, 1851, **122**, 186, 267.

---

[1] *J. prakt. Chem.*, 1867, **10**, 257.
[2] *Compt. rend.*, 1883, **96**, 1056.

CHAPTER II

THE RAW MATERIALS AND PROCESSES OF MANUFACTURE OF CEMENTS

THE foregoing historical sketch has shown how the requirements of building and engineering construction, in combination with local geological conditions, have led to the invention and manufacture of a considerable number of substances and mixtures capable of being used as cements. Some of these products are only suitable for use in brickwork, &c., which is exposed to atmospheric influences alone, whilst they undergo gradual disintegration if submerged in water. Others, the so-called hydraulic cements, resist the action of water, and even set when immersed in a plastic condition. The extensive use of masonry and concrete in the protection of sea-coasts and in the construction of piers and harbours also calls for cements which will resist the destructive action of the salts contained in sea-water, and further varieties of cement, suitable for decorative surface treatment, &c., tend to assume greater importance as the practice of constructing buildings of reinforced concrete without external casing makes greater headway. The number of varieties of cement is therefore likely to increase rather than to diminish, many of the older, and in some respects inferior, products being enabled to hold their own by such advantages as the local availability of their ingredients, their nearness to the place of consumption, or their relatively low cost of production. Nevertheless, the consumption of the products of the highest class continually increases relatively to the others, and this relative increase appears likely to continue.

The materials to be dealt with may be classified as follows:

1. **Lime,** prepared by calcining limestone. The simple term lime is properly confined to those products which consist of almost pure calcium oxide, and slake readily in contact with water. They yield the simplest variety of mortar when slaked and mixed with sand or other inert material.
2. **Hydraulic lime,** prepared by calcining argillaceous limestone. The clayey substances which are present in hydraulic limes deprive them of the property of slaking readily, but enable them to set when immersed in water. The above two classes pass insensibly into one another through limes of intermediate composition.
3. **Natural cement,** prepared by calcining a naturally occurring mixture of calcareous and argillaceous substances at a temperature below that at which sintering takes place. "Roman cement" and "rock cement" are members of this class.
4. **Portland cement** is best defined in the terms of the British Standard Specification, as a product obtained by intimately mixing together calcareous and argillaceous materials, burning them at a clinkering temperature, and grinding the resulting clinker.
5. **Iron-Portland cement** is a mixture of Portland cement prepared as above with granulated blast-furnace slag.
6. **Granulated Slag-cement**[1] is a product consisting wholly or principally of granulated basic blast-furnace slag.
7. **Pozzolanic substances** are not themselves cements, but when mixed with lime they form a hydraulic

---

[1] Generally known by various trade names. It must not be confused with the product formerly called slag cement, which was a mere mixture of lime and ground slag.

mortar. They may be (*a*) natural, including various kinds of volcanic deposits, or (*b*) artificial, including various ignited argillaceous substances, and certain varieties of blast-furnace slag.

8. **Gypsum cements,** prepared by dehydrating gypsum. These include the plasters, and special forms of cement of which gypsum is the principal constituent.

The materials just enumerated are very frequently classed as limes (1 and 2); cements (3 to 6); and plasters (8). In discussing their manufacture and properties, it will be convenient to depart from the above order, and to assign the chief prominence to Portland cement, partly because this material has assumed an importance in recent years which is continually increasing, partly also because it has received the greatest share of scientific attention. From its chemical and physical character it is better suited to systematic investigation than any of the less well-defined products, whilst its study is capable of throwing light on their nature. Next in scientific interest stands slag cement, a comparatively new product, presenting many chemical problems which still await solution.

PORTLAND CEMENT.

Portland cement is prepared, in all but a few exceptional cases, by igniting a mixture of two raw materials, one of which is partly composed of calcium carbonate and the other of aluminium silicates. The most typical materials answering to this description are limestone and clay, both of which occur in nature in a great number of varieties. The opinion which was at one time held, that the quality of the product was dependent on the density and hardness of the limestone used, has no justification at the present day, when improvements in the processes of manufacture have eliminated the conditions which gave rise to it, and the choice of a limestone is now governed chiefly by considerations of local availability, dolomitic limestones, however, being generally excluded. The industry has tended to establish itself in neighbourhoods where two suitable raw materials occur in close proximity, as on the banks of the lower Thames and Medway, where chalk and alluvial mud are used, and in the Midland counties, where the blue Liassic limestone is interstratified with shale. Analyses of these materials are given in Tables I. to IV.

Chalk is a soft limestone of organic origin, being almost entirely composed of the calcareous skeletons of foraminifera, and is an exceedingly convenient source of lime. As found in the south-east of England it contains bands of flints, which have to be removed before the chalk can be made into a mixture for cement. This removal is very simply accomplished in the wet process, the flints simply accumulating at the bottom of the wash-mills, and being removed periodically. The grey chalk, which is also used, is less pure, but is still to be regarded as essentially calcium carbonate.

In Northern Kent, the clayey material used together with white chalk is the alluvial mud of the Medway, whilst in Sussex the Gault clay, which contains a considerable proportion of calcium carbonate, serves the same purpose. Analyses of these materials are given in Table III., p. 22. Liassic limestone and shale, as used in the Midlands and South Wales, have compositions approximating to those given in Tables II. and IV., but are subject to considerable variation. The presence of iron pyrites (FeS_2) in these materials is a decided advantage.

In the north-east of England the usual materials are a local clay, containing less organic matter than the Medway mud, and chalk brought to the works from the Medway district, or from Sussex.

A special position among Portland cement materials is occupied by the Cambridgeshire marl, a deposit occurring at the base of the chalk, and immediately above the greensand. This deposit has a composition which approximates very closely to that of an artificial Portland cement mixture. It is therefore occasionally utilised for the production of a natural cement. The greater part of the local deposit is, however, treated by the more rational process, the materials obtained from different neighbouring strata being mixed in the proper proportions before burning. Calcareous marls are also of great importance on the Continent. Their composition varies widely in different districts, and it is impossible to make general statements respecting them.

Lastly, reference should be made to certain exceptional materials, which have only a limited application in the manufacture of Portland cement, but nevertheless present certain features of interest. There exist, in the first place, a few calcareous marls of such composition that if heated to sintering, a product is obtained in which the proportions of the components do not differ appreciably from those of the artificial cement. A marl of this class, from the shore of the Black Sea, has the composition :[1]—

	Per cent.
SiO_2	13·48
Al_2O_3	4·77
Fe_2O_3	1·35
CaO	44·45
MgO	0·10
SO_3	trace
Loss on ignition	35·64

Similar marls are found in the Tyrol and in Dalmatia, and have considerable local importance as sources of cement. The value of such cements, as compared with those prepared from artificial mixtures, has been much

---

[1] Ljamin, quoted by C. Naske, *Die Portlandzementfabrikation.*

discussed,[1] but it is obvious that accidental variations of composition in the pit or quarry must affect the composition, and therefore the quality of the product, in the absence of the means of control which is afforded by the deliberate mixing of two different materials, the relative proportions of which can be varied as is found desirable.

Several different varieties of raw material are also employed in North America. True chalk and soft limestones occur in certain detached areas in the United States, but hard limestones are also used, their introduction having been made possible in recent years by the improvement of grinding machinery. They are used in conjunction with various clays, shales, or even, in at least one instance, with roofing slate, the scrap obtained from the quarry being employed. Chemically regarded, slate is only an indurated shale, and is therefore perfectly suitable for use as a raw material of cement.

The greater part of the cement produced in the United States is, however, manufactured from highly argillaceous limestones, frequently known as "cement rock." One half of the total production is localised in the Lehigh district of Pennsylvania and New Jersey, where the Trenton (Lower Silurian) limestone forms the principal raw material. Where deficient in lime, it is mixed with a suitable proportion of pure limestone, thin beds of which frequently occur in association with it. The cement-rock is considerably richer in magnesia than any of the materials employed for the purpose in England, as it rarely contains less than 2 to 3 per cent. MgO. The underlying beds of magnesian limestone are useless for the production of Portland cement. Some analyses of cement-rock, suitable for the preparation of Portland and natural cements respectively, are given in Tables V. and XII.

The fact that by-products obtained in several industrial chemical processes consist largely or principally of

---

[1] See S. Habianitsch, *Tonind. Zeit.*, 1906, **30**.

calcium carbonate has suggested the utilisation of certain of them as raw materials for the manufacture of cement. Amongst these are the alkali waste remaining after the recovery of sulphur, some varieties of which have been mixed with clay and converted successfully into cement, whilst others have proved to contain too high a proportion of calcium sulphate to yield a sound product. The attempt has also been made to use sewage sludge in the same way, but the physical condition of the sludge here introduces serious difficulties in addition to those caused by the presence of sulphur compounds and other impurities.

The use of blast-furnace slag in conjunction with limestone is far more important, but is more conveniently considered together with other methods of preparing cement from slag (p. 35).

An outline may now be given of the most important methods of manufacture.

TABLE I.

AVERAGE ANALYSES OF KENTISH CHALK.

	White.	Grey.
	Per cent..	Per cent.
SiO_2	0·80	4·59
Al_2O_3	0·21	2·64
Fe_2O_3	0·07	1·33
CaO	55·03	50·70
MgO	0·23	0·29
SO_3	...	...
Loss on ignition	43·66	40·45
Total	100·00	100·00
Calculated—		
$CaCO_3$	98·25	90·55
$MgCO_3$	0·44	0·56

TABLE II.

AVERAGE ANALYSIS OF BLUE LIAS LIMESTONE.

	Per cent.
SiO_2	11·39
Al_2O_3	3·47
Fe_2O_3	0·56
CaO	45·34
MgO	0·50
SO_3	0·90
FeS_2	0·37
Alkalies and loss	37·47
Total	100·00
Calculated—	
$CaCO_3$	80·97
$MgCO_3$	1·01

TABLE III.

ANALYSES OF MEDWAY MUD AND GAULT CLAY.

	Medway Mud.	Gault Clay.
	Per cent.	Per cent.
SiO_2	60·66	42·12
Al_2O_3	15·05	14·51
Fe_2O_3	9·63	6·58
CaO	1·15	15·76[1]
MgO	1·79	1·63
SO_3	0·20	1·45
FeS_2	0·21	...
Soluble salts	2·50	...
Alkalies and loss	8·81	17·95
Total	100·00	100·00

[1] Principally present as calcium carbonate.

TABLE IV.

Analyses of Liassic Shale, Warwickshire.[1]

	I.	II.
	Per cent.	Per cent.
SiO_2	38·00	17·00
Al_2O_3	14·85	5·99
Fe_2O_3	4·75	4·16
CaO	17·78	36·10
MgO	3·42	1·18
SO_3	1·28	0·59
Loss on ignition	19·92	34·98
Total	100·00	100·00

TABLE V.

Analyses of Typical American Raw Materials for Portland Cement.[2]

	Limestone.		Marl.		Clay.		Shale.	
	1	2	3	4	5	6	7	8
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
SiO_2	3·53	2·14	0·52	0·20	59·15	61·68	65·25	49·93
Al_2O_3	1·14	1·46	0·51	0·50	19·85	19·60	21·06	25·33
Fe_2O_3			0·53	0·60	8·30	3·12	3·40	6·05
CaO	54·45	58·24	51·66	50·12	3·03	2·40	0·84	3·12
MgO	0·44	1·04	1·37	0·83	1·36	1·77	1·78	1·65
SO_3	...	...	0·89	0·56	...	0·43	...	0·38
Loss on ignition	38·74	37·12	44·52	47·19	8·02	7·18	6·10	10·19
Total	98·30	100·00	100·00	100·00	99·71	96·18	98·43	96·65
Calculated—								
$CaCO_3$	97·23	94·35	92·25	89·50				
$MgCO_3$	0·92	2·18	2·87	1·74				

---

[1] Calculated from D. B Butler, *Portland Cement*, London, 1899.

[2] J. C Russell, *Ann. Rep. U S. Geol. Survey* 1901, **22**, iii. 629.

The raw materials are incorporated to form a homogeneous mixture by either the dry or the wet process, of which the first is applicable to every class of material, although perhaps not to all with equal convenience, whilst the second is only applicable to friable materials, of which chalk and Medway mud are the most typical. The second, as being the earlier in date, and that still employed in the original home of the industry, may be described first. It is characterised by yielding a more intimate mixture of the two kinds of particles than is attainable by any other method. In American works the dry process is steadily superseding the wet.

Where the wet process is employed, the materials, such as chalk or marl, and mud, are thrown into circular vats, commonly made of concrete and sunk beneath the surface of the ground. A number of radial arms, attached to a vertical central spindle, carry iron rakes which break up the lumps of solid matter as the arms revolve. The attachment of the rakes to the arms is not rigid, but is made by means of chains. The quantity of water admitted is so large as to render the whole contents sufficiently liquid to overflow through a coarse sieve into another vessel. The flints present in the chalk remain in the mixing vessel, and assist in the reduction of the materials to a fine state of division. Where somewhat harder materials are used, this apparatus is occasionally replaced by submerged edge-runners. The liquid cream known as "slip" or "slurry" is passed through a wet tube-mill to complete the breaking up of the coarser particles, and is then, if thin, transferred to settling tanks, where it can free itself from a part of the excess of water. In order to ensure uniformity of composition, large mixing vessels are now used, in which the charges obtained from several wash-mills may be united and continually agitated by mechanical means. Slight variations in the composition of different charges are equalised by the use of such mixers, the capacity of which is sometimes several hundreds of tons of solid matter. The finished slip or slurry contains the chalk and clay in a state of such fine division that only 2 to 5 per cent. is retained by a sieve having 5000 meshes per sq. cm. (180 per linear inch). The quantity of water employed depends on the character of the raw material, amounting to as much as 85 per cent. if much coarse sand is present, but being little above 40 per cent. if the soft chalk and mud or clay are almost free from mechanical impurities other than flints.

For heating in stationary kilns, it is necessary to dry the slurry, whilst it may be employed directly in rotatory kilns, as described below. The drying is accomplished, for the sake of economy, by means of the waste heat escaping from the kilns, the pasty slurry being spread on the floors of drying chambers heated from below. Like clay under similar conditions, the plastic mass shrinks greatly in drying, and cracks into blocks of a size convenient for handling and loading into the kiln.

The dry process, of which a number of varieties exist, dispenses with the use of water, and brings about the amalgamation of the materials by grinding only. To ensure satisfactory grinding and mixing, the limestone and shale or their equivalents are dried after having been coarsely crushed. Vertical drying stoves are being generally replaced for this purpose by inclined rotating cylinders. Materials containing a large quantity of water may also be dried and utilised satisfactorily in the dry process. The materials are now weighed, mixed in the proportions indicated by analysis, and ground together. The mills devised for the grinding of hard substances exhibit a great diversity of type. Millstones have been entirely abandoned, and modern mills have grinding surfaces of manganese steel or chilled iron, the moving portions having the form of pendulums or of heavy balls pressing by centrifugal force against an outer horizontal ring, or of rollers kept up to the ring by strong springs. Tube and ball mills, in which flints or steel balls are carried upwards by the motion of a rotating cylindrical container, and fall back on the substance to be ground, are also very effective. The fine powder is separated from insufficiently ground particles, either by passing through sieves or, in some modern plant, by means of a current of air.

In this process, again, the subsequent treatment of the mixture depends on whether stationary or rotary kilns are to be used. If the latter, the powdered mixture is introduced directly into the kiln, but where the rotary arrangement has not been adopted, a much more complicated treatment is necessary, owing to the impossibility of heating a fine powder in an ordinary kiln, which requires compact blocks between which the hot gases can pass freely. The powder is therefore consolidated by moistening with water, usually to the extent of 8 to 10 per cent., and forming into bricks by pressure in a brick-making machine. These bricks have then to be dried again by waste heat. In some Continental works, slurry made by the wet process, which has become stiff by long settling in tanks, is also moulded into bricks.

The dry process can be carried out with greater economy of fuel than the wet, as the large consumption of fuel required to evaporate the water used in preparing the slurry is avoided in the former process. In spite of this obvious advantage, the dry process has not succeeded in displacing the wet one completely. Local conditions have to be taken into account, and where the raw materials at hand resemble in character those employed on the Thames and Medway, wet mixing has certain important points in its favour. In the first place, the chalk contains numerous flints, the removal of which is necessary if dry grinding is to be employed, and this removal is a troublesome and costly operation. These flints are actually of service in wet washing, as they assist in triturating the material, and are easily removed when they have accumulated. Secondly, the alluvial mud of the Medway, and deposits which resemble it, are extremely sticky and tenacious, and the moisture is only removed from them with great difficulty. Hard limestone, on the other hand, requires dry grinding, and where this material and shale are employed, the dry process of manufacture is the natural one to adopt, but it does not follow that it is the best under all circumstances.

The ignition of the raw material, if stationary kilns are used, is conducted by means of coke. The old-fashioned type of kiln, still to be seen in small works, is roughly conical in form, and is charged with alternate layers of coke and lumps of dried slurry or pressed bricks. Combustion is maintained by natural draught, and the whole process of burning lasts four or five days. The consumption of fuel is naturally very high, and the temperature varies greatly from one part of the kiln to another. In the improved forms of vertical kiln, the escaping hot gases pass through a chamber containing the solid raw material, which is thus strongly heated before entering the actual zone of combustion, whilst the finished clinker, accumulating in the lower part of the kiln, gives up much of its heat to the air passing through on its way to the layers of fuel, this regenerative effect resulting in a great economy of fuel. This Dietzsch type of kiln is still erected where the quantities to be dealt with are not sufficiently large to justify the employment of rotary kilns, with their largely increased output. Its action is continuous.

Another type of stationary kiln, the Hoffmann ring kiln, was borrowed from the brick-making industry for application to the ignition of cement. It consists of a series of chambers, arranged in an oval ring, and communicating with a central chimney. Fuel and bricks, the latter being stacked so as to allow air to circulate freely, are placed in the chambers. Whenever the contents of one chamber are at their highest temperature, the products of combustion are passing through several chambers just in advance of it, and heating their contents to the temperature required for combustion, whilst its supply of air is being drawn through several chambers immediately in its rear, which are in course of cooling down after being fully heated. At the same time, some chambers in other parts of the ring are being charged, and others emptied of their contents. The process is continuous, and the zone of combustion travels progressively round the ring.

The product, which has been heated to the sintering point, at which partial fusion of a small proportion of the mass takes place, cementing the unmelted particles together, is called "clinker." If correctly burnt, it is extremely hard, compact, although containing innumerable minute pores and gas cavities, and dark grey in colour, with a slight blue or green shade. Owing to unequal heating, stationary kilns are always found to contain a proportion of under-burnt clinker, which has to be removed by hand-picking when the kiln is being emptied. It was formerly thought that cement clinker might also be overburnt, a state of things resembling the "dead-burning" of lime or plaster being brought about. This idea is a mistaken one. Provided that the composition of clinker is correct, it is not injured by strongly heating, even to the point of fusion, although its speed of setting may be modified thereby. Should the overheating occur in contact with firebrick or other acid material, however, silica is taken up and a glassy, acid product is formed, which is without value as a cement.

The most important advance in cement manufacture which has been made in recent years is the introduction of the rotary kiln[1] in place of the stationary type. The

---

[1] Objections have been raised against the use of the word "rotary," and "rotatory" has been proposed in its place. The shorter form is, however, the earlier in point of date, and is also to be preferred on etymological grounds.

action of the rotary kiln is continuous, and the duration of the process is enormously reduced, the raw materials entering the kiln at one end and thoroughly sintered clinker passing out at the other. The kilns are cylindrical in form, built up of steel plates, and supported in an inclined position by friction rollers, being slowly rotated by means of toothed rings. The fuel used in the earliest forms of rotary kiln was producer gas, but this was soon abandoned, and at present, whilst some favourably situated American works employ petroleum, and a few others natural gas, the most general fuel is powdered bituminous coal. The coal is first thoroughly dried by waste heat, is finely ground in pendulum or tube mills, and is then injected into the lower end of the kiln by a current of compressed air. Very thorough combustion takes place, and a high temperature is reached near the burner. The ash of the fuel is carried through to the chimney by the escaping gases.

The lining of the kiln must consist of a highly refractory material. Ordinary siliceous firebrick is unsuited for the purpose, owing to its tendency to react with the basic clinker. Even if the acidity is reduced, and a highly aluminous firebrick used, the lining is still liable to fuse in contact with clinker. This was one of the principal difficulties encountered at the time of the introduction of the rotary kiln into the cement industry.[1]

Bauxite bricks are chemically satisfactory, but are very weak and friable. Magnesia bricks are very resistant to heat and to the action of clinker, but their conductivity for heat is unduly high, so that the steel casing of the kiln suffers, and their great expansion on heating and contraction on cooling cause them to break or fall out of place. The difficulty has now been overcome by protecting the firebrick lining with a coating of cement clinker,

---

[1] W. H. Stanger and B. Blount, *Proc. Inst. Civil Eng.*, 1901, **145**, 44, and discussion.

which is rammed into place while at the full working temperature. The chemical interaction with the firebrick causes the inner and outer linings to become intimately united, and any defects which develop are readily repaired by means of clinker. A firebrick containing a relatively high proportion of alumina is most suitable for this purpose. In America it is customary to use bricks containing as much as 40 per cent. of alumina.

The mixture of materials enters the cylinder at the upper end in the form of semi-liquid slurry if the wet process is used, or of powder if the process is a dry one. The temperature increases progressively from the upper to the lower end of the kiln, and the reactions occurring in it may be divided into three stages. In the first the materials are simply dried, the moisture being removed by the hot products of combustion, and carried away to the chimney. In the second stage, any organic matter derived from the clay is burnt off, and the temperature rises so far (above 800°) that the calcium carbonate is decomposed into carbon dioxide and lime. In the third stage the lime thus formed reacts with the alumina and silica of the clayey matters present, producing a sintered mass of clinker, which contains the complex substances composing Portland cement. The final temperature reached is near or above 1400°. The clinker has the form of granules of the size of peas or rather larger. It escapes at the end of the kiln, and passes through cooling cylinders, where it gives up most of its heat to a current of air, which is employed for the blast, thus increasing the efficiency of the fuel.

The rotary kiln is designed for continuous working, and for dealing with large quantities of material at a time. It requires ample storage-room in order to ensure uninterrupted working. Owing to the uniformity of temperature within a given zone of the kiln, practically the whole of the clinker is equally burnt, and there are no underburnt masses to be removed by hand, as is the case with the product from the older types of kilns. In other respects there is no essential difference between the products of the two forms of kiln except that the ash of the fuel remains mixed with the clinker when stationary kilns are used, increasing its weight by about 5 per cent., whilst this is lost when the rotary kiln is used. As will be shown later, this difference is of importance in determining the rapidity with which the finished cement sets, but it does not cause any fundamental distinction between the two products. Uniformity of quality is much more characteristic of cement from rotary than from stationary kilns, and the necessity of eliminating defective material by a tedious process of hand-picking is done away with.

It is necessary to grind the clinker to a fine powder in order to obtain a commercial product. As is shown in a later chapter (p. 134), the quality of cement is greatly improved by increased fineness of grinding, and the increased demand for a finely-ground cement in recent years has led to important modifications in the forms of grinding machinery employed in the industry. Not only millstones, but also edge-runners and rollers, have become obsolete, and have been superseded by Griffin and similar mills working on the pendulum principle, or by ball and tube mills. Tube mills are now very commonly employed for the final grinding, after a preliminary reduction in other appliances. The separation of the coarsest particles before admission to the tube mills is accomplished either by sieves or by air-separators. In the most modern plants a regulated quantity of steam is admitted into the tube mills during the final grinding in order to modify the setting properties of the cement (see p. 126). This quantity of steam is so small as to be completely absorbed by the ground clinker, so that no clogging is produced.

The foregoing very brief account indicates the main features only of the process of manufacture of Portland cement, so far as is necessary for an understanding of its properties. The mechanical details, for which reference must be made to special works on the subject, vary with the nature of the materials dealt with, the local conditions of labour and transport, and the date at which the plant was laid down. In all modern works the handling of the raw materials and clinker is entirely mechanical, by means of screw conveyers, bucket elevators, and similar contrivances. Provision is also made in well-arranged works for the withdrawal and collection of the suspended dust, which was formerly so objectionable a characteristic of cement works, leading not only to unhealthy conditions within the buildings, but poisoning and disfiguring the whole neighbourhood in which the industry was carried on. By the aid of exhaust fans and dust-collecting apparatus the air is now kept free from dust, and a considerable quantity of cement, which was formerly wasted, is now saved to the manufacturer.

Analyses of some typical British, German, and American Portland cements are given in Tables VI., VII., and VIII.

TABLE VI.

Analyses of English Portland Cements.

	I.	II.	III.	IV.	V.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Insoluble in HCl .	0·37	1·14	1·50	1·23	0·42
SiO_2 .	23·23	22·94	19·64	23·32	23·34
Al_2O_3	6·28	7·12	9·55	6·64	9·12
Fe_2O_3 .	3·30	3·24	3·70	2·20	
CaO . .	62·17	60·70	61·72	61·96	62·95
MgO . .	1·10	1·25	1·14	0·68	1·05
SO_3 . . .	1·13	1·36	0·85	1·24	1·01
CO_2+H_2O . . .	1·42	1·18	1·18	2·54	1·42
Alkalies and loss	1·00	1·07	0·72	0·19	0·69
Total	100·00	100·00	100·00	100·00	100·00

I. is the mean of two very similar cements from Kent, II., III. are also Kentish brands, and cement IV. is from Bedfordshire. V. is an average analysis of rotary kiln cement, high in lime.

TABLE VII.

Analyses of American Portland Cements.[1]

	I.	II.	III.	IV.	V.	VI.	VII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
SiO_2	21·99	20·75	20·88	21·61	23·25	22·14	22·47
Al_2O_3	7·24	7·72	7·91	7·88	5·32	7·32	6·94
Fe_2O_3	3·39	2·59	2·69	3·18	3·27	3·02	2·79
CaO	62·53	62·75	62·98	62·56	63·14	62·36	60·42
MgO	2·37	2·61	2·85	2·37	3·01	1·61	3·23
SO_3	1·19	1·66	1·46	1·52	1·32	1·58	1·67
Undetermined	1·29	1·92	1·23	0·88	0·69	1·97	2·48
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00

TABLE VIII.

Average Analyses of German Portland Cements.

	I.[2]	II.[3]
	Per cent.	Per cent.
Residue insoluble in hydrochloric acid	1·40	1·22
SiO_2	20·87	21·27
Al_2O_3	7·63	7·25
Fe_2O_3	2·98	3·07
CaO	62·99	63·31
MgO	1·55	1·56
SO_3	1·85	1·71
Sulphide S	0·10	0·13
Total	99·37	99·52

---

[1] R. L. Humphrey and W. Jordan, *Bull. U.S. Geol. Survey*, 1908, No. 331, 11.

[2] H. Burchartz, *Mitt. k. Material-Prüf. Amt.*, 1910, **28**, 1.

[3] *Verh. Ver. deut. Portlandzementfabrikanten*, 1907.

The ordinary Portland cement has a greenish-grey colour, and after setting yields a more or less buff-coloured mass. This property excludes its use for ornamental purposes unless the surface is subsequently treated with some other preparation. For this reason, attempts have been made to manufacture white Portland cement, and several such preparations are now on the market. The first condition of obtaining a white product is the exclusion of iron from the materials used. So far as the raw materials are concerned, this has been found quite practicable. White chalk and certain varieties of limestone may be obtained, containing not more than the faintest traces of iron. The supplies of suitable clay are much more limited, being chiefly confined to kaolin (China-clay) and felspar. Cryolite (sodium aluminium fluoride) is also added. The presence of very small quantities of manganese is said to have a marked influence on the colour of products of this class. The principal difficulty which is encountered in their manufacture is the exclusion of contamination by iron during the processes of mixing, burning, and grinding. Particulars of the methods actually adopted are not readily available, but the fact that Portland cements, setting to form a mass as white as plaster of Paris, are now commercially obtainable, shows that the difficulties mentioned have been overcome.

Iron-ore Cement.

A material differing in certain respects from Portland cement, whilst belonging to the same class, is the so-called iron-ore cement, which has recently attracted attention outside of its original home, Germany, owing to the decision to employ it in large quantities in the construction of the Panama Canal, this decision being based on its power of resistance to sea-water. The cement is prepared in the same manner as Portland cement, the clay in the original mixture being replaced wholly or partly by iron ore. Although such an admixture was proposed as far back as 1854 for the purpose of improving the qualities of cement intended to be exposed to sea-water, the manufacture was found to be impracticable until after the introduction of the rotary kiln, as the high specific gravity of iron ores renders their incorporation in the wet way impossible, separation into two layers taking place, whilst their lack of plasticity prevents them from yielding the coherent bricks required for the old dry process. These difficulties disappear when the materials are fed in the form of dry powder into the rotary kiln. The cement thus produced has the following composition:[1]—

SiO_2	23·26
Al_2O_3	1·67
Fe_2O_3	8·20
CaO	64·84
MgO	0·66
SO_3	1·08
	99·71

CEMENTS FROM BLAST-FURNACE SLAG.

The slag obtained as a by-product in the manufacture of pig iron in the blast-furnace has, as its essential components, the same oxides as Portland cement, namely, lime, silica, and alumina. As the slag is mainly a waste matter, the production being far in excess of the small demand which exists for it, the prospect of converting it into a valuable cement is an attractive one. The attempt has been made in several different ways, three of which have assumed industrial importance.

1. Slag, granulated in water and finely ground, is found to form a good pozzolanic material for addition to lime in the preparation of mortar, or it may be mixed with lime in the factory.
2. Ground slag, mixed with limestone in suitable pro-

---

[1] W. Michaëlis, *Cement and Eng. News*, 1907, **19**, 140.

portions to form a Portland cement, is calcined, the slag simply replacing the clay in the ordinary mixture.

3. Slag of a certain composition is granulated under special conditions, and is then found to possess, after grinding, the properties of a Portland cement.

When the slag is merely granulated and ground, being mixed with lime only at the moment of preparation of the mortar, its function is exactly the same as that of trass, pozzolana, or any similar material, and does not call for special remark. A considerable quantity of a mixture known as slag or pozzolanic cement was, however, manufactured at one time by mixing granulated slag and lime at the place of manufacture. In any case, the granulation of the slag is an essential part of the process, and is carried out in practice as rapidly as possible by running into water. Part of the sulphur which is always present in blast-furnace slags in the form of sulphides is removed by the action of water on the hot material, and is evolved in the form of hydrogen sulphide. Granulation is also necessary in order that the material may be sufficiently friable to be ground.

It was formerly considered that only highly basic slags, obtained from blast-furnaces producing grey foundry pig, could be utilised in this way, but it has proved possible to employ slag from white iron with equal success, if due attention be paid to the difference in composition of the mixture.

The granulation is generally performed by running the slag into an inclined water-trough, or by directing a jet of water against the issuing stream of slag. The next operation, the removal of adhering water, is necessary before the slag can be ground. The porous character of the granules makes the drying process a difficult one, if conducted as usual in rotating drums. It is more economical to divert a part of the stream of liquid slag into a trough over which water plays, a brittle pumice-like mass being produced, which retains sufficient heat to dry the granulated portion.[1] The slag is then ground, and intimately mixed with the lime in a ball-mill. Hydraulic lime gives better results than fat lime, being less liable to cause unsoundness.[2] The lime is slaked before mixing with the slag, and coarse particles are removed by sifting after mixing.

Cement is now very extensively manufactured from slag in the United States by method 2. The composition of the cement is perfectly under control, the method of manufacture being exactly the same as when Portland cement is prepared from limestone and clay. Only a comparatively small quantity of limestone has to be added, as the slag already contains a quantity of lime approaching that required. The slag is granulated and dried, and in this state is readily ground and mixed with the limestone. A small quantity of slaked lime is added to render the mixture sufficiently coherent to be pressed into bricks. Where rotary kilns are employed, labour is greatly economised, the granulated slag, after passing through a rotary drier, being ground in a ball-mill and then mixed in the required proportions with the dried and ground limestone. The final mixing and grinding is performed in tube-mills containing flint pebbles. The fine powder is then fed into rotary kilns in the usual way, and the clinker is ground, first in mills of the centrifugal type, and finally in tube-mills. A little gypsum is added during the last grinding.[3]

The German product known as "Eisen-Portland-

---

[1] T. C. Hutchinson, *J. Iron Steel Inst.*, 1903, i. 216.

[2] E. C. Eckel, *Mineral Industry*, 1902, **10**, 84. Details of the process are also given by C. von Schwartz, *J. Iron Steel Inst.*, 1900, i. 141; 1903, i. 203; Jantzen, *Stahl u. Eisen*, 1903, **23**, 361.

[3] W. M. Kinney, *Proc. Eng. Soc. W. Pennsylvania*, 1909, *Iron and Coal Trades Rev.*, 1909, **79**, 543.

zement," which may be rendered "Iron-Portland Cement," has been the subject of much controversy. As at present manufactured,[1] it is composed of 70 per cent. of Portland cement and 30 per cent. of granulated slag. The Portland cement is manufactured by the process just described, granulated slag being mixed with limestone by grinding and heated to sintering. The remaining 30 per cent. consists of slag, granulated, dried, and ground. Only highly basic blast-furnace slags are suitable for this purpose, and their composition, together with that of the Portland cement prepared from them and of the Iron-Portland mixture, is shown in Table IX.

TABLE IX.

	Granulated Slag.	Portland Cement Product.	Iron-Portland Mixture.
	Per cent.	Per cent.	Per cent.
SiO_2	27–35	20–26·5	20–25
$Al_2O_3 + Fe_2O_3$ . .	8–20	6–14	9–15
CaO	44–52	58–65·5	54–60
MgO . .	0·6–2·5	1–3	0·6–5·0
SO_3	1·2–3·0	0·2–2·5	0·8–2·7
Alkalies . . .	...	0·2–2·5	...

It is evident that this product differs in some important respects from Portland cement as ordinarily defined. Portland cement is prepared by heating a mixture of calcareous and argillaceous materials to sintering. This is true of the product shown in the second column of figures above, but not of the mixed product shown in the third column. This product might be regarded as a mixture of cement with a pozzolanic material, were it not that granulated slag of the above composition differs from other artificial pozzolanas in

---

[1] *Eisen-Portlandzement, Taschenhandbuch*, 2nd edn., Dusseldorf, 1904.

having hydraulic properties, although its hardening only takes place very slowly. Iron-Portland cement is regarded by its makers as a mixture of two varieties of Portland cement, one of which is relatively rich, and the other relatively poor, in lime. This view is not consistent with the usual definition of Portland cement, and it is better to regard the two products as distinct. The designation "Iron-Portland" is not likely to lead to confusion, and has now been generally adopted. The cement is a mixture of the products of two chemical processes, and not, like the older material, the product of a single process, and its chemical composition is an average one, representing the mixture of two different kinds of particles.

The third product, to which the name slag cement is most strictly applicable, is prepared by granulating slag under special conditions, and grinding it without further calcination. The granulation is not performed by running the slag into water, as in the processes just described, but by allowing the stream of molten slag to fall on rapidly revolving iron drums. Several forms of drum have been devised.[1] The slag is thrown off by centrifugal action in the form of globules, which are cooled by the air, but not so rapidly as in the granulation by water. At the same time, the slag is sprayed with water containing certain salts in solution, such as alum or magnesium sulphate. The action of these salts, to which the inventor attached great importance, is still almost unexplained, and it is even uncertain whether it is to be attributed chiefly to chemical or to physical causes. The catalytic influence of soluble salts on cements is referred to later (p. 126), but it is not easy to picture the manner in which they influence the constitution of the granulated slag.

One of the most modern plants of this type[2] is provided with ladles which convey the molten slag from the

---

[1] See C. von Schwarz, *J. Iron Steel Inst.*, 1908, i. 137.

[2] Coltness Iron Co., see *Iron and Coal Trades Review*, 1909, **79**, 694.

blast-furnaces to the granulators, which consist of drums rotating within an outer, water-jacketed casing. The stream of falling slag, immediately before reaching the drum, encounters a fan-shaped stream of water containing 5 per cent. of magnesium sulphate, chimneys being provided for the removal of the steam and sulphurous fumes. In order to eliminate differences of composition existing between the slag from different furnaces, the granulated slag from several furnaces is mixed before grinding.

The slag granulated in this way is no longer hard and glassy, but porous and friable. It is readily ground, and after being mixed with small quantities of lime and gypsum to regulate the setting, it is reduced to a fine powder by ball-mills, followed by tube-mills.

Table X. contains analyses of two samples of granulated slag of German origin,[1] and one of cement made by this process in Scotland.

TABLE X.

	Granulated Slag.		Cement.
	I.	II.	
	Per cent.	Per cent.	Per cent.
Insoluble residue	3·95	1·25	0·2
SiO_2	29·87	35·12	26·5
Al_2O_3 . . .	12·72	10·29	15·0
FeO	0·82	0·76	0·2
CaO . .	46·88	47·25	50·5
MgO .	2·85	2·83	2·9
SO_3	trace	0·12	1·3
Sulphide S	2·74	2·49	1·8
Alkalies .	...	...	0·5
MnO . . .	...	...	0·3
Loss on ignition	1·89	1·23	0·6
Total . .	101·72	101·34	99·8

---

[1] H. Séger and E. Cramer, *Tonind. Zeit.*, 1904, **28**, 1687.

A part of the calcium is present as calcium sulphide.

Slag cement of this class differs from Portland cement in containing much less lime and much more alumina. The proportion of lime is in fact so small that a cement of the same composition would be useless if only heated to sintering. This fact alone shows that an essential difference must exist between the two types of cement, the one sintered and the other fused and granulated. Several processes have been proposed for enriching the slag by adding lime while the whole is in a fluid state, but the impracticability of incorporating lime, which greatly diminishes the fusibility, with a viscous liquid such as slag, is obvious. The manufacture of cement from slag by the above or a similar process, in spite of the time that has elapsed since it was first proposed, must be regarded as being still in its infancy, and its further development is a matter of great scientific and technical interest.[1]

NATURAL CEMENTS.

Natural or rock cements differ from Portland cement in being prepared from a rock containing lime, silica, and alumina in approximately correct proportions instead of from an artificial mixture of limestone and clay. The oldest cement of this type is that designated by the misleading name of "Roman cement," prepared from the septaria or argillaceous nodules dredged up from the sea-bottom, particularly near Harwich and near Sheppey, on the French coast near Boulogne, and in Holland and Germany, &c. These cements are lightly calcined, and have a dark brown colour owing to the presence of considerable quantities of ferric oxide.

---

[1] Important papers dealing with the manufacture of cement from slag are, in addition to those already cited: H. Wedding, *Stahl und Eisen*, 1908, **28**, 219; H. Detienne, *Ann. Mines, Belg.*, 1903; H. Passow, *Die Hochofenschlacke in der Zementindustrie*, Würzburg, 1908; M. Lepersonne, *Rev. univ. des Mines*, 1909, [iv.] **25**, 274.

American rock cements are characterised by the very high percentage of magnesia in the lightly calcined varieties, thus distinguishing them sharply from the British natural or Roman cements. Analyses of septaria and Roman cement are given in Table XI., and of American cement rocks and the cements prepared from them in Table XII.

The preparation of natural cement is carried out in a very similar manner to that of Portland cement, except that the calcination is generally performed at a lower temperature. This is particularly the case with Roman cements, the calcination of which takes place at 1170–1210°, whilst some of the American rock cements are calcined at as high a temperature as Portland cement, and consequently yield a clinker of very similar character. The composition of the product naturally depends on that of the cement-rock used, and is more variable than that of cements prepared from an artificial mixture, the proportions of which may be varied from time to time in accordance with chemical analysis.

In the usual American process, the rock from several different strata is usually mixed for a single charge, the intention being to correct an excess of lime or magnesia in one portion by adding another which contains an excess of silica. As the materials are not ground before their introduction into the kiln, each lump of rock is ignited separately, and the substances in excess do not enter into chemical reaction with one another. It is only after ignition and grinding that the materials become thoroughly mixed, and the product is therefore a mixture of particles differing widely in composition, and is in all respects the same as a mixture of several separately manufactured cements. Evidently little dependence can be placed on a product of this kind, and it is not surprising to find that the production of natural cements is diminishing relatively to that of Portland cement. It is unnecessary to do more than refer to the practice, unfortunately not yet entirely obsolete, of exporting some of the Belgian natural cements of this class under the fraudulent denomination of Portland cement.

TABLE XI.[1]

	Harwich.		Sheppey.	
	Septaria.	Cement.	Septaria.	Cement.
	Per cent.	Per cent.	Per cent.	Per cent.
Insoluble matter	25·6	10·5	20·2	7·8
[including SiO_2]	[21·3]	[8·8]	[16·5]	[6·5]
SiO_2	0·6	17·4	0·7	19·4
Al_2O_3	1·1	4·6	4·3	7·3
Fe_2O_3	6·3	12·4	11·6	9·2
CaO	32·4	46·1	29·3	48·2
MgO	2·7	3·7	3·3	2·7
Na_2O+K_2O	1·1	1·0	1·0	1·0
CO_2+H_2O	30·2	4·3	29·6	4·4
Total	100·0	100·0	100·0	100·0

TABLE XII.

	Cement Rock.			Natural Cement.		
	I.[2]	II.	III.[3]	IV.[2]	V.	VI.[3]
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Insoluble matter	15·37					
SiO_2		18·10	24·29	22·75	26·50	24·30
Al_2O_3	11·38	6·40	4·54	16·70	9·40	7·22
Fe_2O_3					2·00	5·06
CaO	25·71	36·40	20·76	37·60	53·50	33·70
MgO	12·45	1·70	12·50	16·65	2·40	20·94
SO_3						
Loss and alkalies	35·09	37·40	37·91	6·30	6·20	8·78
Total	100·00	100·00	100·00	100·00	100·00	100·00

---

[1] C. Knauss, *Dingl. polyt. Journ.*, 1855, **135**, 361.

[2] R. S. Tarr, *Economic Geology of the United States*, New York, 1894.

[3] F. H. Lewis, *Mineral Industry*, 1898, **6**, 89.

In America, the rock formerly used for the preparation of natural cement is now employed in certain districts as one of the materials of an artificial Portland cement mixture, and the product then ceases to be a natural cement, and is rightly classed as a true Portland.

Either vertical open kilns or continuous kilns are used, many natural cement plants using simple kilns similar to those formerly employed for burning lime. It is necessary to submit the product as it issues from the kilns to hand-picking, in order to reject those portions which are either too strongly or insufficiently burnt. It is remarkable that the extent to which burning must be carried is dependent in so high a degree on the composition of the cement rock that it is the practice in some American works to reject all material which has been heated to a sintering temperature, whilst in others these portions are reserved for the preparation of the best quality of cement. Aeration or steaming must precede grinding, the latter being preferable, as it brings about disintegration of the portions rich in lime and hence facilitates grinding.

The grinding machinery is frequently of the same type as in Portland cement plants. In many works, however, millstones built up of blocks of rock emery held in position by metal cast round them are used.

LIME.

The calcination of limestone to form either fat or hydraulic lime may be discussed very briefly. Chalk and other pure limestones are calcined in stationary kilns resembling in principle those described under the heading of Portland cement, unless a very pure product, free from admixture with the ash of the fuel, is desired, in which case kilns are used with separate calcination and combustion chambers, the heat from the burning fuel having to pass through a separating partition. This method naturally requires a greater consumption of fuel than the method of direct calcination.

This dissociation of the calcium carbonate of limestone is a reversible process, which ceases when the pressure of carbon dioxide attains a certain value depending on the temperature. Hence, any method of preventing the accumulation of carbon dioxide in the kiln facilitates the decomposition, and the plan which has proved the best in practice is the injection of steam into the lower part of the kiln. There is no chemical reaction in this process, the steam merely having the effect of diluting the carbon dioxide, reducing its partial pressure, and at the same time hastening its removal from the kiln.

Hydraulic limes, such as those obtained from the blue Liassic limestone, are prepared in the same way as quicklime, care being taken that the temperature does not rise so high as to form either a sintered or a vitreous product, which would be "dead-burnt." This sintering is the more likely to occur, the higher the proportion of siliceous or clayey matter in the limestone.

An exceptional type of hydraulic lime is that known as "chaux du Teil," prepared by calcining a limestone found on the Rhone, in the central part of southern France. This limestone consists almost entirely of calcium carbonate and silica, the latter being in a finely divided and soluble form, without alumina, and the lime prepared from it has a high reputation for work exposed to sea-water. Analyses of Lias lime and chaux du Teil are given in Table XIII.[1]

Whilst most hydraulic limes are despatched in the condition in which they come from the kilns, the practice adopted at the Teil works, and since followed by many Continental manufacturers, of slaking the lumps, and screening the powder thus formed in order to remove

---

[1] B. Blount, Art. "Cement," *Encyc. Brit.*, Suppl., vol. 26, 633.

uncombined and inert matter, has much to recommend it, a product slaked at the works in this way being much more uniform than one merely slaked as required.

TABLE XIII.

	Chaux du Teil.	Blue Lias Lime.
	Per cent.	Per cent.
Insoluble in HCl. .	0·3	2·39
SiO_2 . . .	21·7	14·17
Al_2O_3 . . .	1·8	6·79
Fe_2O_3	0·6	2·34
CaO	74·0	63·43
MgO	0·7	1·54
SO_3	0·3	1·63
CO_2	0·6	3·64
H_2O		2·69
Alkalies and loss .	...	1·38
Total . . .	100·0	100·00

TABLE XIV.

	Pozzolana.[1]		Santorin Earth.	Trass.[2]	
	Pratolungo	Vesuvius.		Rhenish.	Rhenish.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
SiO_2 .	46·24	48·45	64·34	53·08	59·3
Al_2O_3 .	19·26	17·81	10·88	18·28	12·2
Fe_2O_3	11·18	3 49	6·44	0·48	8·5
FeO . . .	...	3·35	...	3·33	...
CaO .	9·82	12·09	3·62	1·25	6·2
MgO . .	2·84	3·02	2·77	1·31	1·9
Na_2O . . .	2 66	5·46	6·05	3·44	3·3
K_2O . . .	2·77	5·01	4·83	4·17	3·5
H_2O and volatile matter	6·10	0·60	1·50	12·65	3·5
Total .	100·87	99·28	100·43	97·99	100·4

---

[1] G. Gallo, *Gazz. chim. ital.*, 1908. **38**, ii. 156.

[2] O. Feichtinger, *Chem. Technologie*, Brunswick, 1885, p. 82.

POZZOLANIC MATERIALS.

The volcanic products known as pozzolana, trass, &c., consist of a mixture of silicates. The true pozzolanas are mainly amorphous, but contain crystals of leucite, augite, and mica distributed through them. Santorin earth contains pumice, quartz, and felspar. Rhenish trass is more compact, although some inferior qualities are light and porous, like pumice. The dense trass is finely ground before being brought into use, and then forms a bluish-grey powder.

Materials of this class are variable in composition, and the analyses in Table XIV. are only to be regarded as typical.

GYPSUM CEMENTS.

The well-known plaster of Paris is only one of a number of cements, the essential constituent of which is calcium sulphate, prepared by dehydrating gypsum at a moderate temperature. The deposits of native gypsum are used, of which the best known is that forming the hill of Montmartre in Paris, whence the name of the plaster. The gypsum is broken up and calcined. It is necessary to avoid contact with the fuel, which would bring about the reduction of a part of the calcium sulphate to sulphide, thus introducing a very undesirable impurity. For this reason, plaster kilns have rather the form of ovens than of lime or cement kilns. The nature of the process of dehydration is described later (p. 104). Superheated steam has been used as a dehydrating agent with good results.

A second method of preparing plaster is that known as "boiling." The gypsum, instead of being heated in lumps, is finely ground and placed in an iron vessel or kettle, heated from below. The water is readily evolved, and as it escapes from the fine powder, the mobility of the particles produces an appearance like that of a boiling liquid. The powder is stirred thoroughly by mechanical means until the process is complete. The escaping steam carries much dust with it, and a flue leading into a dust-separator must therefore be provided.

Both the oven and the kettle processes are discontinuous, and are therefore less economical than calcination in rotating cylinders, which is now superseding the older processes. The hot material issuing from the rotary calciners passes into calcining bins, in which the last portions of water are given off.

Care has to be taken in the preparation of ordinary plaster that the temperature of calcination does not exceed 200°, for if heated more strongly gypsum becomes "dead-burnt" and loses its property of setting with water. Under certain conditions, however, a useful product may be obtained by heating gypsum to a considerably higher temperature. This is the method adopted in the manufacture of the so-called "flooring-plaster" (German Estrich-Gyps) which is largely employed on the Continent, although almost unknown in this country, and differs from plaster of Paris in setting much more slowly, and also in yielding a much harder mass. This variety of plaster was at one time much used in neighbourhoods where gypsum was abundant, as a mortar for brickwork, in the form of a mixture with sand.

In the manufacture of flooring plaster,[1] gypsum of good quality is heated in a kiln so arranged that the hot gases from the fuel pass through the piled-up lumps of raw material. The temperature is maintained at about 500°, and the heating must not be continued for more than four hours in the usual form of kiln, as more prolonged heating brings about the conversion of gypsum into the inactive, dead-burnt variety. The product is used in a less finely-ground condition than ordinary plaster.

---

[1] F. A. Wilder, *Report Iowa Geol. Survey*, 1901, **12**, 195.

Gypsum also forms a constituent of a number of compound cements. Selenitic cement, also known as Scott's cement, is a mixture of hydraulic lime with 2 to 5 per cent. of gypsum. The mixture may be prepared by grinding together in the dry state, or merely by dissolving the gypsum in the water used to slake the lime. Another series of gypsum cements consists of plaster impregnated with various salts, either during or after the burning process, for the purpose of yielding a harder plaster, and one less readily attacked by moisture. Such cements are used for producing a smooth white surface in internal building work. Alum or borax may be used as the impregnating salt. If the first, the lumps of plaster taken from the kiln after heating to redness are steeped in a solution of alum and again heated to redness, and are afterwards finely ground. Alum is the agent generally employed, and the product is then known as "Keene's cement." It is necessary to use a pure gypsum, as even small quantities of iron salts give rise to reddish-coloured veins in the product. Parian cement is prepared by incorporating borax with gypsum, either in the same manner, or by mixing powdered gypsum and borax before calcining.

For details of the manufacture of cements, reference should be made to the following works:—

C. Naske, *Die Portlandzementfabrikation*, 2nd edn., Leipzig, 1909.

G. R. Redgrave and C. Spackman, *Calcareous Cements*, 2nd edn., London, 1905.

A. Moye, *Der Gips*, 2nd edn., Leipzig.

R. K. Meade, *Portland Cement*, Easton, U.S.A., 1906.

E. C. Eckel, *Cements, Limes, and Plasters*, New York, 1905.

A. C. Davis, *Portland Cement*, 2nd edn., London, 1910.

P. C. H. West, *Portland Cement*, London, 1910.

Among older works the following is very valuable:—

C. Feichtinger, *Chemische Technologie der Mörtelmaterialen*, Brunswick, 1885.

CHAPTER III

THE CHEMICAL COMPONENTS OF CEMENTS

ALTHOUGH most of the substances of which hydraulic cements are composed contain three or more elements in a state of combination, we may introduce a considerable simplification into their study by regarding them as produced by the association of simple binary compounds. As most of the elements present, both metallic and non-metallic, are undoubtedly combined with oxygen, we may adopt the usual device of mineralogists in dealing with silicates and other oxygen-salts, and represent the complex compounds as being built up of oxides, some of which are basic and others acid in character. This method, which is practically that of Berzelius, differs considerably from that adopted in the exposition of inorganic chemistry in most modern text-books. The development of the structural theory, and the widespread use of the hypothesis of ionic dissociation, have led to the representation of salts as combinations of positive and negative ions. This view, however, based as it is on the behaviour of aqueous solutions, is of little assistance in the treatment of silicates and similar compounds, which are practically unknown to us in solution. We are almost completely ignorant of the molecular weights of compounds of this class, and we are therefore unable to decide how far differences of molecular complexity may be responsible for observed differences of physical properties and chemical behaviour. Under these conditions the ordinary conceptions of chemical structure become inapplicable, and the attempts, so frequently made, to explain reactions involved in the manufacture or the setting of cement by processes of isomerisation or polymerisation, are entirely speculative and without serious value.

On the other hand, the associations of oxides in silicates, alumino-silicates, &c., bear a close resemblance to the associations of metals in alloys. We may have in alloys simple mechanical mixtures, solid solutions, or definite inter-metallic compounds, or all of these together, and special methods have been devised for the investigation of such systems, based on thermal and microscopical analysis, and on the quantitative study of physical properties.[1] In metallic alloys, as in the compounds contained in cements, the components are frequently closely similar, so that we are unable to distinguish them definitely as electro-positive and electro-negative, and, in both cases, structural theory fails us as a means of explanation. These analogies suggest an analogy of method, and we find in fact that the most important advances in the chemistry of cements are now being made by the cautious application of the methods of metallography. It is necessary to observe, however, that the experimental difficulties are much increased in the case of cements. This is mainly due to the high temperatures at which most of the substances to be studied fuse, and to their low conductivity for heat as compared with that of metals and alloys. The latter condition gives rise to errors in thermal measurements, as it is difficult to ensure equality of temperature throughout the mass employed, and the accurate measurement of critical temperatures is hindered. The consequence of the infusibility of the materials is that, in the manufacture of cement by present methods, the temperature of complete fusion is not attained,[2] the product being only "sintered," that is,

---

[1] See the author's *Metallography* (London, 1910).

[2] Blast-furnace slag is an exception, being formed in the liquid state. In this case, however, the rapid cooling of the product in its manufacture gives rise to departure from conditions of equilibrium (see p. 97).

heated to the melting-point of the most fusible portion of the reacting mixture. The chemical changes which take place are therefore arrested at an incomplete stage, and the final product does not contain the components in a state of equilibrium. The same remark applies to the hardening of cement, the chemical changes involved remaining incomplete after the lapse of many years or even centuries. It is therefore necessary to employ caution in applying the conclusions of physical chemistry, based on the study of systems in equilibrium, to mixtures of this kind. Fortunately, it is generally possible to determine the direction in which the condition of the system departs from one of equilibrium, and if this precaution be remembered, cements offer a most fertile field for investigation by methods akin to those of metallography.

Another department of physical chemistry which is in a position to throw light on the chemical behaviour of cements is that which deals with the properties of colloids. Although the fundamental researches of Graham on the properties of colloidal solutions date from 1850, it is only in quite recent years that marked progress has been made in their investigation. The microscopical examination of cements mixed with water has shown that colloidal substances are first formed, and that the separation of crystalline products takes place subsequently. The recognition of this fact gives a new aspect to the process of setting, which must now be regarded as proceeding in the presence of a colloid. The process is discussed from this point of view in Chapter V.

The remainder of this chapter contains a brief account of the properties of those oxides which may be considered as the components of cements, and also of the simpler compounds formed by their association in pairs.

CALCIUM OXIDE.

Calcium oxide, or lime, has the formula CaO. It is an essential component of all the cements with which we have to deal, and is mostly derived from the decomposition of calcium carbonate, $CaCO_3$. The latter compound occurs in a practically pure state as chalk and marble, and mixed with varying quantities of impurities as limestone. When heated, calcium carbonate dissociates into gaseous carbon dioxide and solid lime, $CaCO_3 \rightleftarrows CaO + CO_2$, the dissociation pressure becoming equal to that of the atmosphere at 812°, so that at temperatures above this the carbon dioxide may be completely driven off. This reaction is carried out in the lime kiln in the manufacture of pure lime and hydraulic lime, and in the cement kiln in the manufacture of cement. The product is white, amorphous, and friable. Its specific gravity varies from 3·08 to 3·30, being greater, the higher the temperature at which the lime was burnt. The chemical reactivity of lime, like its specific gravity, depends on the temperature at which it is prepared. Lime which has not been heated above 1000° "slakes" instantly on the addition of water, whilst a more strongly ignited product requires a considerable time for hydration. A similar inactivity is observed towards steam or carbon dioxide.

If heated sufficiently strongly in an electric furnace, lime may be fused. The melting-point has not been determined satisfactorily, but cannot be below 3000°. The molten lime solidifies to a crystalline mass, having perfect cubic cleavage, specific gravity 3·32, hardness 3–4 on Mohs's scale, and refractive index 1·82. A lump of such lime, placed in water, is dissolved very slowly at the surface, the hydration being so gradual that no appreciable rise of temperature is observed. On the other hand, the finely powdered crystals, mixed with water, appear to be inert, but after a few minutes the reaction sets in with explosive violence.[1] It appears, therefore, that the decrease in the reactivity of lime with increasing temperature of ignition is due less to a molecular change than to shrinkage and consequent reduction of surface. It is found that loose powdered lime, if kept for any length of time at 1400°, agglomerates to form crystals, which continually increase in size. Lime prepared at a low temperature is loose and porous, so that a large surface is presented to the action of the water, and hydration takes place very rapidly. The more strongly burnt lime is denser, and offers a smaller surface in proportion to its mass, the action is therefore confined to a smaller area and proceeds more slowly. Crystalline lime, being dense and non-porous, is naturally the least reactive.

This effect of high temperature must not be confused with another, observed in impure limes, derived from limestones containing clay. If the temperature be allowed to rise too high during the manufacture, the product slakes with difficulty, and is said to be "dead-burnt." In such a case, however, the temperature is still far below that needed to produce dense, and therefore inactive, lime, and the effect is due to a different cause, namely, the combination of a part of the lime with the clayey impurities, yielding a product intermediate in character between pure lime and hydraulic lime. At lower temperatures, these impurities remain uncombined as mechanical admixtures. There is, therefore, for each limestone an appropriate temperature of ignition, depending on its composition.

Lime does not occur in the free state as a constituent of well-burnt Portland cement. The effect of "free" lime, and the methods by which its presence may be

---

[1] A. L. Day, E. S. Shepherd, and F. E. Wright, *Carnegie Inst. Publ.*, 1906; *Amer. J. Sci.*, 1906, [iv.] **22**, 265. This important memoir will be often referred to in the sequel.

detected, are discussed in Chapter VI. The greater part of the lime is undoubtedly present in combination with other oxides, but another part may very possibly be present in a state of solid solution. Such solid solutions play a most important part in the physical chemistry of metallic alloys, and analogy would lead us to expect their presence in cements. Lime held in such a state of solution would be less reactive than when free, and would not exhibit the phenomenon of slaking, or violent combination with water.

CALCIUM HYDROXIDE.

The product of the hydration of lime by water is calcium hydroxide, $Ca(OH)_2$. We are justified in writing its formula in this way, instead of CaO,H_2O, because calcium hydroxide is a base, soluble in water, and amenable to investigation by ordinary chemical methods, and because it is found to present a complete analogy with other metallic hydroxides. It decomposes into lime and water at about 400° :

$$Ca(OH)_2 \rightleftarrows CaO + H_2O,$$

and is therefore not found in cements or other products which have been strongly heated. It is obtained in the slaking of lime as a white, amorphous powder, of specific gravity 2·078, this value probably varying with the character of the lime from which it was prepared. If crystallised slowly as in the hydration of cements, it forms large, well-developed crystals, which may be recognised by means of the microscope.[1] Tabular crystals of this kind have been isolated from cements after setting, and have been found to be hexagonal, with

---

[1] H. Le Chatelier, *Recherches sur les Mortiers Hydrauliques* (Paris, 2nd edn., 1904). This work contains the most important of the author's earlier papers, and will be generally quoted for convenience.

basic cleavage, $a : c = 1 : 1{\cdot}20$. Their specific gravity is 2·254, and hardness 2–3.[1]

Calcium hydroxide reacts with carbon dioxide to form calcium carbonate:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$

and this reaction plays an important part in the hardening of mortar. It only takes place in the presence of moisture. This is found to be true of other reactions of calcium hydroxide, the reason being that this compound is soluble in water, and successive small quantities of it are dissolved and precipitated by the other reacting substances. The solubility of slaked lime in water is small, but by no means inconsiderable, amounting to 1·34 grams per litre at 10°. It diminishes as the temperature rises, being only 0·88 grams per litre at 60° and 0·60 grams at the boiling-point.[2]

MAGNESIUM OXIDE.

Magnesium oxide or magnesia, MgO, is only present in small quantities in ordinary cements, being then derived from magnesium carbonate present in the original limestone in the form of dolomite, $CaCO_3,MgCO_3$. Limestones containing more than a very small proportion of dolomite are unsuitable for the preparation of Portland cements (see p. 20).

Pure magnesium oxide, if not heated to too high a temperature, possesses distinct hydraulic properties. Light, porous magnesia combines with water to form the hydroxide $Mg(OH)_2$, but without setting, whilst dense magnesia prepared at a full red heat sets, yielding a coherent mass, although of low tensile strength.

Magnesia does not form solid solutions with lime, the two compounds crystallising independently from their

---

[1] S. F. Glinka, *Zeitsch. Kryst. Min.*, 1909, **46**, 303.

[2] A. Guthrie, *J. Soc. Chem. Ind.*, 1901, **20**, 223.

fused mixtures. The double carbonate, dolomite if ignited at 300–400°, so as to decompose the magnesium carbonate while leaving the calcium carbonate unchanged, yields a product which sets with water and becomes very hard. A mixture of calcium and magnesium oxides, prepared by igniting dolomite very strongly, does not slake, but if finely powdered and mixed with water sets rapidly, and has been used as a substitute for plaster in making casts.

Magnesium hydroxide is only very slightly soluble in water, and in the solid state is very little acted on by carbon dioxide.

Silicon Dioxide.

Silicon dioxide, or silica, SiO_2, is the most abundant of all minerals, and is a component of the vast group of silicates, among which are the clays. It is present in all cements in a state of combination, and is then derived from the clay used as a raw material. It is also one of the components of pozzolana, and is used in the form of sand as a constituent of mortar.

Pure crystalline silica occurs in nature as quartz, and then forms hexagonal crystals, $a:c=1:1{\cdot}10$, specific gravity 2·653, hardness 7. The melting-point is about 1600°, but the molten quartz is so viscous unless much more strongly heated that the exact point is difficult to determine. When cooling from the liquid state, silica has a great tendency to assume a glassy form, without crystallising. If cooled under favourable conditions crystals are formed, but these crystals prove to consist, not of quartz, but of tridymite, another crystalline modification of silica which occurs in nature, and has a specific gravity of 2·318. Tridymite is only stable above 800°, and changes at lower temperatures into quartz, but the transformation is exceedingly slow unless some other substance, which accelerates the change, be present. Glassy silica is much less dense than either of the crystalline modifications, having a specific gravity of only 2·213; its crystallisation is therefore accompanied by a contraction of 16 per cent.

Quartz is chemically a very inert substance at ordinary temperatures, but when strongly heated it reacts vigorously with bases. Sand behaves in mortars as an indifferent material, binding the particles of lime or cement together mechanically, but not entering into chemical reaction with them. At high temperatures silica behaves as an acid oxide, and is capable of combining with bases to form silicates, and of expelling weaker acids from their compounds. Quartz will react with lime in the presence of water if heated under pressure, and this fact is of importance for the manufacture of sand-lime bricks (p. 204). The readiness with which action takes place is in the highest degree dependent on the surface presented by the quartz. For instance, a perfect crystal weighing 12·8 grams lost 0·25 per cent. in weight when heated with a lime paste for 48 hours at 180° in an autoclave, whilst a similar crystal, ground so finely as to leave no residue on a 100 sieve, lost 12·4 per cent. in weight under the same conditions. Further reduced to an impalpable powder by prolonged grinding, the quartz became so active as to be converted into colloidal hydrated silicic acid by merely boiling with water.[1]

A distinction is commonly drawn between soluble and insoluble silica, the former being readily attacked by caustic alkalies or by lime water, but there is no rigid line of demarcation between the two. Such substances as kieselguhr (infusorial earth) owe a large part of their reactivity to their highly porous character, presenting a large surface to the action of the reagent. Some forms of soluble silica contain combined water, but this fact apart, the differences of reactivity are to be referred rather to

---

[1] W. Michaëlis, paper read before the German Portland Cement Manufacturers, Berlin, March 9, 1909.

physical differences of texture and porosity than to actual differences of chemical character.

The combination of silica with water gives rise to the compounds known as silicic acids, which yield silicates by their reactions with bases. A great variety of formulæ have been assigned to these acids, but as no member of the series has yet been obtained in a crystalline condition, it is very doubtful whether they are to be regarded as more than colloidal hydrates, derived from one or two simple hydroxides. The silicic acids obtained by the decomposition of various natural silicates are now being compared by several investigators,[1] with results which are not yet decisive. We may therefore use the general formula, SiO_2,xH_2O, for the silicic acids, without attempting to determine the manner in which the water is combined. It appears to be established that the silicic acids prepared by the action of acids on different silicates differ from one another, but the colloidal character of the products renders all attempts to represent their differences by structural chemical formulæ unjustifiable.

ALUMINIUM OXIDE.

Aluminium oxide, or alumina, Al_2O_3, occurs in nature as corundum and in several other modifications, but none of these have any importance in connection with cement. On the other hand, alumina in a state of combination is a component of almost all natural and artificial cements. It behaves sometimes as an acid, and sometimes as a basic oxide, and in some instances it is difficult to decide whether it is to be reckoned among the acid or the basic components of a particular system. We may regard

---

[1] G. Tschermak, *Zeitsch. physikal. Chem.*, 1905, **53**, 349; *Sitzungsber. k. Akad. Wiss. Wien*, 1906, **115**, i. 217; *Zeitsch. anorg. Chem.*, 1909, **63**, 230; 1910, **66**, 199; J. van Bemmelen, *ibid.*, 1908, **59**, 225; E. Jordis, *ibid.*, 1905, **44**, 200; O. Mügge, *Centr. Min.*, 1908, 129; H. Le Chatelier, *Compt. rend.* 1908, **147**, 660.

it either as basic or as indifferent in the clays, in which it is combined with silica, and as acid in the aluminates, in which it is combined with lime or other bases.

Aluminium hydroxide, $Al(OH)_3$, is generally associated with variable quantities of water, forming a colloid. Although this compound may possibly be produced in the hydrolysis of aluminates, which is one of the processes constituting the setting of cement, it is probable that the reaction does not actually proceed so far, and that the hydrolysis results in the formation of calcium aluminates of indefinite composition, the proportion of lime occasionally becoming so small that the residue differs little from aluminium hydroxide.

FERROUS AND FERRIC OXIDES.

The oxides of iron have only a subordinate importance in the chemistry of cements. Ferrous oxide, FeO, is of a distinctly basic character, and may occur in combination with silica or other acid oxides in the raw materials. The part which it plays is entirely a subordinate one. If any unoxidised ferrous compounds remain in the cement clinker, the ferrous oxide must be regarded as replacing an equivalent quantity of other bases, such as lime. If air or oxygen obtains access to the mass, the ferrous oxide is converted either into ferric oxide, Fe_2O_3, which enters into reaction with the basic components, or into the black magnetic oxide, Fe_3O_4, which is chemically inactive, and only affects the colour of the product.

Ferric oxide, Fe_2O_3, on the other hand, has distinctly acid properties, closely resembling alumina in its chemical behaviour. The pure oxide melts at about 1565° in an oxidising atmosphere, and crystallises in rhombohedra resembling the native mineral. Ferrites may be prepared by fusing the oxide with bases.

CALCIUM SILICATES.

The compounds of lime and silica, being the most important constituents, not only of Portland, but of most other calcareous cements, have naturally been the object of numerous investigations. We may pass over those which make use of reactions in the presence of water. Products have been obtained by the addition of a soluble silicate to a solution of a calcium salt, or by mixing colloidal silicic acid with lime water, and analyses have been published from which formulæ have been constructed. Silicic acid is, however, so weak an acid that its salts are very extensively hydrolysed by water, and the precipitates thus obtained vary in composition, not only with the concentration of the reacting substances, but also with the extent to which washing is carried, and even with the time during which the solution and the precipitate are allowed to remain in contact.[1] It is certain that the substances thus described are more or less heterogeneous mixtures of compounds, often only partly crystalline and partly colloidal.

Much more satisfactory results have been obtained by bringing the reacting substances into contact at a high temperature, preferably one at which complete fusion can take place. It is not, however, sufficient to conclude from the homogeneous appearance of a solidified mixture that a definite compound has been obtained. A homogeneous solid solution may have been formed, or the structure may be so minutely heterogeneous, and the microscopic constituents so intimately intermixed as to escape observation. Two methods of determining the true character of the product are available, and are the same as those employed in the investigation of alloys, namely, thermal analysis and microscopical examination.

---

[1] E. Jordis and E. H. Kanter, *Zeitsch. anorg. Chem.*, 1903, **35**, 82, 336.

In the method of thermal analysis, mixtures of the two components in varying proportions are heated to fusion and allowed to cool, the melting and freezing temperatures being determined by means of a thermoelectric or of an optical pyrometer. Curves are then drawn, representing the variation of the freezing or melting point (the latter is usually the more easily determined in the case of silicates) with the composition. In the microscopical study, thin slices of the products are ground until transparent, and are then examined by transmitted light, either simple or polarised, as in the petrological study of igneous rocks. The most satisfactory results are obtained when the two methods are employed concurrently.

The members of the lime-silica series vary greatly in fusibility, but no mixture of these components melts below 1400° C., a temperature the attainment of which in laboratory experiments presents difficulties. It is necessary to heat by means of an electric resistance furnace, and to enclose the materials in a crucible of platinum, or, in the case of the less fusible mixtures, of iridium. Even under these circumstances it is impossible to fuse lime or the mixtures very rich in lime, which only become fluid at the temperature of the arc.

It is necessary to distinguish clearly between the true melting-point and the softening-point. In mixtures of two substances which do not form solid solutions with one another, the variation of the freezing-point with the composition of the mixtures is shown in Fig. 1. The freezing-point of the substance A is lowered by the addition of the substance B, and that of B by the addition of A. The mixture C, which has the lowest freezing-point of the series, is known as the *eutectic*. A mixture, the composition of which lies between A and C, begins to freeze at a temperature indicated by the point *d*, depositing crystals of the substance A. The removal of these crystals as the temperature falls alters the composition of the portion remaining liquid, until this reaches the eutectic proportion, when it solidifies at the temperature represented by point C. Conversely, if a solid mixture is heated, a part of it begins to melt as soon as the temperature represented by C is reached. As the temperature rises, the now liquid eutectic acts as a solvent for the portion remaining solid, and the last part of the mixture melts when the temperature *d* is reached. Now, if we have a solid mixture consisting of crystals of A with a small quantity of the eutectic, the melting of the latter will not be sufficient to render the mass liquid, but will cause some degree of softening. The larger the proportion of eutectic present, the softer the mass will become when heated to a temperature slightly above C. The softening-point of a mixture is therefore the temperature at which the eutectic present melts, and the degree of softening is an indication of the proportion of eutectic in the mixture.

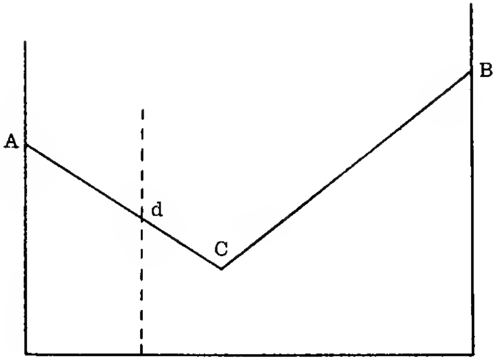


FIG. 1.

Solidification of a Eutectiferous Mixture.

Temperatures are frequently measured for industrial purposes by means of the so-called Séger cones, small pyramids with sharp edges, composed of clayey materials mixed in different proportions. When a certain temperature, which is constant for each cone, is reached, softening takes place, and the edges lose their sharpness, soon followed by the bending and drooping of the sharp apex. Attempts have been made to determine the melting-points of cements, slags, and similar products by forming them into such pyramids, and heating them in a muffle furnace together with Séger cones of known softening-point. Such a method of working is without scientific value. The effect observed is dependent on the melting-point of the eutectic and on the proportion in which it is present. The results thus obtained may differ by several hundred degrees from the true melting-point. For example, mixtures of lime and silica have been examined in this way, with the object of constructing a melting-point curve of the series, by P. Rohland and by O. Boudouard.[1] The figures given by the latter author for the melting-points of mixtures containing 60 to 80 per cent. of lime are almost certainly from 300° to 800° too low, the figures given merely representing the softening of a eutectic melting at 1430°, which is present in such mixtures.

An exceedingly careful series of determinations is due to Day and Shepherd, and is contained in the memoir cited on p. 54. The mixtures were heated in an iridium crucible in an electric resistance furnace, and the temperatures at which fusion occurred were determined by means of a Holborn-Kurlbaum optical pyrometer. These authors' results, which were controlled by a chemical and microscopical examination of the mixtures after solidification, are utilised in preference to others in the following discussion. Their equilibrium diagram is reproduced in Fig. 2.

Calcium metasilicate, CaO,SiO_2, is the best known member of the series. The mineral wollastonite, which

---

[1] *J. Iron Steel Inst.*, 1905, i. 339; *Rev. de Métallurgie*, 1905, 2, 441.

forms monoclinic crystals, has this composition. A fused mixture of lime and silica in this proportion, however, does not solidify to wollastonite, but forms pseudo-hexagonal crystals, known as pseudo-wollastonite. The latter substance is also formed when wollastonite is strongly heated, the change taking place with absorption of heat, but without any appreciable change of volume, both substances having the specific gravity 2·91.[1] Calcium

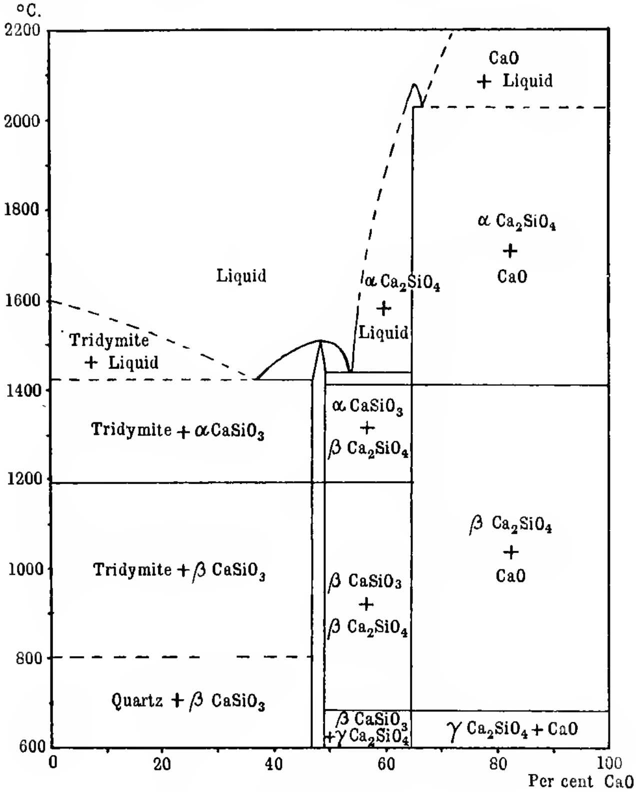


FIG. 2.

Equilibrium Diagram of Calcium Silicates.

---

[1] E. T. Allen and W. P. White, *Amer. J. Sci.*, 1906, [iv.] 21, 89.

metasilicate thus exists in two modifications, one of which (*a*) is stable between the melting-point, 1512°, and the transition-point, 1180°, whilst the other (β) is stable at all temperatures below the transition-point. Water is practically without chemical action on the metasilicate, a finely ground specimen absorbing only 0·9 per cent. of water in the course of several years' immersion,[1] although a considerable increase of volume takes place.[2] It is not a constituent of Portland cement clinker. A hydrated form of it, however, containing a variable amount of water, has been prepared by several different methods, and has been assumed to be present in cements and mortars after setting. It appears, in fact, to be the only calcium silicate which is capable of existing in the presence of water or of lime-water.[3] Hydrated silica, even in the presence of a large excess of lime, does not take up any more lime than corresponds with the metasilicate.

Calcium orthosilicate, $2CaO,SiO_2$, is undoubtedly present in cements and in slags. When prepared in a pure state it melts at about 2080°. The solidified mass, which is at first very hard, has the remarkable property of cracking and rapidly disintegrating at the ordinary temperature, falling into a fine, white powder, which has practically no hydraulic properties. This behaviour is observed, even in mixtures containing considerable proportions of foreign substances, and has been shown to be characteristic of this compound. The orthosilicate actually exists in three modifications, of which the α-form, which constitutes the mass immediately after solidification, crystallises in monoclinic prisms, with a hardness of 5–6. This modification is only stable above 1410°, below which it changes, without

---

[1] K. Zulkowsky, *Stahl u. Eisen*, 1907, **27**, 1098.

[2] O. Schott, *Dissert.*, Heidelberg, 1906.

[3] H. Le Chatelier, *Mortiers hydrauliques*, 1904, 52; E. Jordis and E. H. Kanter, *Zeitsch. anorg. Chem.*, 1903 **35**, 82.

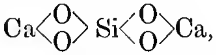
appreciable alteration of volume, into the orthorhombic β-form. At about 675° a second change takes place, the monoclinic γ-form being produced. Whilst the specific gravity of the α-orthosilicate is 3·27, and that of the β-form nearly the same, the γ-form has the low specific gravity of 2·97, so that its formation is accompanied by an increase of volume of practically 10 per cent. The disintegration is thus accounted for. The cooling of the mass is too rapid, under ordinary conditions, to allow the change from α or β into γ to take place. At the ordinary temperature, therefore, the orthosilicate is in an unstable condition, and tends to pass spontaneously into the stable γ-form. If this change begins at any point it spreads rapidly through the mass, heat being developed, and the great increase of volume which accompanies the change results in the shattering of the crystals into dust. It should be said that the β-crystals undergo this change more readily than the α, so that by quenching the mass from above 1410° so rapidly as to prevent the change from α to β from taking place, we obtain a more stable product than if we quench from below 1410°, within the range of stability of β. It will be shown below (p. 100) that the stability of the orthosilicate is greatly affected by the presence of other substances in a state of solid solution, and that mixtures within certain limits of composition, if quenched rapidly, may be preserved indefinitely without undergoing disintegration, and then possess hydraulic properties. This fact is of great importance in the treatment of blast-furnace slag.

The attempt has been made on several occasions[1] to explain the difference between the properties of the silicate $2CaO,SiO_2$ when quenched and when cooled slowly by assuming a specific difference of chemical constitution.

---

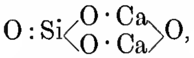
[1] K. Zulkowsky, from 1863 onwards. See his *Erhärtungstheorie der hydraulischen Bindemittel*, Berlin, 1901; A. Meyer, *Tonind. Zeit.*, 1902, **26**, 1895.

The modification which does not set with water is regarded as a true orthosilicate:



$$\mathrm{Ca}\!<^{\mathrm{O}}_{\mathrm{O}}>\mathrm{Si}\!<^{\mathrm{O}}_{\mathrm{O}}>\mathrm{Ca},$$

whilst the hydraulic substance obtained by sudden quenching is considered to be a basic metasilicate,



$$\mathrm{O}:\mathrm{Si}\!<^{\mathrm{O}\cdot\mathrm{Ca}}_{\mathrm{O}\cdot\mathrm{Ca}}>\mathrm{O},$$

the anhydride structure of which is in accordance with its tendency to undergo hydration. Such explanations, however, are purely speculative, in the absence of any trustworthy means of determining the chemical constitution of substances of this class, and it is safer to regard the orthosilicate as a polymorphic substance, capable of existing in three modifications, and to leave it for the present an open question whether the differences between the α, β, and γ forms are of a chemical or a purely physical character.

Hydrated calcium orthosilicates are unknown, water decomposing the compound, with formation of the metasilicate and calcium hydroxide.

The two silicates described above are the only compounds of lime and silica, the existence of which has been established with certainty, although several others are to be found in chemical literature. Certain of these, such as the silicate $4CaO,3SiO_2$, known as åkermanite, have been proved to be mixtures. A greater interest, however, attaches to the tricalcium silicate, $3CaO,SiO_2$, which has been assumed, since the early publications of Le Chatelier, to be the principal active constituent of Portland cement. It is certain that a mixture of the components in the calculated proportions, if heated to a sufficiently high temperature, yields an apparently homogeneous product, which has all the properties of a true cement. Great care is necessary in the preparation of the materials to obtain such a result, as the quantity of lime which is taken up is considerably less than that required by the formula, unless the components are very finely ground. Occasionally, such a mixture has been obtained in such an intimate form that the optical examination of thin slices indicates homogeneity of composition.[1] A very careful study with accurate optical appliances has shown, however, that such preparations consist of an intimate crystalline intergrowth of calcium oxide and calcium orthosilicate, which is readily mistaken for a homogeneous substance.[2] The evidence is practically conclusive against the formation of a tricalcium silicate from mixtures of lime and silica alone, or of a solid solution of lime in dicalcium silicate under the same conditions. It would be wrong to conclude from this that a tricalcium silicate is never present in cements or slags, as the presence of other substances—alumina, ferric oxide, alkalies, &c.—may give rise to profound modifications of the equilibrium, and it is quite conceivable that such a compound, incapable of existence in the two-component system, may be stable in presence of other substances capable of forming solid solutions with it. The microscopical appearance of crystals of alite (p. 86) lends some support to this view, the presence of a small quantity of aluminate being sufficient to render the crystals homogeneous.

CALCIUM ALUMINATES.

Most investigations of calcium aluminates have been conducted with products obtained by the interaction of substances in aqueous solution, but the instability of the compounds thus formed renders the results less certain than those obtained by the study of fused mixtures. A

---

[1] C. Richardson, *Portland Cement*, Atlantic City, 1903 ; S. B. Newberry and M. M. Smith, *Bull. Soc. d'Encouragement*, 1903, 641.

[2] Day, Shepherd, and Wright, *loc. cit.*

recent thermal investigation[1] on the same lines as that dealing with the calcium silicates described above has shown that several definite aluminates are formed, as is represented in Fig. 3. The two lowest aluminates, $3CaO,5Al_2O_3$ and CaO,Al_2O_3, are not likely to be present in cement, but the compound $5CaO,3Al_2O_3$, which has the comparatively low melting-point of 1386°, may sometimes be one of the constituents. It has distinct hydraulic properties, but its behaviour appears to depend on the rate of cooling from the liquid state, a rapidly cooled specimen being stable, whilst a slowly cooled specimen

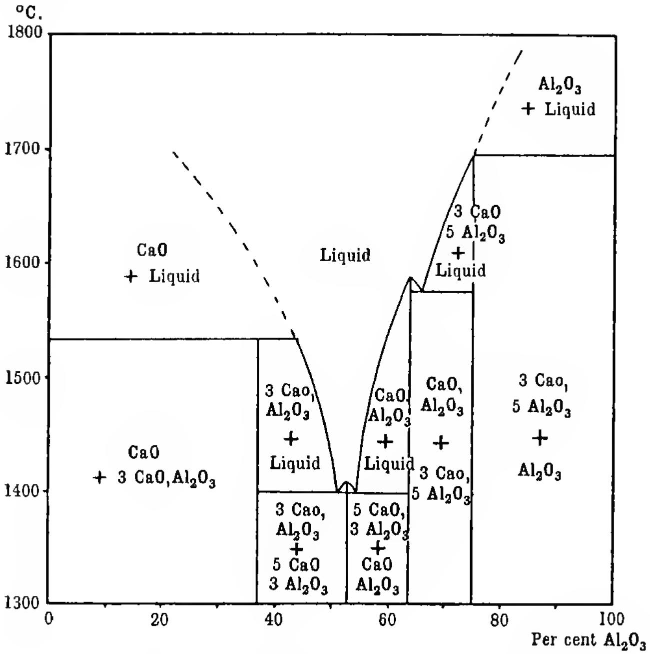


FIG. 3.

Equilibrium Diagram of the Calcium Aluminates.

---

[1] E. S. Shepherd, G. A. Rankin, and F. E. Wright, *Amer. J. Sci.*, 1910, [iv.] **28**, 293.

undergoes disintegration after setting.[1] The most important compound of the series is **tricalcium aluminate,** $3CaO,Al_2O_3$, which is formed from molten mixtures at 1531°, and has the specific gravity 3·04 and hardness about 6. It crystallises in the regular system and has no distinct cleavage, the fracture being conchoidal. If doubly refracting crystals are observed, lower aluminates are present. It has hydraulic properties, but test-pieces prepared with it expand after setting, although it is possible that this is due to the difficulty, in laboratory experiments, of obtaining preparations free from uncombined lime.

The only member of the series which has been definitely shown to be capable of existence in a hydrated form is the tricalcium aluminate, although several other salts have been described. It is obtained by dissolving the anhydrous aluminate in water and adding lime-water to hinder the hydrolysis of the somewhat unstable compound. It forms spherulitic clusters of slender crystals,[2] $3CaO,Al_2O_3,xH_2O$, the value of x being uncertain owing to the difficulty of isolating the crystals in a pure state. Different observers have found $x=8$ to 12.

A single magnesium aluminate[3] exists, having the formula MgO,Al_2O_3. Its melting-point is too high to be measured with accuracy.

Calcium Ferrites.

The ferrites of calcium play quite a subordinate part in most cements, which contain only small quantities of iron compounds. It is nevertheless desirable to take them into account in considering the constitution of a

---

[1] H. K. G. Bamber, *Trans. Concrete Inst.*, 1909, **1**, 106.

[2] H. Le Chatelier, *Ann. des Mines*, 1887, [viii.] **12**, 345.

[3] Shepherd, Rankin, and Wright, *loc. cit.*

cement, whilst it has been found possible to prepare true hydraulic cements from lime and ferric oxide alone.

A thermal analysis of mixtures of lime and ferric oxide[1] carried out similarly to Day and Shepherd's investigation of the calcium silicates, has shown that **calcium metaferrite**, CaO,Fe_2O_3 is only formed with difficulty, mixtures of this composition being generally heterogeneous after solidification. It is very stable towards water or acids, and is certainly devoid of hydraulic properties. The compound $3CaO,Fe_2O_3$ is hydraulic, whilst mixtures corresponding with **calcium orthoferrite**, $3CaO,Fe_2O_3$, like calcium orthosilicate, fall to powder after cooling. This points to a polymorphic change which has not yet been investigated.

The chemical inactivity of calcium ferrites in contact with water or solutions of salts is taken advantage of in the manufacture of cements intended for exposure to sea-water.

A hydrated calcium ferrite having the composition $3CaO,Fe_2O_3,xH_2O$ has been obtained by the action of lime-water on precipitated ferric hydroxide,[2] and may probably be present in cements containing iron after setting, as it is apparently also formed by the slow hydrolysis of ferrites richer in lime.

ALUMINIUM SILICATES.

Compounds of alumina with silica do not present themselves, so far as is known, in cement clinker or in hardened cement, the alumina in which is always present in combination with bases. The clay which forms so important a raw material of the cement industry consists, however, essentially of substances which approximate in composition to aluminium silicates. It is incorrect to regard ordinary

---

[1] S. Hilpert and E. Kohlmeyer, *Ber. deut. chem. Ges.*, 1909, **42**, 4581; *Metallurgie*, 1910, **7**, 193, 225.

[2] K. Zulkowsky, *Chem. Industrie*, 1901, **24**, 420.

clays as impure varieties of the definite mineral kaolinite, $Al_2O_3,2SiO_2,2H_2O$, which is a crystalline constituent of kaolin or china clay, a material which now finds a limited application in the cement industry, in the manufacture of white Portland cement (p. 34). Clay formed by the surface weathering of rocks under ordinary surface conditions is entirely different, both in its nature and in its origin, from kaolin. It has been shown[1] that clays, and the clayey constituents of many limestones, &c., are composed of crystalline fragments of undecomposed mineral silicates, together with amorphous (colloidal) products of alteration, in which the ratio of silica to alumina is always higher than in kaolinite. The plasticity of clay depends entirely on the colloidal properties of these constituents.

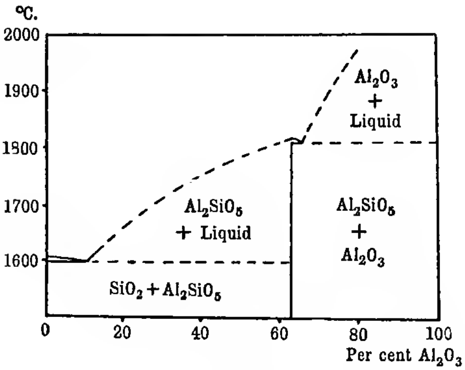


FIG. 4.

Equilibrium Diagram of the Aluminium Silicates.

The affinity between silica and alumina at high temperatures is so small that whatever compounds are present in the mixtures used for cement burning are readily decomposed by the lime with which they are heated, calcium silicates and aluminates being formed.

---

[1] J. M. van Bemmelen, *Zeitsch. anorg. Chem.*, 1910, **66**, 322. References will be found in this paper to earlier work on the subject.

There is also no reason to suppose that re-combination of silica and alumina takes place in cement during setting. The only compound of the series which can exist in fused mixtures is sillimanite, Al_2O_3,SiO_2, which forms well-crystallised prisms of specific gravity 3·03 and hardness 6–7. Two other minerals of the same formula occur in nature, namely, andalusite and cyanite, but both of these are converted into sillimanite when heated to 1300°. An equilibrium diagram, showing the relations of sillimanite to alumina and silica, is shown in Fig. 4.[1]

ALKALIES.

The quantity of alkalies present in cements is always small. We may assume them to exist in the form of sodium and potassium silicates, which form either solid solutions or glasses with other constituents of the cement. The existence of either compound in a free state is highly improbable, and there is no evidence of the formation of any definite double silicates. The mixtures of sodium and potassium silicates with the silicates of the alkaline earths have a great tendency to assume the glassy condition on cooling,[2] and whether glassy or crystalline, their effect on the microscopical and other properties of the clinker would be inappreciable. The presence of any considerable quantity of alkalies would have the effect of increasing the fusibility of the clinker, and at the same time of reducing its tendency to crystallise.

In contact with water, such compounds are readily hydrolised, so that alkaline compounds are set free on mixing with water. As will be shown in Chapter V., even small quantities of these salts may have an important influence on the setting properties of the cement.

---

[1] Shepherd, Rankin, and Wright, *loc. cit.* In this and the preceding diagrams, Figs. 2 and 3, those curves which are somewhat uncertain, owing to the difficulties of the thermal investigation, are drawn in dotted lines.

[2] R. C. Wallace, *Zeitsch. anorg Chem.*, 1909, **63**, 1.

SULPHIDES.

Calcium sulphide, CaS, is often present to a very small extent in cements, and is then derived from the reducing action of the fuel on calcium sulphate contained in the raw materials or formed, in a stationary kiln, from sulphur compounds in the fuel. Calcium sulphide is more characteristic, however, of blast-furnace slags. If the cement contains ferrous iron, this is converted into the green ferrous sulphide, which is generally considered to be objectionable from its liability to undergo oxidation, accompanied by expansion of volume.

MORE COMPLEX COMPOUNDS.

The number of native minerals containing three or more of the oxides described above to which chemical formulæ have been assigned is exceedingly large, and it is natural to seek to transfer these formulæ to the substances composing cement clinker. Such an application must be made with caution. The formulæ of minerals of this class rest as a rule upon the results of chemical analysis alone, whilst thermal investigations are essential to establish the identity of a chemical individual. It is certain that in many minerals described under distinct names the components are not present in a state of chemical combination, but in one of solid solution. We are not justified in assigning a definite chemical formula to a mineral species until its individuality has been proved on other grounds than that of mere homogeneity of structure. Researches in the metallography of alloys have demonstrated the value of thermal analysis in distinguishing between solid solutions and definite compounds, and the chemistry of the silicates still awaits a similar systematic treatment for its establishment on a thoroughly scientific basis. The experimental difficulties in the way of such an investigation have been alluded to above, but these difficulties are being gradually overcome, the special equipment of the Geophysical Laboratory at Washington having more particularly proved its value in work of this kind.

Calcium silicates and aluminates form solid solutions together which are discussed in the next chapter. No double compound is as yet known to exist. Calcium aluminate and calcium ferrite form solid solutions, and Le Chatelier states[1] that a definite compound, $3CaO,Al_2O_3,Fe_2O_3$, crystallising in long red needles, is also formed, any excess of aluminate in the mixture becoming visible as distinct colourless crystals.

Le Chatelier also considers it probable that a calcium magnesium aluminate exists, basing this conclusion on the fact that fused mixtures of the two aluminates are less readily attacked by water than calcium aluminate. This is, however, also consistent with the formation of a series of solid solutions.

Calcium and magnesium metasilicates form a single definite compound, the double **metasilicate**, $CaO,MgO,2SiO_2$, which melts at 1380° and forms crystals of specific gravity 3·275, identical with the mineral diopside.[2] A complicated series of solid solutions is also formed. Mixtures of the orthosilicates behave rather differently. Only mixtures containing less than 19 per cent. Mg_2SiO_4 disintegrate completely on cooling, as the pure calcium orthosilicate does, and from 25 per cent. onwards even partial disintegration is not observed. A double compound, MgO,CaO,SiO_2, identical with the native mineral **monticellite**, is formed in these mixtures. If more than 50 per cent. of magnesium orthosilicate is present, crystals of that compound, identical with the mineral **forsterite**, are found.[3]

---

[1] *Op. cit.*, p. 61.

[2] E. T. Allen, W. P. White, F. E. Wright, and E S. Larsen, *Amer. J. Sci.*, 1909, [iv.] **27**, 1.

[3] Hermann, *Mitt. k. Material-Prüf. Amt.*, 1906, **24**, 246.

CHAPTER IV

THE CONSTITUTION OF CEMENTS

In discussing the constitution of manufactured cements, it will be convenient to limit our remarks at first to two products, viz. Portland cement and the cement prepared by granulating blast-furnace slag. The technical importance of other materials, such as hydraulic limes, Roman cements, and "natural" cements, continually diminishes in proportion to that of the more thoroughly burnt products, and their chemistry is moreover of less interest, their components being largely the same as those of Portland cement, but in a less complete state of combination. Their chemical characteristics will be briefly summarised at the close of the chapter, together with an account of the materials employed as pozzolana.

One fundamental difference between the two typical cements selected for treatment presents itself at the outset. In the manufacture of Portland cement, the materials employed are heated together to a temperature at which sintering takes place, but the heating stops considerably short of complete fusion of the mass. On the other hand, the slag produced in the blast-furnace is formed from the reacting materials at a sufficiently high temperature to render it completely liquid, in which state it issues from the furnace. Now, chemical reactions between solid substances, even when these are very intimately mixed, proceed very slowly, and are likely to be incomplete after the longest period during which heating is continued in technical practice. One of the most conspicuous advances in the manufacture of

Portland cement since its invention in 1824 has been the progressive increase in the temperature of burning. Each successive improvement in the form of the cement kiln has had the effect of raising the temperature attained, and manufacturers now aim at thorough sintering, that is, at the liquefaction of the most fusible eutectic in the mixture. The question naturally suggests itself to the chemist, accustomed to heat his materials to fusion, whether it may not be possible to carry the improvement still further, and to heat the reacting materials so strongly as to melt them, thus ensuring a perfectly homogeneous and thoroughly combined product? Portland cements have been prepared on a laboratory scale, using platinum or iridium vessels and electric furnaces, and the dense, crystalline products thus obtained have proved to be true cements. The homogeneity of the product would have great advantages, especially those of complete trustworthiness and of the absence of those puzzling changes of setting properties which are apt to occur during the storage of even the most carefully prepared sintered cements. The passage from laboratory conditions to those of technical practice is admittedly a difficult one, but it would be rash to assume that it will not be made. The production of very high temperatures is now a necessary element of several metallurgical and other industries, and many of the problems connected with it have been solved. Consequently, although the temperature required to fuse cement is higher than that attainable in a kiln, it is quite possible that means may be found, either of enriching the air supply by removal of a part of its nitrogen, or of employing electrical heating as an auxiliary to the combustion of fuel.[1] The next step of fundamental importance in the Portland cement industry may prove to be in this direction.

[1] See B. Blount, *J. Soc. Chem. Ind.*, 1906, **25**, 1020. The fusion of cement had been previously suggested by W. Michaëlis.

The essential components of Portland cement are, as stated in the last chapter, lime, alumina, and silica, whilst magnesia and ferric oxide are only of subordinate importance. To determine the manner in which these oxides are associated and combined with one another in the clinker and finished cement has been the object of a very large number of investigations, proceeding along several different lines of approach. It is not proposed to review in this place the work which has been done, or the numerous and conflicting hypotheses which have been proposed to explain the facts observed.[1] Some of these, based on laborious and careful experiments, and devised with great ingenuity and scientific knowledge, have now merely an historical interest, having been rendered obsolete by the discovery of new facts or by the advances in our knowledge of physico-chemical laws, whilst others have been devised for the explanation of some limited class of facts, without proper consideration having been given to other facts inconsistent with the hypothesis. Like other branches of technical chemistry, the chemistry of Portland cement is unfortunately overburdened with contributions to its literature which have no permanent scientific value. It is impossible to speak dogmatically at the present time of the constitution of cements, and the most that can be done here is to give a summary of the most trustworthy investigations, to make some attempt to indicate the present state of our knowledge, and to indicate the directions which offer the greatest prospect of success in the future.

The author whose publications have had the greatest influence in determining the ideas held as to the constitution of hydraulic cements is H. Le Chatelier, whose

---

[1] Reviews and bibliographies of the subject are given by O. Schmidt, *Der Portlandzement*, Stuttgart, 1906; E. Jordis and E. H. Kanter, *Zeitsch. angew. Chem.*, 1903, **16**, 463, 485.

first paper on the subject appeared in 1883.[1] We owe to him the application to cement of the methods of petrography, as employed in the study of rocks. By the systematic investigation of microscopical sections, combined with chemical processes of attack, he was able to indicate with considerable certainty the character of the principal constituents, and to distinguish between those concerned in the initial setting and in the subsequent hardening of the cement. His work on setting is considered in the next chapter. His conclusions as to the microscopic structure were subsequently confirmed by the entirely independent work of Törnebohm,[2] who gave distinctive names, now very generally adopted, to the component "minerals" observed in thin sections of cement clinker. Synthetic experiments were also made by S. B. Newberry,[3] C. Richardson,[4] and O. Schott.[5] The following account is derived from their memoirs, supplemented by those of G. Gallo[6] and by recent observations of the author.

Cement clinker as ordinarily prepared is not a homogeneous substance, but consists of a fine-grained mixture of several solid phases. It is therefore impossible to draw conclusions of any value from a study of its chemical reactions alone. The observed action of a reagent in such a case is the sum of its reactions with the separate constituents, and depends on the proportions in which they are respectively present. Hence the only methods capable of yielding trustworthy results are those which enable us to deal with the individual constituents separately. The

---

[1] *Compt. rend.*, 1883, **96**, 1056; *Ann. des Mines*, 1887, [viii.] **12**, 345, and later papers.

[2] *Ueber die Petrographie des Portlandzements*, Stockholm, 1897.

[3] S. B. and W. B. Newberry, *J. Soc. Chem. Ind.*, 1897, **16**, 887.

[4] *Portland Cement from a Physico-Chemical Standpoint*, Atlantic City, 1903.

[5] *Dissertation*, Heidelberg, 1906.

[6] *Gazz. chim. ital.*, 1908, **38**, ii. 142, 156.

conditions have a close parallel in the case of the igneous rocks. It would be impossible to determine the structure of a granite by observing its behaviour towards reagents, using either fragments of the rock or a fine powder. The reactions with the quartz, felspar, and mica respectively would be superimposed and confused, and the resultant action would give only a meaningless average. Two methods of overcoming this difficulty are employed by petrographers. The rock may be crushed to such a degree of fineness as to release the constituent crystal grains, and the powder thus obtained suspended in liquid of suitable densities, so bringing about a separation of the lighter and heavier minerals. In skilled hands, this method is capable of giving very accurate results. It has been applied to cement,[1] but with less success, principally owing to the close intermixture and friable character of the constituents, rendering a separation impossible until the whole has been reduced to a fine flour, when the particles no longer settle satisfactorily after suspension in heavy liquids. The minerals composing such a rock as granite are comparatively tough, and are detached by a moderate degree of fine grinding, and it is only when these conditions are fulfilled that satisfactory results can be obtained by the suspension method.

The second method, which is more generally applicable, consists in examining prepared sections by means of the microscope. The specimen is reduced to such a degree of thinness by careful grinding that it becomes sufficiently transparent for examination by transmitted light. This is the usual practice in the study of rocks, and has been employed by many investigators in dealing with cements. A modification of the method is that employed in metallography, and consists in polishing a single surface only of the specimen, developing the structure by etching with a suitable reagent, and examining

---

[1] Törnebohm, *op. cit.*

by reflected light. These two methods, together with a third of occasional utility, which consists in examining the powdered substance by transmitted light, either alone or in a transparent medium, will now be described.

The grinding of thin sections for microscopical work was first employed in a published memoir by H. Witham in 1831,[1] in the study of fossil plants, but its introduction as a means of systematic research is undoubtedly due to H. C. Sorby,[2] who based upon it a method of identifying minerals in igneous and sedimentary rocks. Its application to petrography has given rise to an elaborate technique, enabling the operator to deal with brittle and friable rocks as well as with those which are hard and tough.

In preparing a section of cement clinker, a chip of suitable size, such as 1·5 × 1·5 × 0·2 cm., is ground on one of its faces until approximately flat. A carborundum block, used for grinding tools, is a convenient surface on which to perform the rubbing. Moistening with water must be avoided, on account of the readiness with which the cement is acted on chemically, but a little turpentine may be used to facilitate the grinding. A second carborundum block of finer grain is used to remove the scratches caused by the first, and the surface is finally polished with rouge and turpentine on a plate of glass. The smooth, mirror-like surface thus obtained is cemented to a small piece of thick glass by means of prepared dry Canada balsam, softened by heat. When firmly attached, the glass is used to support the specimen during the process of grinding the second face, which is treated in the same manner as the first. When the section is sufficiently thin, the second face is polished, and the Canada balsam

---

[1] *History of Fossil Vegetables*, Edinburgh, 1831. Witham learnt the method from William Nicol, who devised it in 1827.

[2] *Quart. J. Geol. Soc.*, 1858, **14**, 453.

softened by heat; the section is then pushed off the glass support, washed with turpentine, mounted on a microscope slip with a solution of Canada balsam, and covered with a cover-glass.

The grinding of so friable a substance as cement is much facilitated if the specimen is first boiled in a solution of Canada balsam in benzene or chloroform and dried before grinding. The pores are in this way filled up, and the toughness and tenacity of the specimen is greatly increased.

Both Le Chatelier and Törnebohm observed four different kinds of crystals in sections thus prepared. The names proposed by Törnebohm, of *alite, belite, celite,* and *felite,* have been generally adopted. Of these crystalline constituents, alite and celite are the most important, and probably the only essential.

Alite presents itself in sections in fairly well-defined crystals, whilst celite appears principally as a filling material between the alite grains. This circumstance at once suggests that the alite is the principal product, formed by a chemical reaction between the materials in the kiln, and that the celite represents the more fusible portion, which has been liquefied at the temperature of sintering and has then solidified as a eutectic mixture. Celite is darker in colour than alite, the difference being attributed to the accumulation of the iron of the cement in this constituent. The explanation is based on the fact that an increase in ferric oxide, but not in alumina, gives rise to an increase in the amount of celite. All the micrographic constituents of Portland cement, however, give the reaction for iron with an acid solution of potassium ferro-cyanide.

Alite is practically colourless in thin sections, and is found by optical measurements to belong to the rhombic system, although the crystals have a marked tendency to assume approximately hexagonal forms. Sharp outlines are found in well-burnt cements; rounded and indefinite forms point to insufficient burning of the clinker. The quantity of alite increases with the proportion of lime in the cement, so that cements low in lime contain a preponderatingly large proportion of celite.

Belite is an accessory constituent, found principally in cements poor in lime. It resembles alite, but has a darker colour, and commonly exhibits fine striæ, intersecting at angles of 60°. All its properties indicate that it contains less lime than alite, and the fact that such crystals are sometimes observed to be in a state of partial disintegration has suggested that they consist of, or at least contain as one of their constituents, the unstable dicalcium silicate (p. 67).

Felite forms rhombic crystals, and is not very frequently observed. It is found in blast-furnace slag, especially in that which has partly disintegrated. It seems probable that belite and felite are two forms of a single solid solution, corresponding with the hydraulic and non-hydraulic forms of dicalcium silicate respectively.[1] Felite may contain magnesium when this is present in the clinker, as it is found that calcium orthosilicate can hold a considerable quantity of magnesium orthosilicate, amounting possibly to 19 per cent., in solid solution, without alteration of crystalline form.

One of the means of determining the chemical nature of these crystalline constituents consists in examining a series of preparations of progressively varying composition, and observing the variation in the relative proportions occurring in the microscopic sections. Richardson, using laboratory preparations from pure materials, found that a mixture in such proportions as to allow three molecules of lime to each molecule of silica, and three molecules of lime to two molecules of alumina, contained both alite and celite, whilst a mixture containing much less lime showed an increased quantity of celite. Richardson

---

[1] H. Kappen, *Tonind. Zeit.*, 1905, **29**, 370.

concluded that alite was a solid solution of tricalcium silicate in tricalcium aluminate, and celite a solid solution of dicalcium silicate in dicalcium aluminate, both solutions having only a certain limit of concentration, as further additions of calcium aluminate caused the appearance of a new micrographic constituent. Such a condition never presents itself in commercial cements, which contain only a relatively small proportion of alumina.

Le Chatelier made the interesting observation that the "grappiers" or hard nodular masses which resist slaking in hydraulic limes, and yield a true cement when ground, consist almost entirely of alite, with a minimum quantity of inter-crystalline matter. The analyses which follow are given in his memoir:

	SiO_2.	CaO.	Al_2O_3.	Fe_2O_3.	CaO : SiO_2.
	Per cent.	Per cent.	Per cent.	Per cent.	Ratio.
Grey grappiers, Paviers .	26·0	66·0	3·0	1·2	2·75 : 1
,, ,, Teil . .	26·0	66·0	3·5	0·8	2·75 : 1
Green ,, Senonches .	25·5	68·0	3·6	0·7	2·85 : 1

the last column giving the ratio of the equivalents of lime and silica. As this ratio is not far below 3, the conclusion drawn from these figures was that alite was essentially tricalcium silicate, retaining only a small quantity of aluminate as an impurity. The fact that it is possible to obtain an alite almost free from alumina does not prove, however, that the alite of ordinary clinker is free from alumina, as it is characteristic of a solid solution that its composition may be varied within limits without change in appearance.

Crystals of pure alite were prepared by O. Schmidt and K. Unger[1] by heating a mixture containing about 67 per cent. of lime to fusion, when the whole mass became crystalline, and drusy cavities were found into

---

[1] O. Schmidt, *op. cit.*, p. 102.

which crystals of alite several millimetres in length projected. These alite crystals were proved microchemically to contain alumina as well as lime and silica. Two analyses gave the following results:—

	CaO.	SiO_2.	Al_2O_3.	FeO.	MgO.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
I.	67·33	23·50	3·83	2·28	2·34
II.	67·50	23·36	3·73	2·36	2·55

The ratio of acids to bases is very nearly 1:3.[1] The microscopical examination of these large crystals proved them to be completely homogeneous, so that we are fully justified in regarding them as a solid solution of calcium silicate and aluminate, but not in assigning to them any definite chemical formula. The general mass of the clinker was composed of similar alite crystals separated by microcrystalline aggregates of celite, which we have seen reason to regard as a eutectic mixture. This mass contained more alumina, slightly less lime, and considerably less silica than the alite, but it was not found possible to isolate pure celite for analysis.

The porous and friable character of Portland cement clinker makes the preparation of thin slices for microscopical examination by transmitted light a tedious and difficult matter, as the sections are apt to break into pieces before a sufficient thinness is reached. Consequently, sections of clinker commonly show a certain overlapping of the crystals, and it is only here and there, particularly in the neighbourhood of the air-cavities, that single isolated crystals can be observed and examined in polarised light, without errors due to the overlapping of

---

[1] The whole of the iron being in the ferrous state, we may include it in the bases. The total of the equivalents of bases then becomes 0·429 and that of the acids 1·293. This is preferable to Schmidt's mode of regarding the results.

different structural elements. These practical difficulties are avoided by adopting the method, already familiar to metallographists, of examining a single polished and etched surface by reflected light. Metals and alloys do not become transparent, however thinly they may be ground, and the method to be described is therefore the only one applicable to them. Specimens prepared in this way are better adapted to reproduction for the purposes of a permanent record by photography than transparent sections, and are for this reason also to be preferred.

One surface of the specimen selected, having been ground flat on a carborundum block as described above, is more finely smoothed by rubbing to and fro on the emery papers 000 and 0000 used in metallography. It is then polished with rouge or alumina on a piece of stretched "beaver" cloth, and finally cleaned by gentle rubbing on a clean piece of the same cloth. If now examined with a lens, the surface will be seen to have a good mirror-like polish, free from scratches. Under higher magnification, the outlines of the crystals may be dimly discernible, but the contrasts are too weak for convenient study. The structure is developed by rubbing lightly on a stretched cloth moistened with water, a little fine alumina being used as a polishing material. A few minutes of this treatment render the structure distinctly visible. For the further resolution of structure, a 1 per cent. solution of hydrochloric acid in alcohol is used.

For examination under a hand lens, diffused light falling on the specimen from a window at the side gives better results than a beam from a lamp, but when an objective of higher power is used, illumination by light from the side is very unsatisfactory, and it is necessary to make use of the appliance known as a vertical illuminator. In its most convenient form, the vertical illuminator consists of a short brass cylinder, which screws into the body tube of the microscope just above the objective, as shown in Fig. 5. A horizontal beam of light from an incandescent gas lamp or a Nernst electric lamp is thrown by means of a lens into the lateral opening of the illuminator at A. It then falls on a thin disc of glass B, which is mounted on a pivot about which it can rotate. In its normal position, it is inclined at an angle of 45° to the axis of the microscope and to the entering beam. A part of the light is reflected from the surface of the glass, passes down through the lenses of the objective C, and is focussed by them on to the surface of the specimen D. The reflected rays retrace their path through C, and passing through the glass plate B ascend the body-tube of the microscope, and after traversing the eyepiece reach the eye of the observer. The loss of light at the two reflecting surfaces of the inclined plate is considerable,

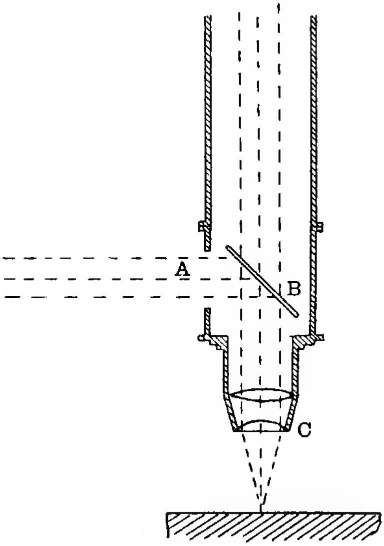


FIG. 5.

Diagram of Microscope arranged for Vertical Illumination.

but the definition obtained is greatly superior to that given by other forms of illumination, in which some form of prism takes the place of the plate. The simple apparatus just described is easily adapted for photomicrographic work, either with a vertical or a horizontal camera.

It is necessary, for examination under vertical illumination, that the surface of the specimen should be accurately perpendicular to the optical axis of the microscope, that is, that it should be parallel with the surface of the stage. This is readily effected by a simple device employed by J. E. Stead in the examination of metallographic specimens. The piece of clinker is laid, with the polished face downwards, on a clean sheet of glass. A brass ring of suitable height, and having exactly parallel ends, is placed round it, and a small piece of artists' plasticine is placed on the specimen. A glass microscope slip is then pressed down on the plasticine until its surface is in contact with the ring (Fig. 6). On inverting the slip, the specimen is found to be attached to it by the plasticine, and the polished surface is parallel with that of the glass. Several rings of suitable height for mounting specimens of varying thickness may be cut from a brass tube by a series of parallel cuts on a lathe.

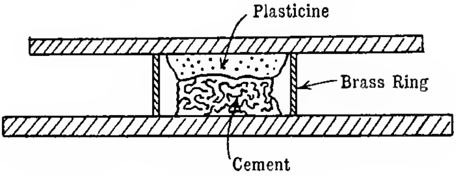
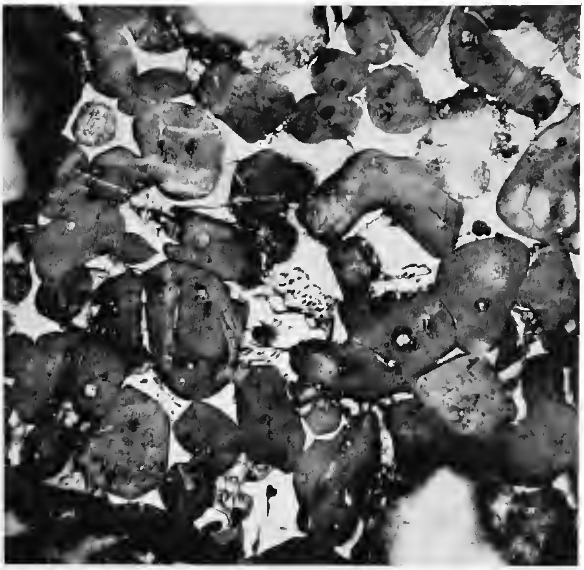


Fig. 6.

Mounting Specimens for Examination by Reflected Light.

The most convenient objective for the observation of cement clinkers is a 6 mm. ($\frac{1}{4}$ inch). It should be specially corrected for use without a cover-glass, as the reflections at the surface of a cover-glass when vertical illumination is used render the structure practically invisible. An eyepiece of medium power is the most convenient.

When an ordinary cement clinker, from a stationary kiln, is examined by the method just described, after etching with weak acid, it is easy to recognise that the greater part of the material is composed of crystals of a single constituent, separated by intercrystalline material. The general character of this structure is seen in Plate I. i. The crystals are those of the principal constituent, which is evidently identical with alite. The dark colour is not inherent in the crystals, but is due to the action of the reagent. Alite is more readily attacked by water and acids than the intercrystalline matter, and is therefore eaten away to some extent during the short period of immersion in the etching reagent, so that the crystals became depressed slightly below the surrounding level. The intercrystalline material is probably identical in the main with what has been described in transparent sections as celite. An examination of the photomicrograph shows that two different substances are present in the intercrystalline matter. That present in larger quantity is grey in colour, and has a dull surface like that of fireclay. The other, which fills the intercrystalline spaces in the same way as the grey material, is white, like hard porcelain. Close inspection reveals that both these substances have, here and there, a structure resembling that of eutectic mixtures in metallic alloys or igneous rocks. If the specimen is etched with water alone, without the application of an acid, the first mentioned material appears darker than the alite crystals, whilst the second has the same white porcelain-like appearance as in the other section. This effect is seen in Plate I. ii., which represents the same specimen of clinker as Plate I. i. The nature of this white substance is uncertain, and demands further



i. Etched with 1 %/₀ HCl. Vertical illumination. × 300 diam.

ii. Etched with water. Vertical illumination. × 300 diam.

CLINKER FROM STATIONARY KILN.

investigation. It is not observed in all clinkers. It is evident that the whole of the valuable properties of the cement reside in the alite, the intercrystalline matter being inert, as is shown by its resistance to water and acids.

Clinker from a rotary kiln has essentially the same structure, but as the heating and cooling processes are much more rapid than in the stationary kiln, and the granules of clinker are small, the structure is finer in grain. Plate II. i. shows a section of rotary kiln clinker, etched with dilute acid. The alite crystals are, as before, dark, and the intercrystalline matter light. The latter appears to be homogeneous, the cooling probably having been too rapid for the development of a distinct eutectic structure. The degree of porosity of the clinker is seen in Plate II. ii., a photomicrograph of the same specimen under a lower magnification. The large dark areas are gas-cavities, and it is evident that, in spite of the hardness of the clinker, its texture is extremely open, like that of pumice.

The Ratio of the Components in Cement.

It follows, from what has been said as to the nature of the constituents of cement clinker, that the relative proportions of the essential components, lime, silica, and alumina, may vary within rather wide limits without entirely changing the character of the cement. Within these limits the properties vary continuously with the composition, but if the limits are passed in either direction, an abrupt change takes place, and the essential character of the cement is altered.

An increase in the proportion of lime yields a stronger cement, until a limit is exceeded, beyond which the cement becomes unsound. An increase in the alumina hastens the setting, and the difference between slow-testing and quick-setting cements, the process of manufacture being the same, is mainly dependent on this factor. Ferric oxide, as has already been noticed, has an exactly similar chemical function to alumina, and in calculating the proportions of a mixture, the sum of these two components, $Al_2O_3+Fe_2O_3$, is taken into account, under the general name of "sesquioxides." Ferric oxide influences the character of the product in two ways which are independent of its chemical behaviour, by its colour, an excess of iron causing a deepening of the colour, and by its effect on the fusibility of the mixture, the ferrites lowering the melting-point more than the aluminates, so that the sintering-point is reached at a lower temperature when a part of the alumina is replaced by ferric oxide.

Alkalies also increase the fusibility, alkaline silicates, like the ferrites, acting as a flux towards the other ingredients. Magnesia also, if present in the clay, facilitates sintering.

Numerous formulæ have been devised to represent the limits of composition within which good Portland cements may be prepared. Le Chatelier,[1] starting from his assumption that the components contained in cement had the formulæ $3CaO,SiO_2$ and $3CaO,Al_2O_3$, considered that the upper limit of lime permissible in a clinker was fixed by the formula

$$\frac{CaO+MgO}{SiO_2+Al_2O_3}=3,$$

the molecular ratios of the components being taken, and not their percentages by weight.[2] The experiments of Newberry and Smith, and others, have shown that cements prepared in the laboratory are sound if the lime does not exceed the above limit, but that a small further addition of lime produces unsoundness. On the industrial scale,

---

[1] *Op. cit.*, p. 76.

[2] The molecular ratios are easily obtained by dividing the percentage by weight of each component by its molecular weight. The principal molecular weights required in cement calculations are: $CaO=56{\cdot}1$;

owing to the imperfection of the ignition, which does not allow the reaction between the components to proceed to completion, the permissible limit is somewhat less. Le Chatelier, considering that calcium ferrites caused unsoundness, omitted the ferric oxide from the reckoning, with the intention of leaving it unsaturated with lime. The great similarity between alumina and ferric oxide makes it desirable to reckon these two components together, and to replace Al_2O_3 in the above formula by $Al_2O_3+Fe_2O_3$, this sum being denoted by R_2O_3. The value 3 is, however, too high in practice, and the present British Standard Specification has as the upper limit of lime

$$\frac{CaO}{SiO_2+Al_2O_3}=2{\cdot}85.$$

This formula neglects the magnesia, a procedure which is justified by the fact that magnesium silicates do not behave as the equivalents of calcium silicates in cement. On the other hand, the total sesquioxides are generally taken into account rather than the alumina alone.

Le Chatelier also devised a formula for the permissible lower limit of lime based on the fact that the presence of dicalcium silicate, being liable to cause spontaneous disintegration, is to be avoided, but the formula was not based on experiment, and the lime limit set by it is so low as to be of no practical value. The manufacturer of a high-class cement aims at approaching the upper limit as closely as is consistent with soundness. A cement

$MgO=40{\cdot}3$; $SiO_2=60{\cdot}3$; $Al_2O_3=102{\cdot}2$; $Fe_2O_3=159{\cdot}7$. A cement containing 63·4 per cent. lime, 1·2 per cent. magnesia, 23·8 per cent. silica, and 6·8 per cent. alumina, has the ratio

$$\frac{\frac{63{\cdot}4}{56{\cdot}1}+\frac{1{\cdot}2}{40{\cdot}3}}{\frac{23{\cdot}8}{60{\cdot}3}+\frac{6{\cdot}8}{102{\cdot}2}}=2{\cdot}63$$

on this basis, or 2·51 if the magnesia is omitted.

prepared in a rotary kiln is capable of holding a rather larger proportion of lime in solution with safety than one made by the older process, on account of the somewhat higher temperature reached, and especially of the more uniform distribution of temperature.

The proportions in the above formulæ are molecular, and a calculation is therefore necessary to convert the ordinary proportions by weight into those required by the formula. Although the labour of such a calculation is small, especially when a slide-rule is used, the necessity has been avoided by the use of formulæ containing only proportions by weight, and such empirical formulæ are in use in many places. The most usual practice, especially in Germany, is to add together the percentages of lime and magnesia (sometimes also that of alkalies) and to divide the total by the sum of the percentages of acids—silica, alumina, and ferric oxide. The total is called the "hydraulic modulus" of the cement.[1] The German Association of Portland Cement Manufacturers requires in its definition of Portland cement that there shall not be less than 1·7 parts by weight of lime (magnesia is not taken into account) to one part of acids.

A cement containing 62·95 per cent. of lime, 23·34 per cent. of silica, 9·12 per cent. of sesquioxides, and 1·05 per cent. of magnesia, has the hydraulic modulus

$$\frac{62{\cdot}95}{23{\cdot}34+9{\cdot}12}=1{\cdot}93$$

if the magnesia is neglected, or 1·97 if magnesia is reckoned with the bases. Le Chatelier's ratio for the same cement is 2·44.

Yet another mode of expressing the composition has been proposed by S. B. Newberry,[2] who, taking into

---

[1] The expression is due to W. Michaëlis.

[2] *Cement Age*, 1905, 75.

account the fact that a cement rich in silica may safely contain more lime than one rich in sesquioxides, fixes the upper limit by the formula

$$\frac{CaO - R_2O_3}{SiO_2} = 2{\cdot}8,$$

percentages by weight being employed. This value is termed the "lime factor." The lime factor of the cement just mentioned is 2·3. In practice, the value is always considerably below 2·8. Should the sesquioxides be high relatively to the silica (more than 1:2·5), it is desirable to employ a high factor, in the neighbourhood of 2·7, in order to avoid rapid setting.

It is to be noted that such formulæ as the above are really independent of any hypothesis as to the exact composition of the compounds of lime with silica and alumina. Although in some instances first devised on the basis of theoretical ideas, they derive their chief support from analyses of cements which have proved their value in practice. When Portland cements of equally high quality, but prepared from different raw materials and often in different countries, are compared, a remarkable similarity in chemical composition, at least as regards the ratio of bases to acids, is observed. The theoretical bearing of this fact has already been indicated.

Free Lime.

A question which has given rise to much controversy is that of the possible presence of "free lime" in Portland and other cements. An unsound cement is one which undergoes a change at some time after setting, resulting in an expansion of volume, producing cracks or, in extreme cases, complete disintegration of the mass. This effect being observed particularly in cements containing more than a normal proportion of lime, and being very similar to that produced in the slaking of quicklime, was naturally attributed to the presence of uncombined lime in the cement before mixing with water. A method of detecting this "free" lime was therefore desirable. The earlier investigators merely agitated a sample of cement with water and filtered rapidly, then determining the alkalinity of the filtrate. The assumption was thus made that under these conditions the calcium silicates and aluminates were undecomposed. It is obvious, from what has been said above as to the properties of these compounds, that such an assumption is not justified. The calcium compounds contained in cements are so readily hydrolysed that lime is always extracted by water under such conditions. Many attempts have therefore been made to find a reagent or solvent for lime which should be without action on the silicates and aluminates. Solutions of sugar in water, of iodine, hydrochloric acid or ammonium salts in absolute alcohol, or of phenolphthalein in alcohol, acetone or chloroform have been employed by different investigators, whilst others have attempted to determine, from the quantity of heat developed during hydration, the manner in which the lime is combined.[1] It is unnecessary to discuss these methods, as one and all fail to yield any intelligible result, and the requirement that a cement shall "contain no free lime" has now disappeared from practically every specifiation. It is of interest, however, to consider the form in which lime must be present in order to produce expansion after setting. The addition of a small quantity of amorphous quicklime to a cement after grinding does not produce expansion, as slaking takes place rapidly during the process of gauging with water, and the lime is thus rendered harmless. Strongly ignited lime slakes slowly, so that its conversion into the hydrated form may not occur until after the bulk of the

---

[1] W. Ostwald and R. Blanck, *Riga Ind. Zeit.*, 1883.

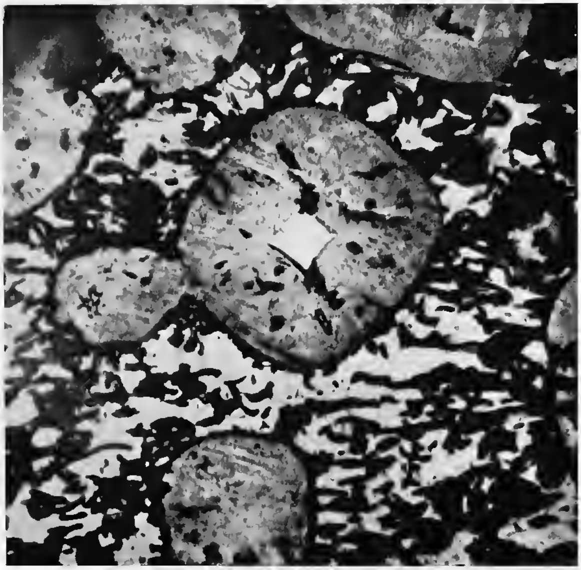
cement is set, and the resulting increase of volume may be sufficient to cause complete disintegration. Thus, by the addition of 1 per cent. of dense lime, prepared by igniting calcium nitrate, to a sound cement, an expansion of 10 per cent. may be produced. Artificial mixtures prepared in the laboratory, containing 70 per cent. of lime, are found by the microscope to contain crystalline cubes of lime, and such mixtures always expand after setting.

We know little of the properties of lime in a state of solid solution, but it appears probable that in this condition it reacts so gradually with water that a marked expansion is not produced, and that the lime causing expansion is that present in excess over the quantity required to saturate the solid solution of calcium silicate and aluminate. A thorough microscopical investigation of the clinker yielding unsound cements is desirable, with the object of determining whether the lime to which the defect is due is always present as a distinct crystalline constituent or not. It is safe to say that no chemical method of estimating or even of recognising free lime in a cement exists. For practical purposes, the term "free lime" should be abandoned altogether, and reliance should be placed, as is done in the leading modern specifications, only on carefully considered tests for constancy of volume after setting (see p. 153).

Granulated Slag.

Mixtures containing silicates, such as the blast-furnace slags, have a great tendency to assume a glassy form if cooled rapidly from the liquid state. The phenomenon is one of undercooling. The passage from the liquid to the solid (crystalline) state is accompanied by a rearrangement of the molecules, which take up a definite orientation in the crystals. The viscosity of molten silicates near their freezing-point is so great that this rearrangement does not take place unless a considerable time is allowed. If the time be insufficient, the particles retain their irregular (amorphous) arrangement, and, the viscosity increasing rapidly as the temperature falls, the slag passes from the definitely liquid state to a state in which the rigidity approaches that of a solid, but the slag is devoid of crystalline structure. Such a substance is called a glass. Glasses are thus not solids, in the strict physical usage of the term, but greatly undercooled liquids, having a very high internal viscosity. Below the freezing-point, however, the stable condition is that of a completely crystalline solid, and the glasses, being unstable, must tend continually to pass into the stable state, the tendency being restrained by the viscosity, which hinders the mobility of the molecules. At the ordinary temperature the mobility is very small, and a substance may persist indefinitely in the glassy conditions, although, given favourable conditions, devitrification (the passage of parts of the glass into the crystalline condition) may begin, and having once begun, may proceed more or less rapidly. This change is greatly facilitated by heat, so that, if a glass is heated for some time below its melting-point, devitrification has a greater opportunity of proceeding.

Slag which has been granulated in water has undergone such a rapid cooling as to be almost completely glassy. The slag granulated by projection from a revolving surface is less suddenly quenched, and is able to undergo partial change into the crystalline condition. Hence, if we examine slag granulated in this way microscopically, we find that different granules have different structures. Some are almost completely glassy, whilst others have developed a distinctly crystalline structure. We may apply the same methods of examination as when we are dealing with Portland cement, etching with a



i. Granulated slag. Commencement of devitrification.
Etched with 1 °/₀ HCl. Vertical illumination. × 300 diam.

ii. Eutectic structure in granulated slag.
Etched with 1 °/₀ HCl. Vertical illumination. × 300 diam.

dilute alcoholic solution of hydrochloric acid. Plate III. i. represents a portion of a granule which is mainly glassy. At certain points, however, devitrification has set in, and in the photomicrograph several points are seen, at which the development of radiating bundles of crystals about a centre (a crystal resembling melilite) has begun. Such spherulitic arrangements of crystals are common in devitrified glasses. Among igneous rocks, for example, rhyolites often exhibit such a spherulitic structure in course of development from an originally homogeneous glassy mass.

Some granules, with a more distinctly stony texture, prove on examination to have a more or less definite crystalline structure. Plate III. ii. shows an area lying between the crystals in such a specimen, in which a distinct eutectic structure is to be seen. The remainder of the surface examined consists of a very fine ground mass, evidently representing an early stage in the devitrification, whilst scattered crystals and patches of eutectic indicate a more advanced stage of the process. It is impossible to decide, without considerable further investigation, whether this eutectic is identical with that recognised in slowly cooled Portland cement clinker or not. It is certain that slag, either granulated or slowly cooled, does not contain any crystalline constituent resembling alite, the latter substance only being present in products rich in lime, that is, containing lime in excess of the quantity required to form dicalcium silicate. Many minerals have been recognised in crystalline blast-furnace slags, including augite and other members of the pyroxene group. Large prisms of a substance usually referred to gehlenite or to melilite (calcium aluminium silicates of the ortho-series) are among the most frequent constituents observed in microscopic sections. The crystals found in granulated slag lack the characteristic prismatic form of gehlenite and melilite, and their identity is doubtful. Only basic slags are suitable for granulation and conversion into a true hydraulic cement, and from these slags melilite is generally absent.[1]

There are two possible explanations of the difference between granulated and slowly cooled slag. One explanation is that the rapidly cooled material contains a basic calcareous constituent in a state of supersaturated solution, whilst on slow cooling the solution decomposes, giving up the excess of lime in the form of a basic substance. Free lime has been suggested, but it is unlikely that in a material containing altogether only 40–50 per cent. of lime, that compound should be liberated in a free state. The second explanation depends on the occurrence of polymorphic change in dicalcium orthosilicate (p. 66). The granulated slag would then contain the α-form, stable at high temperatures, whilst the slowly cooled material would have undergone the transformation, either during cooling or shortly afterwards, into the β-form. Both processes may occur simultaneously, but it is to be noted that the second explanation does not account satisfactorily for the difference in hydraulic properties, although the attempt to do so by means of assumed differences of molecular structure of the two modifications has been made (see p. 68).

NATURAL AND ARTIFICIAL POZZOLANAS.

All natural pozzolanas are of volcanic origin. They belong to the class of volcanic tuffs, and consist of a mixture of glassy and crystalline particles. The most abundant constituent is frequently a porous glass like pumice, but fragments of many crystalline minerals are also found. Tuffs are not identical in composition with the original volcanic lavas, but have evidently undergone

---

[1] See an elaborate series of analyses and photomicrographs by M. Theusner, *Metallurgie*, 1908, **5**, 657. The fullest account of the composition of blast-furnace slags is that by W. Mathesius, *Stahl und Eisen*, 1908, **28**, 1121.

considerable chemical alteration. This alteration is now generally considered to be due to the action of superheated steam below the earth's surface. The effect of the subterranean action has been to reduce the original rock to a fine sand or dust, at the same time converting much of the original material into a more chemically reactive modification, whilst lime and other basic components were removed by the combined action of steam and carbon dioxide.[1] The conversion has proceeded further in Italian pozzolana and in trass than in Santorin earth.

Some light is thrown on the genesis of natural pozzolana by a study of the artificial materials employed as substitutes. Powdered tiles, brickdust, and burnt ballast consist alike of strongly heated clay, that is, of impure aluminium silicate. A native aluminium silicate, such as kaolinite, $Al_2O_3,2SiO_2,2H_2O$, is inactive towards lime, but if dehydrated and heated to 700–800° it is converted into a true pozzolana,[2] and readily reacts with lime-water to form calcium silicates and aluminates. It is evident that the effect of the heating has been to loosen the combination of silica and alumina, and to set these components practically free. Under such conditions the alumina loses the weakly basic properties which it possessed in the kaolinite, and becomes an acid, comparable in strength with the silica which accompanies it. The altered condition is recognisable by the solubility in alkaline solutions which heating confers on the previously insoluble kaolinite.

The impure clays used in the making of bricks, tiles, and ballast, behave in an exactly similar way. The ferric oxide present in them reacts like the alumina. Silica, alumina, and ferric oxide are all present, to a considerable

---

[1] W. Michaëlis, *Chem. Zeit.*, 1896, **20**, 1024.

[2] O. Rebuffat, *Gazz. chim. ital.*, 1900, **30**, ii. 182. Michaëlis gives the temperature as 600–700°.

extent, in the natural pozzolanas in the active form, and are therefore soluble in alkaline solutions.

Natural cement and hydraulic limes do not lend themselves to the microscopical method of study, as they are not sufficiently compact to yield satisfactory sections. Even a cursory examination shows that they are mixtures of lime with substances formed from clay by ignition. They may therefore be regarded, in a general manner, as mixtures of lime with some form of pozzolana, the mixture being of course very intimate on account of the close intermixture of constituents in the clay or cement rock previously to burning. Any explanation, therefore, which can be given of the behaviour of Portland cement and of pozzolanic materials may be extended, with little modification, to cover the case of natural cements and hydraulic limes.

CHAPTER V

THE SETTING AND HARDENING OF CEMENTS

THE practical utility of all calcareous cements depends on the power which they possess, when mixed with water, of forming a coherent mass, which in course of time gives up the excess of water contained in it, and becomes hard and mechanically resistant. Such cements are employed in the form of powder, and when mixed with an appropriate quantity of water yield at first a plastic mass, capable of being moulded or spread over a surface, as in the construction of brickwork or masonry. The passage to the hard condition frequently takes place in two stages. In the first stage, the mass loses its plasticity and becomes more or less friable, so that if moulded or re-mixed with water the plasticity is not restored, or is restored only partially. In the second, consolidation takes place, the mass constantly increasing in hardness, until a stony texture is finally obtained. In the case of hydraulic cements, the change is accompanied by the disappearance of the permeability for water. These two stages are distinguished as the processes of "setting" and "hardening" respectively. In certain cases, such as that of plaster, no such division is observed, the setting process being a simple one.

The mechanism of the changes referred to is by no means the same in all classes of cements. The production of a coherent mass from a powdered solid and water may take place in several different ways, of which the following are of importance in this connection:—

1. The crystallisation of a substance from a super-

saturated solution, producing a mass of interlaced crystals;

2. The desiccation of a colloidal, semi-solid mass, or "gel";
3. A chemical reaction between two or more substances in presence of water, giving rise to a product which is (*a*) crystalline, or (*b*) colloidal.

The processes 3*a* and 3*b* may proceed simultaneously in the same cement.

Beginning with the first of these possible modes of setting, we find it well exemplified in the case of calcium sulphate, or **gypsum.** As far back as 1765, Lavoisier showed[1] that the setting of plaster of Paris was due to the recombination of the burnt gypsum with the water of crystallisation of which it had been deprived by heat, the hydrated salt then forming a confused mass of crystals, the intergrowth of which gave strength to the hardened plaster. The further explanation of the process is of later date, and is due to Le Chatelier. Further work has elucidated minor points, but has, in the main, confirmed the conclusions of these two chemists. The principal facts may be briefly summarised.

Gypsum, as found in the mineral condition, whether massive or in well-developed crystals, as selenite, has the composition $CaSO_4,2H_2O$. The water of crystallisation is lost when the solid is heated under atmospheric pressure, three-fourths of it being given off at 128°:

$$2[CaSO_4,2H_2O] = 2CaSO_4,H_2O + 3H_2O.$$

The remaining one-fourth is only lost at 194°. In the ordinary burning of plaster of Paris, the temperature is not allowed to rise above 130°, at which the dihydrate is converted almost completely into the hemihydrate. The same product may be obtained in the laboratory by

---

[1] *Compt. rend.*, 1765; *Oeuvres compl.*, iii. 122.

warming gypsum to 40-50° for 18 hours with concentrated nitric acid. Thus obtained, it forms distinct rhombic crystals. The hemihydrate dissolves readily in water, forming an unstable supersaturated solution, which tends to deposit crystals of the dihydrate, and such a deposition having begun at some point the series of changes continually repeats itself, the hemihydrate dissolving, becoming further hydrated, and then depositing crystals of the dihydrate. It is characteristic of crystals separating from such a supersaturated solution that they tend to group themselves in radiating bundles, each of which starts from some point as a centre. When ordinary plaster sets, the quantity of water used in mixing is so small that the particles are in close contact, and the resulting crystals form a confused and dense mass, the strength of which is due to the interlocking of these bundles of radiating prisms. It is impossible to obtain a clear photograph of such a mass, but by employing dilute alcohol instead of water, we may cause the hydration to take place so slowly that the crystals have time for development, and aggregates of an appreciable size are obtained. Plate IV. i. represents crystals of gypsum obtained in this way. The quantity of liquid is so large in proportion to that of solid that the centres of crystallisation are rather widely separated, and the prisms formed do not become interlocked. Under such conditions, the gypsum formed is not coherent. The presence of a strictly limited quantity of water is necessary to hardening, in order that crystallisation may take place from a strongly supersaturated solution. If plaster is mixed with a large excess of water, hydration takes place quite readily, but the crystals separate from a comparatively dilute solution, and the resulting mass, consisting of entirely isolated prisms, is loose and incoherent. The quantity of water generally used in mixing is not capable of dissolving more than one-thousandth of the calcium sulphate with which it is in contact, but by this process of dissolving the hemihydrate and depositing the dihydrate it suffices for the conversion of the whole.

The existence of the supersaturated solution on which the above explanation depends is not a mere inference, but may be proved by an experiment originally due to C. Marignac.[1] A quantity of plaster is shaken with water for five minutes and is then rapidly filtered. The filtrate is five times more concentrated than a saturated solution of gypsum, but it soon becomes turbid, deposits crystals, and ultimately attains the normal concentration.

As the specific gravity of the hemihydrate is 2·75, and that of the dihydrate is 2·32, the setting is accompanied by a contraction of about 7 per cent.[2] This appears at first sight to be contrary to experience, as the utility of plaster in the preparation of casts is known to depend on its power of filling the mould by its expansion and so taking a sharp impression of its surface. It appears probable that the setting really involves two distinct processes. The crystals of the dihydrate which at first separate are not identical with gypsum, which is monoclinic, but consist of a second, rhombic modification, which subsequently passes into the stable form.[3] It was found by van't Hoff that the process was actually accompanied by a large contraction, followed by a smaller expansion. Microscopical examination also proves that such a change from a rhombic to a monoclinic modification of gypsum really occurs.

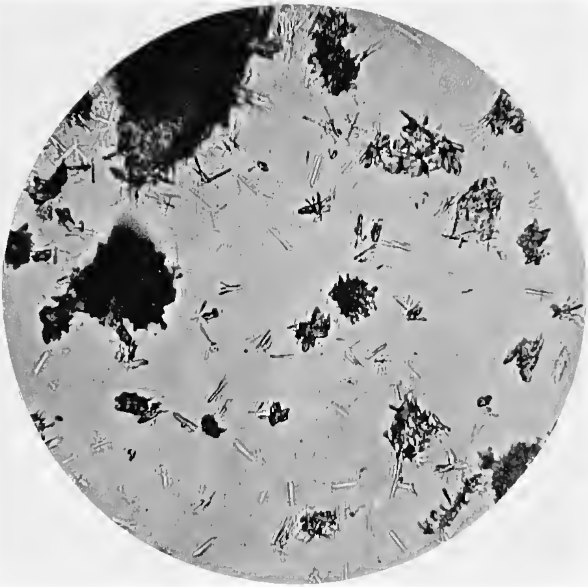
The above account fairly represents the course of events in the setting of ordinary plaster of Paris. The re-

---

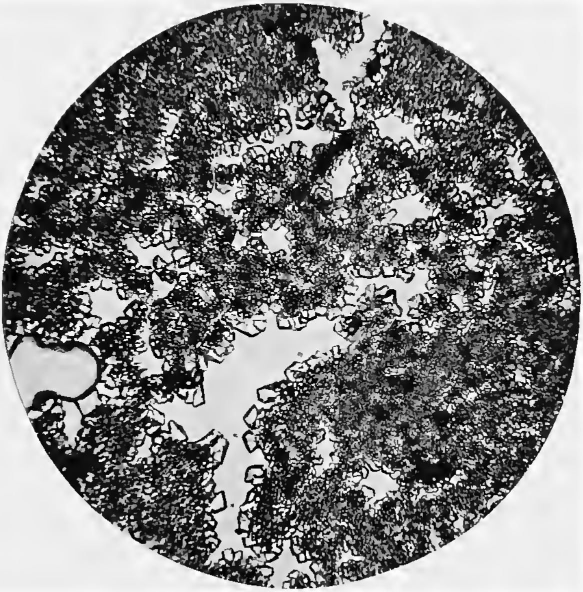
[1] *Arch. sci. phys. nat.*, 1873, **48**, 120.

[2] $2CaSO_4,H_2O = 290$; $H_2O = 18$; $CaSO_4,2H_2O = 172$; volume before setting $= \frac{290}{2·75} + \frac{3 \times 18}{1} = 159·5$; volume after setting $= \frac{2 \times 17}{2·32} = 148·1$, a contraction of 7 per cent.

[3] W. A. Davis, *J. Soc. Chem. Ind.*, 1907, **26**, 727. This memoir contains a review of the subject and references to the literature.



i. Crystals of gypsum
formed by the hydration of plaster. × 90 diam.



ii. Crystals of calcium carbonate
formed by the exposure of a solution of lime to the air.
× 90 diam.

lations between calcium sulphate and its several hydrates are, however, far less simple than they were formerly supposed to be.[1] Some of the modifications which have been observed are without practical interest, but others are of importance in connection with plaster and certain cements related to it. It is well known that if the temperature is allowed to rise too high in the burning of plaster, the gypsum becomes "dead burnt," and no longer hardens with water. In this case the whole of the water of crystallisation is expelled, and the anhydrous calcium sulphate thus obtained, like the native mineral anhydrite, $CaSO_4$, is not capable of forming a supersaturated solution, owing to the extreme slowness with which it dissolves in water, and therefore cannot set. Very slow dehydration of gypsum at a moderate temperature also yields an anhydrous product, differing from anhydrite in dissolving in water and in hardening, although more slowly than plaster of Paris. This soluble anhydrous calcium sulphate is a constituent of the hard plasters used for flooring, of the so-called "Estrich gypsum," and of most of the medieval plaster cements, all of which are characterised by comparative slowness of setting, and by attaining considerable hardness if kept moist during the process of setting. The details of the hardening of such plasters have been comparatively little studied. An account of some experiments in this direction is given by Gary.[2] It is known that the hydration of flooring plaster may require months for its completion. The addition of Estrich gypsum to ordinary plaster retards the setting of the latter, and this device may be employed to prepare a plaster having any desired rate of setting.[3]

The setting of plaster may be considerably modified

---

[1] See J. H. van't Hoff, E. F. Armstrong, W. Hinrichsen, F. Weigert, and G. Just, *Zeitsch. physikal. Chem.*, 1903, **45**, 257, for a summary of a long series of investigations on this subject.

[2] *Mitt. k. Material-Prüf. Amt.*, 1904, **22**, 50.

[3] O. Frey, *Tonind. Zeit.*, 1910, **34**, 242.

by the presence of soluble salts in the water used for mixing it. Some salts, such as potassium sulphate, accelerate the conversion of the hemihydrate into gypsum, whilst others, such as borax, retard it. It has been found[1] that the substances which accelerate the change are those which increase the solubility of gypsum, and conversely, that those which retard the change lessen the solubility. This action of catalytic agents is of great importance in the setting of cements. The same catalyst may affect different cements in very different ways. For example, potassium sulphate, which greatly accelerates the setting of plaster, retards that of lime and Portland cement.

The rapidity of setting is also influenced to a very marked degree by the addition of substances which interfere with the formation of crystals, that is, substances of a colloidal character. The addition of a sufficient quantity of such a colloid as gelatin to ordinary plaster completely inhibits the formation of crystals, whilst the addition of a much smaller quantity merely retards the setting. The "retarders" added in the manufacture of wall-plaster, for the purpose of prolonging the time during which the plaster may be manipulated without injury, are of a gelatinous character.

This mode of setting by crystallisation from supersaturated solution is not peculiar to calcium sulphates. Many other salts capable of existing in an anhydrous and in a hydrated form behave in the same way. The experiment is readily performed with sodium sulphate, or with the double sulphate of potassium and calcium. The ready solubility of these salts in water renders them useless as cements, but anhydrous barium metasilicate sets by a process of simple hydration, forming a cement of exactly the same character as plaster:

$$BaO,SiO_2 + 6H_2O = BaO,SiO_2,6H_2O.$$

---

[1] P. Rohland, *Zeitsch. Elektrochem.*, 1908, **14**, 421.

Although the existence of a solution of the anhydrous modification, supersaturated with respect to the hydrate, has not been directly proved, there can be no reasonable doubt that the mechanism of the process is identical with that of the setting of plaster.

The hardening of a **lime mortar** is totally different in character from that of plaster. No chemical reaction is involved, as the hydration of the quicklime is completed in the process of slaking, before the mortar is mixed. When the reaction $CaO + H_2O = Ca(OH)_2$ takes place, the quantity of water present is only sufficient to dissolve a small part of the lime, and not to allow of crystallisation. Crystals of calcium hydroxide are indeed found in many specimens of hardened lime mortar, but they owe their formation to subsequent solution in water and re-deposition, and are not a primary product of hydration. During slaking we must imagine the lime to form a solution with water, which is excessively supersaturated, and has only a momentary existence. Under such conditions the product of the reaction takes a colloidal form,[1] or, to use an older expression, it is amorphous instead of being crystalline. The hardening of the mortar then consists simply in a loss of water by the colloid. The process may be followed in the case of a thoroughly gelatinous colloid, such as silica prepared by the slow evaporation of its colloidal solution. The transparent jelly gradually loses water, becoming dull and opalescent. On further drying it becomes white like porcelain, and finally hard and dull white. The hardening of gelatinous silica is entirely due to desiccation. Lime does not form, like silica, a colloidal solution, but when freshly slaked it is to be regarded quite strictly as a colloid, and like other colloids, it loses water slowly and gains in mechanical strength at the same time. The drying of a plastic clay is another familiar example

---

[1] P. P. von Weimarn, *Zeitsch. Chem. Ind. Kolloide*, 1908, **3**, 282.

of the desiccation of a colloid. The dry mass thus formed is comparatively impervious to water, and the dried clay only takes up water again with considerable difficulty. The same thing is true of lime. Mortar made from fat lime has no hydraulic properties, but this is not due to the absorption of water to reform the original colloid, but to the solubility of lime in water, which causes it to be gradually washed out of the hardened mass.

The desiccation of a colloid is accompanied by considerable contraction of volume. Gelatinous silica, clay, or any other colloidal substance, if spread in a layer and dried, cracks into irregular fragments as the water disappears by evaporation, and similarly, a plastic mass of lime would shrink so much in drying that it would crack and lose its form. The shrinkage is lessened by mixing with an inert substance, such as sand, the particles of which become coated with lime, which adheres to them tenaciously. The cohesion of the dried colloid and its adhesion to the sand surfaces are the causes of the mechanical strength of mortar, which is able to resist not only the tensile stresses due to shrinkage, but also the external stresses applied to the mortar (see p. 166).

A further reaction occurs when lime mortar is exposed to air for any length of time. Carbon dioxide is absorbed, and a part of the calcium hydroxide is converted into calcium carbonate. The presence of moisture is essential to this reaction, as dry carbon dioxide is without action on dry lime. The calcium carbonate thus formed is crystalline, and the crystals, formed by slow growth in a colloidal medium, are closely interlaced, and form a coherent mass. This subsequent reaction is not essential to the formation of a hard mortar, as is sometimes supposed. The only essential process is the desiccation of the colloid, and the hardening by conversion into carbonate is merely a secondary reaction. It is confined to the outer layers of a mass of mortar, and by the formation of an impervious coating, hinders the access of carbon dioxide to the interior. It is therefore not surprising that mortar taken from old Roman buildings, if uninjured, is found to consist mainly of calcium hydroxide, even 2000 years of exposure to the atmosphere having been insufficient to convert more than a superficial layer into carbonate. Plate IV. ii. represents the crystallisation of calcium carbonate at the surface of a specimen of moist lime on a microscope slide, where air containing carbon dioxide has access to the preparation.

The slow hardening of lime mortar was formerly attributed, at least in part, to another cause, namely, to a chemical reaction between the lime and the silica (sand), forming calcium silicate. This is not the case. Lime does not combine with silica in the form of quartz under ordinary conditions of temperature and pressure. It is true that certain forms of silica react with lime under these conditions, as described below under pozzolana, but the silica is then present in a form differing from quartz in its far greater chemical reactivity. The fact adduced in support of the above statement, that ancient mortars commonly prove on analysis to contain considerable quantities of combined silica, is explained by the common practice in ancient times of adding pozzolana or other substances containing active silica to the mortar, or in some instances to the use of felspathic sand in place of pure quartz sand.

The formation of a crystalline compound by the chemical interaction of two substances may also lead to the formation of a hard mass, if the conditions are such as to favour the production of a supersaturated solution. An example of this is the magnesia cement or Sorel cement. Magnesite or dolomite is calcined, and the powdered product is mixed as required with a strong solution of magnesium chloride, sometimes thickened with starch, gelatinous silica, or other substance to prevent the solid magnesia from sinking too rapidly to the bottom of the pasty mass. Combination takes place with development of heat to form the compound $5MgO,MgCl_2,xH_2O$.[1] In all probability, the magnesium oxide and chloride first react in solution, and a supersaturated solution of the oxychloride is formed, from which crystals are deposited as in the setting of plaster. The product is hard, but is attacked by water. It is used for cementing glass and metal.

Several similar mixtures are known, and find a limited application as dental cements, &c. Thus zinc oxide yields a hard mass with a solution of zinc chloride or with syrupy phosphoric acid. The product is, in every such case, probably crystalline, although the crystals may be so minute and so closely interlocked as to resemble a glassy mass. Magnesium oxychloride, after setting as above, forms a mass which is microscopically demonstrable to consist entirely of crystals.[2]

The setting and hardening of **Portland** and other **true hydraulic cements** are far more complex in character than those of lime mortars or of plaster, as might be expected from the greater complexity of the burnt material. It is necessary in the first place to abandon the search for a chemical equation which shall express the whole of the changes occurring in the setting. We have to deal with a material which, as shown in the last chapter, is made up of several different constituents mechanically mixed, each of which has a somewhat complex constitution. Owing to the formation of solid solutions, the chemical components (the oxides) are not present in simple molecular proportions. When we consider further that the reaction with water is always very incomplete, so that even the most

---

[1] The value of x is uncertain, different investigators having given different figures.

[2] A. Krieger, *Chem. Zeit.*, 1910, **34**, 246.

perfectly mixed cement contains a large proportion of unchanged material after setting and hardening, and also that the formation of indefinite colloids undoubtedly plays a part, we see that it is hopeless to attempt to represent the process by any simple formula. It would not serve any useful purpose to enumerate the hypotheses which have been proposed, and reference will only be made to two or three which have rendered real service in the study of cements, omitting entirely all those which attribute setting and hardening to the formation of compounds containing definite amounts of water of crystallisation.

It was observed by Le Chatelier, in the important researches already several times cited, that thin sections of hardened cements, prepared with the necessary precautions, contain large, doubly-refracting crystals, which are readily determined to consist of calcium hydroxide. Taking into account the further fact that the only calcium silicate which is stable in contact with water is a hydrated form of the metasilicate, Le Chatelier regarded the principal reaction as consisting in the hydrolysis of a tricalcium silicate, with the formation of calcium hydroxide and hydrated monocalcium silicate. Writing x in place of the definite figure assumed by Le Chatelier for the number of molecules of water of crystallisation, we have:

$$3CaO,SiO_2 + aq. = CaO,SiO_2,xH_2O + 2Ca(OH)_2.$$

Evidently this equation can only represent a part of the change, as the aluminates also share in the hydration, hence they were assumed to form a more basic aluminate with water and a part of the lime.[1]

That free calcium hydroxide is one of the products of setting is a well-established fact. In addition to the

---

[1] The suggestion, essentially correct, that Portland cement is hydrolysed by water into free lime and "such compounds of lime with silica and of lime with alumina as can be formed by those substances in the wet way" had been made by A. Winkler, *J. prakt. Chem.*, 1856, **67**, 444.

microscopical proof referred to above, lime may be detected in water with which cement has been agitated, and an alcoholic solution of phenolphthalein colours a mass of cement pink after setting, proving the presence of a soluble base. The composition of the crystals has also been established by direct analysis after mechanical separation from the hardened mass. There is no such certainty about the microscopical recognition of the silicate and aluminate, the crystals described as such being very imperfectly characterised, whilst the greater part of the mass is apparently amorphous. The first "set" of the cement is attributed to the hydration of the aluminates, the silicates entering much more slowly into reaction and being chiefly concerned in the subsequent hardening.

According to this hypothesis the formation of a coherent mass takes place essentially in the same way as in the setting of plaster, by the production of a supersaturated solution, followed by the growth of interlaced crystals. It is a serious objection to such a view that the mechanical strength attained by hardened Portland cement is so greatly in excess of that attained by plaster, or by any other cement setting by simple crystallisation from a supersaturated solution, that it is hardly possible to conceive of the two processes as being the same in character. The reaction assumed to occur by Le Chatelier does actually occur in the case of barium orthosilicate, which sets with water, the reaction proceeding as follows:

$$2BaO,SiO_2 + 15H_2O = BaO,SiO_2,6H_2O + Ba(OH)_2,9H_2O,$$

being a simple hydrolysis, resulting in the formation of a hydrated barium metasilicate and of barium hydroxide. The resulting mass, at first partly amorphous, soon becomes entirely crystalline. The mechanical strength attained is very small, and the result lends no support to the view that Portland cement sets by means of such a process of crystallisation. Michaëlis has in fact found that cements may be prepared in the same manner as Portland cement, replacing calcium carbonate by barium carbonate, and the product sets perfectly to a hard mass, but the resulting silicates are crystalline and not colloidal, and are disintegrated and dissolved by water, like plaster. The product is therefore of no hydraulic value.

It is only since the introduction of the idea of colloidal precipitates into the chemistry of Portland cement that it has become possible to form a clear and consistent mental picture of the process of setting. The suggestion that "the calcareous hydraulic cements owe their hardening mainly to the formation of colloidal calcium hydrosilicate" was made by W. Michaëlis as far back as 1893,[1] but has been very slow in gaining acceptance. It is only since the great development of interest in the chemistry of colloids in the last few years, marked by the issue of a journal entirely devoted to the subject,[2] that the theory of Michaëlis has received attention. The theory so well explains the phenomena observed, and is in such good accordance with the results of microscopical investigations of cements during and after setting, that it must be held to contain at least the greater part of the truth.[3]

The action of lime on silica in the presence of water leads to the formation of a gelatinous mass, in which both lime and silica are present, but for which it is impossible to obtain a definite formula, the composition varying with the conditions of the experiment. A hydrated calcium metasilicate, containing an uncertain amount of water,

---

[1] *Chemiker-Zeit.*, 1893, **17**, 982.

[2] *Zeitschrift für Chemie und Industrie der Kolloide*, Dresden.

[3] Michaëlis' most recent views are summarised in *Der Erhärtungsprozess der kalkhaltigen hydraulischen Bindemittel*, Dresden, 1909. An English translation has been published by *Cement and Engineering News*, Chicago, 1909.

has been obtained by several investigators, as described on p. 66, but the formation of crystalline substances of this kind is always a secondary change, the initial precipitate being invariably gelatinous.

The formation of a gelatinous product in the action of water on cement may be observed under the microscope.[1] A small quantity of the powdered cement is mixed with water or with a 2 per cent. solution of gelatin to retain the particles in place, on a glass slide, covered with a cover-glass, and kept in a moist chamber, preferably so arranged as to exclude carbon dioxide, which introduces a complication owing to the separation at the edges of crystals of calcium carbonate. If examined from time to time, the originally sharp, angular forms of the particles of cement dust are seen to disappear, each particle becoming surrounded by a zone of transparent or semi-transparent gelatinous matter, which slowly increases in bulk. Plate V. i. shows an ordinary finely ground Portland cement, immediately after immersion in water, and Plate V. ii. represents the same specimen, after remaining in a moist chamber, to prevent evaporation of the water, for twenty-four hours. The great enlargement of the particles, due to absorption of water to form a gelatinous mass, or gel, is obvious.

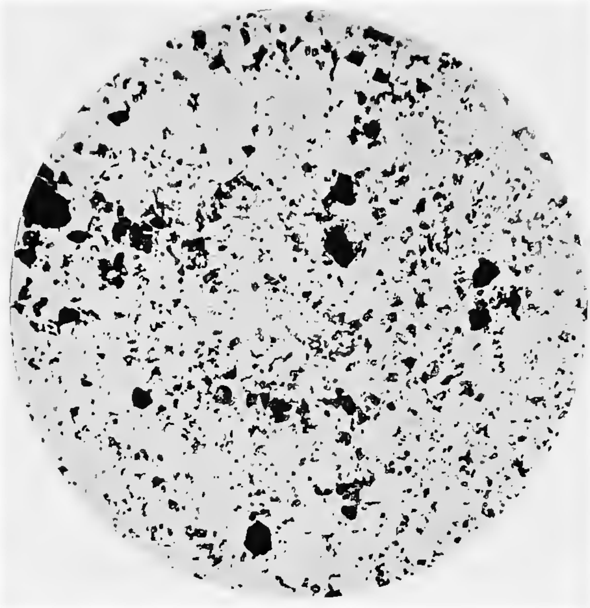
Since the absorption of water by a colloidal mass to form a gel is accompanied by a great increase in the volume of the mass, as is familiarly seen in the swelling of gelatin or starch grains, it has been questioned [2] whether a colloid theory is applicable to cements, which are known not to increase largely in volume during setting. The objection is really based on a misunderstanding.[3] Whilst the individual particles of cement become larger, the total volume

---

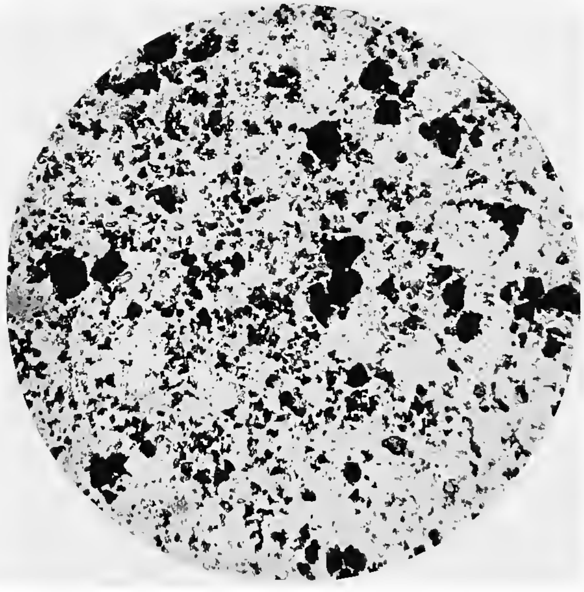
[1] H. Ambronn, *Tonind. Zeit.*, 1909, **33**, 270.

[2] C. Schumann, *ibid.*, 1909, **33**, 465; A. G. Larsson, *ibid.*, 785. See also A. Martens, *Mitt. k. Material-Prüf. Amt.*, 1897, **15**, 109.

[3] H. Kühl, *Tonind. Zeit.*, 1909, **33**, 556; W Michaëlis, *ibid.*, 615.



i. Portland cement, immediately after mixing with water. × 90 diam.



ii. Portland cement, 24 hours after mixing with water. × 90 diam.

cement + water, diminishes during the absorption, as is always the case when colloidal gels swell by absorption of water.[1] The net effect is a small contraction.

The course of events when Portland cement is gauged with water may now be briefly described.[2] We may, for the moment, omit all consideration of the gypsum which is always added in small quantity as a means of controlling the setting, and assume that the cement dealt with is composed entirely of lime, silica, and alumina. The essential hydraulic constituent, alite, is a solid solution of these three components. The action of water on the cement is, at least at first, confined to the alite, which is partly decomposed, the aluminates being first hydrolysed. The solution thus produced is supersaturated, and soon begins to deposit tricalcium aluminate, partly in a colloidal form and partly in crystals, according to the amount of water in the mixture, a large proportion of water favouring the production of crystals and a small proportion the formation of a gel. The excess of lime remains in solution, or a part may be deposited as crystals of calcium hydroxide. This process probably corresponds with the "initial set" of the cement.

The action of water on the calcium silicate contained in alite is much slower, and when hydrolysis occurs, the practically complete insolubility of calcium silicate in water causes it to separate in the colloidal form. The gel produced forms a coating round the cement particles, preventing the further access of water to them except after diffusion through the colloidal coating. If the cement does not become too dry, the reaction continues slowly, more and more of the alite being hydrolysed, and the lime set free being taken up ("adsorbed"[1]) by the gel,

---

[1] See, for example, the measurements of changes of volume during the swelling of starch, by H. Rodewald, *Zeitsch. physikal. Chem.*, 1897, **24**, 193.

[2] The view adopted is mainly due to W. Michaëlis, *op. cit.*, 1909.

which thereby increases gradually in density and hardness, and loses its plastic qualities. The water at first held by the gel is used up in this process of hydrolysis, and the gradual desiccation of the gel, which takes place even when the cement is immersed in water, brings about the gradual hardening of the mass.

When a specimen of hardened cement is ground and polished as described under the examination of cement clinker, a distinct structure is observed after polishing on a moistened cloth disc. Only two constituents are recognised. One forms small, irregular fragments, around and between which the second constituent lies as a filling material. It is not difficult to identify the two substances as unaltered grains of cement and the colloidal product of hydration respectively. Etching with acids reveals a structure in many of the grains, the structure, namely, of unchanged cement clinker. The definitely colloidal nature of the intergranular matter may be proved by immersion in a dilute solution of a dye, such as eosin.[2] Colloidal substances, or gels, absorb dyes, whilst crystals are inert towards them, so that it is possible to stain the colloidal constituents of a mixture without affecting any crystalline substances which are present.

That hardened cement possesses such a structure is itself a proof of the incompleteness of the hydration. The action of water is confined to a layer at the surface of each particle, and although the thickness of this layer gradually increases if the cement is kept moist, the interior of the grain is never reached. The more finely a cement is ground, the more complete is the reaction with water, because a small particle has a greater surface in propor-

---

[1] The term "adsorption" is now commonly employed to denote the withdrawal of a soluble substance from solution by a gel.

[2] E. Stern, *Ber. deut. chem. Ges.*, 1908, **41**, 1742; *Stahl u. Eisen*, 1908, **28**, 1542; *Mitt. k. Material-Prüf. Amt.*, 1909, **27**; 1910, **28**, 173.

tion to its volume than a coarse one. Stern's observations, however, refer to cement of normal fineness, and show that with such material nearly half of the volume of the hardened cement may consist of unaltered particles. Such results are very striking, and furnish a strong argument for the finest possible grinding of commercial cements. The non-hydrated mass in the centre of a particle takes no part in the chemical reactions of hardening, and serves merely as an inert body to which the colloid can adhere, a function which is performed as efficiently and more cheaply by sand.

Even a slight increase in the thickness of the layer of hardened gel probably causes a notable increase of mechanical strength, for an examination of microscopical specimens after seven and twenty-eight days and six months' hardening in water shows that the increase of area of the second constituent relatively to the first is very small, whilst the increase in strength is known to be large. Changes in the composition of the gel may play a part in the increase, as well as the mere growth in thickness.

It is well known that cement which has once hardened, if re-ground and gauged with water, sets a second time, and develops a degree of mechanical strength which, although inferior to that attained at the first setting, is nevertheless considerable. For example, a mass of cement which had lain ten or twenty years under water was finely ground and mixed with three parts of sand. Briquettes of the mortar had a tensile strength, after twenty-eight days, of 7·85 kilograms per sq. cm. (112 lb. per sq. in.).[1]

Even a second re-grinding develops a certain strength, showing that particles of alite still remain unconverted. Some old cement briquettes ground down to flour and extracted with a flourometer (p. 139), the residue being ground each time until the whole had been carried over by the air-current in the form of flour, was found to make

---

[1] H. Séger and E. Cramer, *Tonind. Zeit.*, 1908, **32**, 1746.

a strong mortar.[1] Mixed with ground oolite in the proportions 1:3, it gave a tensile strength of 105 lb. per sq. in. after twenty-eight days, and 105 lb. after two months.

As regards the subsequent conversion of calcium hydroxide into carbonate, the remarks already made in reference to lime mortars also apply to cement mortars. In the presence of moisture, carbon dioxide is absorbed from the atmosphere by the lime, but the action is confined to the surface, and the particularly hard and impermeable character of the cement gel hinders the penetration of the gas to anything more than a small depth. The reaction is unimportant as a factor in the hardening of cements.

THE HARDENING OF POZZOLANIC AND OTHER HYDRAULIC MORTARS

A mortar composed of lime, sand, and a natural or artificial pozzolanic material, hardens by a process which is in principle the same as that of Portland cement. The water dissolves a portion of the lime, so that the particles are surrounded by saturated lime-water. The alumina and silica of the pozzolana then react with the lime, forming a gel, which hardens by desiccation and adsorption of lime in the usual manner.

Pure silica may behave as a pozzolanic material under certain conditions. Experiment has shown that although quartz sand is practically inactive towards lime at the ordinary temperature, yet quartz reduced to an exceedingly fine powder and suspended in water is reactive. Several forms of native silica, including those which contain combined water, such as opal, hyalite, and siliceous sinter, and those of organic origin, such as infusorial earth and tabaschir, are also reactive. All of these modifications are soluble in alkalies, and may be regarded as desiccated gels. They are thus capable of absorbing water to form a true gel, and then of adsorbing lime to form the indefinite,

---

[1] E. P. Wells, *Concrete and Constr. Eng.*, 1908, **2**, 333.

colloidal calcium silicates referred to above. A natural or artificial pozzolana contains both silica and alumina (generally also ferric oxide) in the reactive condition, capable of swelling to form gels, and of hardening by desiccation and adsorption of lime.

The same explanation may be still further extended to the setting and hardening of hydraulic limes and natural cements. The clayey matters contained in these products are converted by burning into pozzolanic, that is, essentially acid, substances, which react in the same way as the silica just mentioned. Both hydraulic limes and that class of natural cements which is produced by burning at a low temperature, may be regarded as very intimate mixtures of lime with some variety of pozzolanic material. Their hydraulic properties depend on (*a*) the acid character, (*b*) the colloidal properties, of the clayey constituents. Their efficiency depends on the degree of availability of the silica, alumina, and ferric oxide that they contain, and may be in great part determined by the solubility of these constituents in alkalies.

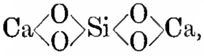
Substances which, on contact with water, become hydrolysed, the less basic residue then assuming a gelatinous form and undergoing the process of hardening described above, have been termed hydraulites.[1] The more basic calcium aluminates and calcium ferrites are of this class, as well as the solid solutions of lime and calcium silicate in cement. A part of the calcium in most of these compounds may be replaced by barium without greatly altering their properties. Moreover, certain other acid oxides yield hydraulites when heated strongly with lime. Thus, mixtures having the composition $4CaO,B_2O_3$ and $4CaO,Al_2O_3,B_2O_3$ are hydraulites, as might perhaps be expected from the close relationship of boric acid to alumina. Even tin oxide, in the mixture $2CaO,SnO_2$,

---

[1] The term is due to Zulkowsky.

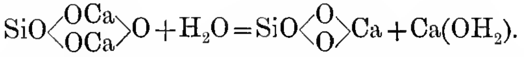
yields a white and hard hydraulite, whilst lead peroxide PbO_2, appears to be incapable of yielding a similar product,[1] and titanium dioxide, TiO_2, is also inactive.[2] It is possible that some of these negative results may be due to the temperature of burning having been insufficiently high to bring about chemical combination. In the case of the plumbate, complete hydrolysis evidently occurred in contact with water.

One puzzling question concerning the formation of hydraulites relates to the behaviour of calcium orthosilicate. Of the two modifications of this compound which are obtainable in ordinary experiments, the β-form, prepared by rapid quenching from a high temperature, is a true hydraulite, and sets with water to a compact mass, whilst the γ-modification, obtained by slow cooling, as the result of the spontaneous disintegration of the β-form,[3] merely yields a mud when mixed with water, and exhibits no tendency to set. This result is difficult to explain on the assumption that the β- and γ-forms are two physical modifications of the same compound. Zulkowsky[4] considers them to be chemically isomeric, the γ-form being a true orthosilicate,



$$\mathrm{Ca}\!\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\!\mathrm{Si}\!\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\!\mathrm{Ca},$$

with little tendency to undergo hydration, whilst the basic metasilicate stable at high temperatures, and only to be obtained at the ordinary temperature by rapid quenching, would be readily hydrolysed, yielding lime and the normal metasilicate:



$$\mathrm{SiO}\!\left<\begin{matrix}\mathrm{OCa}\\ \mathrm{OCa}\end{matrix}\right>\!\mathrm{O}+\mathrm{H_2O}=\mathrm{SiO}\!\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\!\mathrm{Ca}+\mathrm{Ca(OH_2)}.$$

Zulkowsky's theory has considerable plausibility, the two

---

[1] K. Zulkowsky, *Chem. Industrie*, 1898, **21**, 69, 96, 225; 1901, **24**, 317, 345, 369, 420, 445.

[2] A. Glaessner, *ibid.*, 1902, **25**, 186.

[3] See p. 67.

[4] *Zur Erhärtungstheorie der hydraulischen Bindemittel*, Berlin, 1901.

structural formulæ affording an attractive means of distinguishing between the active and the inactive form, but it is necessary to repeat the warning given in Chapter III., against making any assumptions as to the structural formulæ of solid inorganic compounds which are not known in solution, in the present absence of any trustworthy criteria of constitution. Zulkowsky is undoubtedly right in his contention that a number of different hydraulites should be compared, and that general conclusions should not be drawn from the behaviour of a single compound.

It is perhaps permissible to regard the difference between the two modifications from a purely physicochemical point of view. The quenched orthosilicate is in a metastable condition, whilst the slowly cooled, disintegrated compound is stable. It is a general rule that metastable compounds have a higher solubility than the corresponding stable modifications.[1] It is possible that the quenched orthosilicate is sufficiently soluble to yield a (necessarily unstable) solution, from which the gel may be deposited, whilst the stable orthosilicate, on account of its small solubility, does not yield a solution of sufficient concentration to form a colloidal precipitate. The nature of the molecular differences which determine polymorphic modifications is part of a much larger problem, into which it is unnecessary to enter here.

Lastly, it has been suggested that the state of solid solution of the lime may be responsible for the difference in reactivity of the two modifications. If a part of the lime is held at a high temperature in solid solution, and is thrown out of solution in the course of the polymorphic change, this may be held to account for the behaviour of the quenched and slowly cooled silicates on hydration. The thermal investigation of the lime silica mixtures, however, (p. 64) does not lend support to the view that

---

[1] See W. Ostwald, *Lehrb. der allgemeine Chemie.*

the orthosilicate breaks down into lime and a lower silicate at any temperature.

Chemical Factors affecting the Setting of Cements.

When Portland cement became a commercial product, experience proved that the rapidity of setting varied in different specimens of cement. The "setting time" (see p. 145) is a somewhat arbitrary magnitude, being the time which elapses after mixing with water before the mass can resist a certain arbitrarily fixed pressure without deformation. It serves, however, for the comparison of the setting properties of different cements. The distinction between "setting" and "hardening" is also more or less artificial. Nevertheless, the measurements of the heat developed during the process have shown [1] that two maxima commonly occur, corresponding roughly with the beginning of the setting and the hardening process respectively, and pointing to two distinct chemical reactions, one of which sets in much before the other. These two reactions have been identified with the hydration of the aluminates and silicates respectively. The greater the proportion of alumina, the more rapidly the cement sets. The quick-setting properties of Roman and similar cements are due to the large proportion of ferrites and aluminates that they contain.

The older varieties of Portland cement were slow in setting. This was due to several causes which co-operated to produce the same effect. In the first place, being incompletely burnt in some parts of the clinker, the ground product always contained some uncombined lime, which, on mixing with water, dissolved. As the initial setting depends on the hydrolysis of the aluminates, this hydrolysis is hindered, in accordance with the law of chemical mass-action, by the presence of one of the pro-

---

[1] M. Gary, *Mitt. k. Material-Prüf. Amt.*, 1906, **24**, 225.

ducts of hydrolysis in solution. Secondly, the ground cement contained the ash from the fuel, the salts in which exercised a catalytic retarding influence on the setting. The principal agent of this action was found to be the sulphates, derived from the sulphur of the fuel. Calcium sulphate has a remarkable effect in retarding the setting of cement. Its action has been shown[1] to be due to the formation of a definite compound of calcium sulphate and aluminate, calcium sulpho-aluminate,

$$3CaO,Al_2O_3,3CaSO_4,30H_2O\ (?),$$

which is very insoluble in water, so that the aluminate is withdrawn from solution, and converted into a form which takes no part in the setting process. Some doubt may be expressed as to the correctness of the above formula, as a cement is found to be capable of fixing, that is, rendering insoluble, a larger proportion of calcium sulphate than is required by the formula.[2] It is probable that adsorption phenomena complicate the result, a part of the sulphate being adsorbed by the colloidal aluminate.

Cement from rotary kilns does not contain ash from the fuel, and hence sets more rapidly than cement made from the same mixture of raw materials in a stationary kiln. To obviate this difficulty, it has been the general practice to add a small quantity, 1-2 per cent., of gypsum to the product, as a means of retarding setting. It has, however, less effect on such cements than on those made by the older process, a fact attributed by Candlot to the necessity of having a certain quantity of free lime in order that the gypsum may produce its effect. The influence of calcium chloride is greater than that of the sulphate, but no salt other than gypsum has yet been used for the purpose on a large scale.

---

[1] E. Candlot, *Bull. Soc. d'Encouragement*, 1890, 682.

[2] M. Deval, *ibid.*, 1901, 96.

It has already been said that the presence of lime at the moment of mixing with water also retards the setting. It is impracticable to obtain an intimate mixture of the cement with lime by mere mechanical addition at the time of grinding, but the same effect may be produced by the addition of water, which causes a partial hydrolysis of the more basic aluminates. Liquid water cannot be used satisfactorily, hence the process has never been successful, although often proposed. An entirely satisfactory result is obtained, however, by allowing steam to act on the clinker during the final process of grinding. In this process, which is due to H. K. G. Bamber, steam is admitted to the tube-mill. Owing to the friction of the balls and clinker, the temperature in the tube-mill is near to 85°. and the steam raises it still further to about 95°, and the cement is exposed to its action for about two hours. About 1 per cent. of water is absorbed, and the powdered product leaves the mill in a perfectly dry condition. Under these circumstances the cement is brought into a stable state, and a much smaller addition of gypsum suffices to retard the setting time to the required extent. One per cent. of gypsum is generally added, instead of the 2 to 3 per cent. formerly required. The action of the steam must be explained as a partial hydrolysis, at the surface of the ground particles, of the unstable aluminates, accompanied by the slaking of any particles of lime which may have been present in the clinker.

Rohland[1] attributes the action of gypsum to its catalytic influence on hydration, and points out that the salts which respectively accelerate and retard the setting of Portland cement are the same as those which accelerate and retard the hydration of pure lime. This view has much in its favour. It may be said that "catalytic action" is only a

---

[1] *Zeitsch. angew. Chem.*, 1903, **16**, 622.

term to cover our ignorance of the nature of the process, and that in all cases the immediate cause is the formation of a double compound, but there is some advantage in bringing the reactions into line with other, better studied, instances of catalytic influence. The experiments performed by Rohland are not conclusive, and the quantitative effect of different salts on the setting of cement deserves more exhaustive study. Numerous isolated measurements by different observers exist, but it is difficult to draw any definite conclusion from them at present.

Whatever may be the mechanism of the change produced on the addition of gypsum, it is a remarkable fact that the effect passes off when the ground cement is stored, the cement becoming once more quick-setting. On Candlot's hypothesis, that the presence of free lime is necessary for gypsum to produce a retarding effect, this result is explained as being due to the gradual removal of lime from the cement during storage by conversion into calcium carbonate by carbon dioxide from the atmosphere. The addition of a little lime should therefore again produce retardation, and this is found to be generally the case. Opposed to this explanation is the fact that a further addition of calcium sulphate, without lime, also retards the setting. If we regard the action of the gypsum as a catalytic one, the change on storage may be attributed to the combination of the agent with some of the constituents of the cement, rendering it inactive. That large additions of the agent may even have the effect of reversing its action is in favour of this view, such a behaviour being of common occurrence in catalytic reactions.

Cement which has been treated with steam at a high temperature, as described above, is not liable to undergo such changes on storage. The figures of Table XV. refer to a cement from a rotary kiln, ground to such a fineness as to leave only 5 per cent. of residue on a 180 sieve (see p. 136) and stored in bulk in casks.[1]

TABLE XV.

Cement.	Stored.	Setting Time in Minutes.			
		From Cask.		Exposed 48 Hours to Air.	
		Initial.	Final.	Initial.	Final.
Untreated (0·6 p.c. SO_3)	Freshly ground	Instantaneous.	5	Instantaneous.	3
" "	3 weeks	"	3	1	15
" "	8 "	"	3	0·5	10
" "	26 "	1	3	1	3
+1·5 p.c. gypsum (1·3 p.c. SO_3) .	Freshly ground	65	330	2	20
" "	3 weeks	69	240	1	4
" "	8 "	1	3	2	5
" "	26 "	2	60	2	5
Steamed, with addition of 0·75 p.c. gypsum (0·95 p.c. SO_3)	Freshly ground	55	255	40	195
" "	3 weeks	58	320	48	260
" "	8 "	50	410	55	390
" "	26 "	155	510	60	380

These figures show very clearly that the effect of gypsum in retarding the setting of a quick-setting cement disappears on storage in bulk, and very rapidly on exposure to air, so that the cement returns to its original condition, but that cement in which lime and readily hydrolysable compounds have been hydrated by means of steam are stable with a small addition of gypsum, the setting time increasing to some extent with storage or aeration. The effect of the treatment with steam on the soundness of the cement is described later, in Chapter VI.

The spontaneous changes undergone by cement during

---

[1] H. K. G. Bamber, *Trans. Concrete Inst.*, 1909, 1, 106.

storage are yet far from being thoroughly understood. In general, cements become more quick setting on storage, whilst the unsoundness due to free lime tends to disappear. The effect is not only due to the absorption of water and carbon dioxide from the air, for it is often found to take place during storage in closed vessels, out of contact with air. Le Chatelier assumes that in such cases hydrated aluminates or silicates, present in minute quantity on the surface of the grains, give up a part of their water to the lime present in a free state, but the explanation is hardly satisfactory. Another factor should not be forgotten. The solid solutions of which cement clinker is composed are probably only quite stable at a high temperature. The rate of cooling is too rapid for them to reach a state of complete equilibrium, and there must be a tendency for the unstable solutions to break down in course of time, and to rearrange themselves into more stable forms. This might well result in the setting free of the readily hydrolysed aluminates, which are chiefly concerned in the setting. Further, the alkalies present, although in very small quantity, are capable of influencing the setting time. It would be of great interest to discover the form in which they are retained in the clinker, and to determine whether that form persists during storage. The whole question of the spontaneous changes in ground clinker deserves further investigation.

CHAPTER VI

THE PHYSICAL PROPERTIES OF CEMENTS

THE necessity of distinguishing, by means of tests which may be rapidly applied in the laboratory, between different qualities of cement, without having recourse to practical trials demanding much time and trouble, has been the cause of most of the attention devoted to the physical properties of cement. The aim of investigators in this direction has been to fix the values of certain readily determined physical properties for cements which are found to be satisfactory in practice, in order that inferiority of manufacture, or adulteration with inferior material, may be detected by the deviation of the product from such standards.

The properties which have been generally selected for this purpose are: specific gravity; fineness; weight of a given volume or "apparent density"; "setting time"; and constancy of volume during hardening. The mechanical properties of the hardened cement or mortar, and the chemical composition of the material, call for separate treatment. The methods of determining the properties mentioned above, and the results to be expected, are described in the present chapter.

Purely external qualities, such as the colour, are not susceptible of quantitative expression. The colour of Portland cement should be a characteristic greenish or bluish shade of grey, yellow matter indicating insufficient burning. White Portland cement has a dull, chalky white appearance, whilst Roman and other similar cements are of varying shades of brown.

Specific Gravity.

The specific gravity of a substance is defined as the ratio of the weight of that substance to the weight of an equal volume of water. If we use the metric system, in which one cubic centimetre of water weighs one gram, the measurement of the specific gravity is reduced to the determination of the volume in cubic centimetres occupied by a given weight of the substance in grams. In the case of a powder such as cement, this determination may be made by introducing a weighed quantity of the cement into a flask having a certain known capacity when filled to a mark, and then measuring the volume of liquid required to fill the flask to that mark. On account of the action of water on cement, it is obviously impossible to use that liquid for the purpose, and its place is taken by paraffin or turpentine, which must be thoroughly dried by standing over quicklime before use. The determination of the specific gravity of a fine powder is an operation demanding considerable care and some skill, on account of the tenacious retention of air by the powder. In so finely divided a substance as a well-ground cement, each particle is surrounded by an "atmosphere" of adhering air, and this air is not at once dislodged when the particle is immersed in a liquid. Only by very careful shaking and tapping can the air be made to collect in the form of bubbles and to rise to the surface. The flask should not be shaken vertically, as some of the cement is thereby thrown against the sides, where it forms an unsightly coating on the glass.

The most convenient form of flask for determinations of specific gravity is that shown in Fig. 7.[1] It is broad and flat bottomed, with a graduated neck. The capacity, up to the lowest graduation, which is marked 14, is

---

[1] W. H. Stanger and B. Blount, *J. Soc. Chem. Ind.*, 1884, **13**, 455.

exactly 64 c.c. In making a determination, 50 c.c. of dry paraffin are introduced by means of a pipette, so as to avoid wetting the neck. Fifty grams of cement are then weighed out and introduced into the flask through a funnel. After tapping and gently shaking, the level of the liquid meniscus is read off on the graduated neck. The volume of liquid displaced is equal to the volume of the cement. If this is 14 c.c., the meniscus just reaches the first graduation. All ordinary Portland cements give a reading between 14 and 17 c.c. The specific gravity is obtained by dividing 50 by the reading. Thus, if the cement occupies a volume of 15·7 c.c., the specific gravity is $\frac{50}{15 \cdot 7} = 3 \cdot 18$. It is useless to attempt to express the result with greater accuracy by calculating a third decimal place.

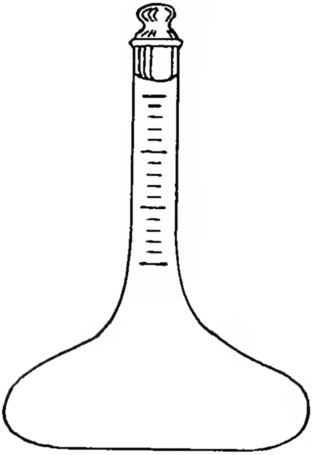


FIG. 7.
Flask for Determination of Specific Gravity.

The practice of introducing the cement first into the dry flask, and then adding the liquid, is not to be recommended, as the air bubbles are much less readily detached in this way. Several other types of apparatus have been proposed, in some of which the liquid is added from a burette until a fixed mark is reached, and the specific gravity is read on the scale of the burette, which is specially graduated, whilst in others a constant volume of liquid is taken, and cement is gradually added from a weighed quantity until the meniscus reaches a fixed mark, the remaining cement being then weighed and the quantity used determined by difference. The method first described is simpler than either, and more accurate than the last method.

A minimum value is prescribed for Portland cement in most specifications. The British Standard Specification requires a specific gravity of not less than 3·15 if the cement is freshly burnt and ground, or 3·10 if it is known to be at least four weeks old since the time of grinding. The latter condition is in recognition of the fact that all cements, when exposed to the air, undergo partial hydration and conversion into calcium carbonate at the surface of the particles, which thus become specifically lighter. This combined water and carbon dioxide may be removed by ignition, and it is therefore the practice, in some laboratories, to make a separate determination of the specific gravity of a sample which has been thoroughly ignited and allowed to cool. The value thus obtained is practically identical with that of the original ground cement.

The importance of the specific gravity as a criterion of the quality of a cement is very frequently over-rated. Cement being a rather dense material, gross adulteration with ashes, ground slag, or other material of decidedly lower specific gravity may be thus detected, but it is incorrect to assume that the presence of insufficiently burnt clinker will be indicated in the same way. Numerous experiments have shown[1] that well-burnt and underburnt clinker have nearly the same specific gravity after grinding. The underburnt product absorbs water and carbon dioxide more readily than good cement, and therefore becomes lighter after storage, but such an indication is uncertain. Even the Belgian natural cements, which it is often necessary to be able to distinguish from true Portland cement, have a normal

---

[1] D. B. Butler, *Proc. Inst. Civ. Eng.*, 1906, **166**, 342.

specific gravity after ignition, although from their great tendency to become hydrated, they are commonly light in the form in which they are brought into commerce.[1]

FINENESS.

The reduction of the clinker to a very fine state of division by grinding increases its value as a cementing material in two ways. In the first place, a fine powder is able to coat the surfaces of grains of sand or other inert material more completely than a coarse one, so that a more intimate contact of the components of the mortar is assured. In the second place, the reaction between the constituents of the clinker and the water used in mixing can only take place at the surface of the solid particles, further action being hindered by the accumulation of a layer of the products of reaction, coating the undecomposed material. Hence, the more finely ground the cement, and the greater the surface exposed in proportion to its mass, the more complete is the reaction with water, and the greater is the cohesion of the resulting product.

The coarser particles only participate in the reactions involved in the setting, to a slight depth below their surface, and the interior of each particle may be regarded as consisting of inert matter, as far as the setting process is concerned. A consideration of the relative costs of cement and sand will show that the particles so rendered inert represent a loss, since their function is equally well fulfilled by the cheaper material, sand. Other things being equal, a finely ground cement will give a stronger mortar than a coarser one with the same proportion of sand.

A few figures will illustrate the effect of very fine grinding on the strength of a cement. The cement as

---

[1] H. Burchartz, *Mitt. k. Material-Prüf. Amt.*, 1907, **25**, 277.

received in commercial condition was transferred to a ball-mill, and ground for varying periods, the products being used to prepare 1:3 mortar with a standard sand. The following tensile strengths were obtained from 28-day briquettes:[1]—

	Lb. per sq. in.
Cement as received	242·7
,, ground for 2 hours	294·4
,, ground for 5 hours	350·5
,, ground for 14 hours	380·6

The increase in strength is here very obvious. Neat cement briquettes, however, do not show this increase of strength, and are sometimes actually weaker, a fact which indicates that the improvement is mainly due to the more complete coating of the particles of sand by the fine powder.[2] The considerable tensile strength obtained when old masses of hydrated cement are re-ground and mixed with water, a fact elsewhere referred to (p. 119), is evidence that under ordinary conditions of grinding the full cementitious value of the material is not utilised.

The grinding of so hard a substance as cement clinker being a costly process, the more finely ground product is more expensive to produce than a coarser one, but in spite of this fact, the advantages of fine grinding are so great that there has been a steady improvement in this respect in the commercial brands of cement since attention was first directed to the matter.

The fineness alone is not a sufficient indication of the quality of a cement. Underburnt or aluminous material is more easily ground than well-burnt clinker, and readily yields a fine product. A cement, however, which

---

[1] J. A. Williams, *Trans. Amer. Ceramic Soc.*, 1908, **10**, 244.

[2] See a series of comparative tests by D. B. Butler, *Proc. Inst. Civ. Eng.*, 1898, **132**, 343.

is shown by other tests to be of good quality, is greatly increased in value by fine grinding, and the test is therefore one of importance which should never be omitted in the examination of a cement. It does not serve to distinguish between cements manufactured by different processes, as Portland, natural, and slag cements are commonly ground to a similar degree of fineness.

The fineness is determined by sifting through sieves having meshes of certain dimensions, and weighing the residue, or portion which fails to pass through each sieve after shaking. The sieves used for the purpose are denoted by the number of holes to the linear inch or to the square centimetre. Such a description is, however, insufficient, as the size of the mesh depends, not only on the number of holes, but also on the thickness of the wire. At present, woven wire gauze is used for the sieves, the wires being so spaced that the distance between two neighbouring wires is almost exactly twice the diameter of the wire. The British standard sieves have 76 and 180 holes per linear inch, the diameter of the wire being respectively 0·0044 inch and 0·002 inch. These two sieves have respectively 5776 and 32,400 meshes per square inch, and are therefore practically identical with the Continental standards of 900 and 4900 meshes per square centimetre, the British sieves having 893 and 5022 meshes in the same area. The gauze must be woven and not twilled.

Fig. 8 is a photomicrograph of a specimen of the fine gauze, having 180 holes per linear inch, woven by Messrs. Greening & Sons, Ltd., Warrington. The even spacing of the wires is essential in a sieve used as a standard.

The gauze is mounted on wooden frames, care being taken to avoid tension, which would distort the mesh. It is advisable to lay the gauze on the rectangular frame, and attach it by screwing thin strips of wood along the edges. Stretching over a cylindrical brass frame, and clamping by means of a ring forced over the gauze, inevitably results in distortion.

A close-fitting lid is used to cover the sieve during shaking. In making the test, 100 grams of the cement are weighed and sifted for 15 minutes, the sieve being shaken continually and frequently tapped to dislodge the particles clogging the meshes. At the end of this time the residue which has failed to pass through is collected and weighed. It is convenient to fit the two sieves together, the coarser being above the finer. A similar frame with wooden bottom serves as a receptacle for the fine particles, and the arrangement is closed above by a lid. In this way, simultaneous tests are made on the two sieves.

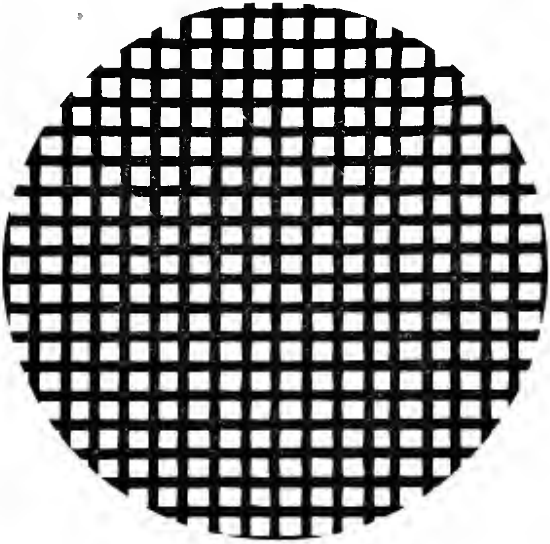


Fig. 8.

Standard Wire Gauze for 180 Sieve (4900 Meshes per sq. cm.) × 28 Diams.

The tedious operation of sifting by hand may be replaced by mechanical sifting, the apparatus employed being a modification of that due to Tetmajer. The sieves are mounted in brass cylindrical frames, attached one above another by means of bayonet catches. The frame holding the sieves in place is caused to rock on hinged arms by a crank, whilst a sharp jerk is applied to it periodically by a cam, which raises the frame against the pull of two springs. At each revolution of the cam, the springs pull the frame down sharply until it strikes the stop. This jerk has the effect of dislodging the particles which have collected in the meshes of the sieves. A counter is connected with the axle, and the machine is stopped after a given number of revolutions. The sifting is not quite as complete as when performed by hand, as the mechanical motion is not a perfect imitation of that given by the hand of a practised operator, but the apparatus may of course be left to itself.

The present British Standard Specification requires that the residue on the 76 sieve (900 per cm.^{2}) shall not exceed 3 per cent., and that that on the 180 sieve (4900 per cm.^{2}) shall not exceed 18 per cent.

There has been a steady improvement in the fineness of grinding of commercial cement during the last thirty years. The average results recorded by C. R. Redgrave and C. Spackman for 1879 show a residue of 10 per cent. on a sieve having 30 meshes per linear inch (140 per cm.^{2}), and 45 per cent. on one with 100 meshes per inch (1550 per cm.^{2}). According to B. Blount,[1] a residue of 10 per cent. on a sieve having 50 meshes per inch (385 per cm.^{2}) would not have been considered unreasonably coarse in 1886.

At the present time the fineness of the best brands of

---

[1] *J. Soc. Chem. Ind.*, 1906, **25**, 1083.

commercial Portland cement is considerably in excess of that required by the specifications. Cement is readily obtainable from a number of English firms which leaves a mere trace of residue on the 76 sieve, and from 10 down to 5 per cent. or even less on the 180 sieve. The same is true of the products of the best Continental works. Practically the whole of the German cements examined at Gross-Lichterfelde during 1909 fulfilled the requirements as regards fineness, the residue on the coarser of the two sieves being usually under 1 per cent.[1] One fifth of the Swiss cements examined at Zürich during 1906 left under 5 per cent. residue on the finer sieve.[2]

In order to determine the proportion of the finest, and therefore most valuable, particles in a cement, tests are occasionally made with still finer sieves. Thus, in certain laboratories, it is the practice to test all samples with a sieve having 200 meshes per linear inch (40000/in.^{2} or 6200/cm.^{2}) or 236 meshes per linear inch (55696/in.^{2} or 8630/cm.^{2}). The finer the sieve employed, the more troublesome is the operation of sifting, owing to the liability of the meshes to become clogged.

The attempt has often been made to determine the proportion of very fine particles, or "flour," by a process of wind-sifting, a current of air being employed to carry away the flour into a separate receiver, the coarser particles being dropped at an intermediate point. The simplest apparatus of the kind is Goreham's "flourometer," in which a current of air is blown through the cement contained in a single conical vessel, and the fine particles are carried up, and out through a lateral discharge pipe. A much more accurate apparatus was devised by M. Gary and Lindner,[3] permitting a separation into four grades.

---

[1] H. Burchartz, *Mitt. k. Material-Prüf. Amt.*, 1910, **28**, 1.

[2] F. Schüle, *Mitt. eidg. Material-Prüf. Amt. Zürich*, 1907, xii.

[3] *Mitt. k. Material-Prüf. Amt.*, 1906, **24**, 72.

Three vertical tubes, conical at the lower ends, are employed, and air is admitted to them by narrow glass tubes reaching nearly to the bottom of the cones. The pressure of the air is kept constant, at 100 mm. of water, a manometer being attached. The apparatus is set in action after 20 grams of cement have been introduced into the first funnel, and after the expiration of a certain time, the residues in the three tubes, and in a fourth vessel which collects the finest flour which is driven beyond the third vessel, are weighed. Repeated determinations with the same cement give very concordant results. Table XVI. contains a comparison of several cements by this method, the vessel I. being that in which the cement is originally placed. It is claimed that grading in this manner provides a means of distinguishing between different products which give similar results on sifting. The differences depend, however, rather on the methods of grinding adopted by the manufacturers than on the composition of the cements, and the test is therefore of doubtful value. The difference between two very similar cements, as regards their proportion of flour, may be determined, but with modern mills it is small, as is shown by the figures in Table XVII.[1]

TABLE XVI.

Cement.	Per cent. Residue on 4900 Sieve.	Per cent. Residue in Vessels.				Per cent. Loss.
		I.	II.	III.	IV.	
Portland	16	68·7	11·3	10·1	5·2	4·7
Iron-Portland . . .	12	63·2	1·5	12·5	18·4	4·3
Blast-furnace slag . .	8	53·9	11·6	12·4	17·3	4·8

The flourometer, although employed in some labora-

---

[1] A. C. Davis, *Proc. Inst. Civ. Eng.*, 1908, **175**, 280.

tories, has not come into general use, and the opinion of most workers is unfavourable to it, as the value of the results obtained does not appear to be commensurate with the trouble involved in making the test. For practical purposes, the cement passing through the finest sieve in use may be regarded as having high cementitious value, and a further classification of this portion according to size of grain appears to be superfluous.[1]

TABLE XVII.

	Residue on 180 Sieve.	Fine Grit.	Flour.	Total.
	Per cent.	Per cent.	Per cent.	Per cent.
Ground by tube-mill .	17·35	22·45	60·20	100
Ground by other mills .	17·53	27·33	55·14	100

LITRE-WEIGHT OR APPARENT DENSITY.

It was formerly a general practice to specify a certain "weight per bushel" for cements. This requirement has been long and deservedly abandoned, as concordant results could not be obtained, and the numerical values were found to be worthless as an indication of the quality of the material. In many laboratories, however, careful determinations are made of the weight of a definite smaller volume, usually one litre, of the powdered cement. The weight of a litre is frequently termed the "apparent density."

It must be pointed out that the "weight of a litre of cement" is an entirely meaningless expression, unless accompanied by an exact statement as to the conditions

---

[1] The grading by means of a current of air or liquid depends not only on the size of the particles, but also on their specific gravity, if unequal. The effect is more marked when a liquid is used than in grading by means of a current of air.

under which the determination is made. It is possible, by varying the manner in which the cement is filled into the measuring vessel, to cause the weight obtained to vary from, say, 1000 grams to 1700 grams, a range of 70 per cent. The weight depends on the form of the aperture through which the cement flows into the measuring vessel, the mode of bringing about its flow, the height through which it falls, and the shape of the measuring vessel, as well as on the state of rest or vibration in which the latter is maintained. All measurements must therefore be made with a standard apparatus and under exactly specified conditions of working.

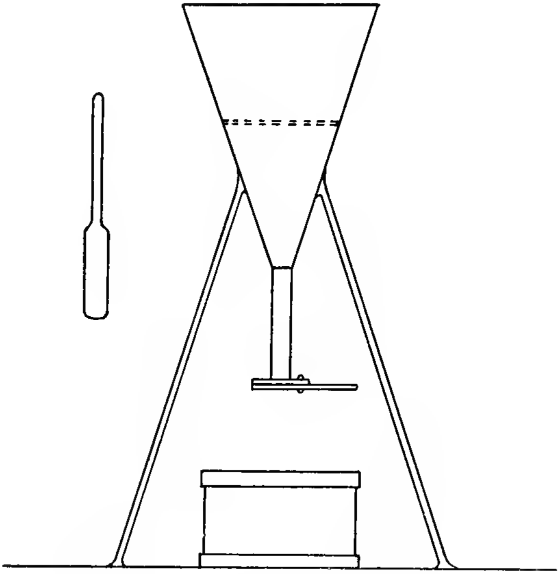


Fig. 9.

Apparatus for Determining the Weight of a Litre of Cement.

A convenient form of apparatus is shown in Fig. 9.

The cement is introduced into the conical sheet-metal funnel, which is provided with a perforated disc half-way down. By means of a wooden spatula, shown at the side, the cement is gently stirred so that it passes through the perforations, and falls down the neck of the funnel into the cylindrical brass vessel below, of internal diameter 12·5 cm. and height 8·15 cm., the capacity of which is one litre. Care is taken to avoid any jarring of the apparatus during the process of filling. In another form of apparatus, used at Zürich, a mechanical screw-feed is employed to deliver the cement to the measuring vessel. The simple arrangement described above is more general.

The weight of a litre of cement shaken down by vigorously tapping the side of the measure is sometimes taken. The weight is naturally much greater than that obtained by filling without shaking.

The weight of a measured volume of powdered cement, determined under standard conditions, is dependent on the specific gravity of the cement, and on the fineness of grinding. If two portions of the same clinker are ground to different degrees of fineness, a litre of the coarser product will be found to weigh less than a litre of the finer particles. How great a difference may be produced in this way is seen in Table XVIII.,[1] which shows the

TABLE XVIII.

Cement.	Weight of a Litre, Shaken.			
	I.	II.	III.	IV.
Portland	1·587	1·548	1·476	1·191
Iron-Portland	1·659	1·651	1·421	1·206

[1] M. Gary, *Mitt. k. Material-Prüf. Amt.*, 1906, **24**, 72.

weight of a litre in kilograms, in the shaken-down condition, of the fractions separated from some cements by the air-separator described in the last section, I. being the coarsest and IV. the finest fraction.

It is not possible to calculate the weight of ten litres, or of a cubic metre, or of any other volume, from the weight of a litre, or conversely. Any alteration of the volume used involves a change in the degree of packing, and it is therefore necessary, in comparing together different cements, to use only weights obtained from the same volumes under the same conditions. In Table XIX. the weights of a number of cements are given, (*a*) filled into a litre vessel without shaking, (*b*) filled into a litre vessel and shaken continuously, (*c*) filled into a vessel holding ten litres.[1]

TABLE XIX.

No.	1 Litre Filled.	1 Litre Shaken.	10 Litres Filled.	$\frac{\text{III.}}{\text{I.}}$
	I.	II.	III.	
1	1·013	1·658	11·05	10·9
2	1·102	1·805	11·98	10·9
3	1·179	1·882	13·23	11·2
4	1·190	1·951	12·63	10·6
5	1·207	1·962	13·64	11·3
6	1·239	1·994	12·89	10·4
7	1·272	2·091	12·89	10·1
8	1·310	2·110	13·50	10·3

The last column gives the ratio of III. to I., which is seen not to be constant. Hence, when the litre weight or apparent density is used as a means of calculating the weight of cement to be used in preparing mortar or concrete of a given composition by volume, the figures must

---

[1] Selected, and the last column calculated, from figures given by H. Burchartz, *Mitt. k. Material-Prüf. Amt.*, 1906, **24**, 291.

be understood as having a rough relative value only. It is not sufficient to multiply the apparent density by the number of litres in a cubic foot, and to accept the product as the weight of a cubic foot of cement. However, the weight of a certain standard cement needed to fill the measure used in the preparation of the mortar having been found once for all, the apparent densities of different samples may be used, on the assumption that the factor does not vary appreciably. This assumption is very nearly true if the quality of the cement only varies within narrow limits, and the determination of the litre-weight is therefore useful as a means of proportioning mortar, but is unsuitable for use as a test of the quality of cement.

When the "weight per bushel" test was used as a means of judging the quality of cement, the heaviest samples were considered the best. At the present time, when a specific gravity test is also applied, provided that the cement is not deficient in specific gravity, the lower its weight per litre the better, since this low "apparent density" is an indication of fine grinding.

As the litre-weight is also dependent on the specific gravity, it diminishes with the age and aeration of the cement, owing to the particles becoming specifically lighter by hydration and carbonation.

DETERMINATION OF THE SETTING TIME.

The chemical changes involved in the setting of cements have been discussed in Chapter V., and it now remains to describe the methods of determining the time occupied in the process of setting. Two periods are distinguished, the "initial set," or interval between the gauging and the partial loss of plasticity, and the "final set," or time required for the gauged cement to acquire such firmness as to resist a certain definite pressure. Formerly, the finger nail was used to produce the pressure, but the use of the standard "needle" introduced by Vicat is now, in its original form or in one of its modifications, almost universal. This instrument consists of a slender cylindrical rod, loaded with a definite weight. In all its usual forms, the cross section of the rod is 1 sq. millimetre. The cement having been mixed with water to "normal consistence," and formed into a cake in a cylindrical mould, the "initial set" is said to have been reached when the needle is no longer able to penetrate by its own weight through the whole thickness of the cake, and the "final set" when the needle, carefully lowered, no longer makes an appreciable impression on the surface.

The determination of the setting time is affected to a very marked degree by a number of circumstances: quantity of water employed in gauging, temperature, hygrometric state of the atmosphere, &c., and comparable results can only be obtained by working under standard conditions.

As regards the quantity of water with which the cement is gauged, a thin mixture sets more slowly than a stiff one, and it is therefore necessary to work to a standard consistence. The quantity of water required is different for different cements. The manner in which the gauged cement behaves when turned over with a spatula is not an accurate guide, and a definite rule is preferable. The following method is fairly satisfactory. About 300 grams of cement are worked to a paste with a quantity of water judged to be correct, the working with a spatula being continued for three minutes in the case of slow-setting, or for one minute in that of quick-setting cements. The paste thus obtained is filled into the split brass or ebonite mould of Vicat's apparatus (Fig. 10) which rests on a glass plate, and the surface is smoothed. The small needle is then replaced by a cylinder 1 centimetre in diameter. The whole moving part of the apparatus weighs

300 grams. When allowed to descend through the mortar by its own weight, the cylinder should come to rest with its base 6 mm. above the level of the glass plate, as indicated by the reading on the scale. Should the reading be higher or lower, the paste is too thick or too thin, and the quantity of water used is altered accordingly.

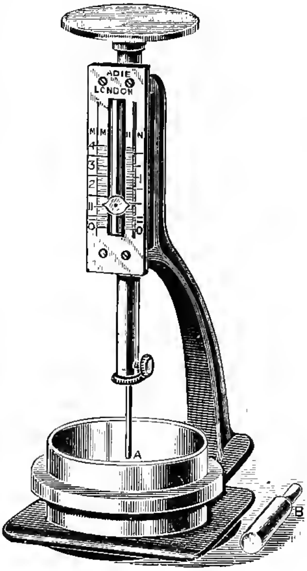


FIG. 10.

Vicat's Needle.

This method of determining the standard consistence, although very generally used, is objected to by many workers, who prefer to trust to personal judgment of the consistence. The Gross-Lichterfelde Testing Station employs a different method. The cement is mixed, with gradual addition of water, until syrupy consistence is reached, so that the paste, lifted by a spatula, runs off in long, thin threads. About 32–38 per cent. of water is required. Further additions of cement are then made, accompanied by vigorous stirring, until the surface becomes glistening, and the paste no longer adheres to the sides of the mixing vessel. In this case, also, much depends on individual judgment.

The temperature of the water should be 15° or 16°, and the tests should be made in a room the temperature of which remains as constantly as possible near to that point. The initial set is then determined with the same apparatus, the thick cylinder being replaced by the needle. At first the needle readily sinks through the mass and comes to rest on the glass plate, and the moment at which it ceases to penetrate completely, and is arrested at an intermediate point, is taken as the time of initial set.

The final set is determined by lowering the needle gently from time to time on to the surface of the cement. As the setting proceeds, the impression made is less and less marked, and the reading is taken when the needle just fails to make an impression. As the cement paste when filled into the mould is always covered with a thin, rather frothy scum, which yields under the needle and renders the determination inexact, it is advisable to invert the pat, and to make the impressions on the under surface, which was originally in contact with the glass plate.

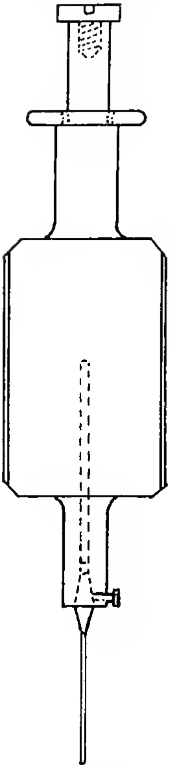


FIG. 11.

Needle prescribed by British 1907 Standard Specification.

The needle prescribed by the British Standard Specification of 1907 is of different pattern, as shown in Fig. 11.[1] The weight is considerably greater, being 1135 grams (2½ lb.) instead of 300 grams. Only the final set is determined. There is no stand, guide, or graduated scale. The apparatus is lifted by the loose collar, lowered gently on to the cement, and the spindle allowed to slide freely through the collar. Another form of the same apparatus has a spherical weight instead of the prismatic one, and a ring by which it may be hung from the finger, and so lowered vertically. The needle should always be applied at several different points, in order to guard against errors due to the possible presence of hard lumps in the cement.

Table XX. shows the influence of temperature on the setting time in minutes of two cements, of which A is a

---

[1] See Appendix I. for Revised British Standard Specification of 1910.

medium-setting cement from a rotary kiln and B a slow-setting cement from an intermittent kiln.[1]

TABLE XX

Cement.	Temp.	Dry Atmosphere.		Under Water.	
		Initial.	Final.	Initial.	Final.
	Deg.				
A	10	155	410	210	480
	15·5	150	270	150	410
	21	105	225	100	350
	29·5	50	95	60	300
	37·5	30	55	45	180
B	10	385	660	480	750
	15·5	215	365	420	600
	21	130	295	300	410
	29·5	95	170	210	360
	37·5	85	115	60	195

The quantity of water used in gauging was in each case 22 per cent.

The attempt has been made to render the Vicat needle self-recording. In Tetmajer's apparatus of 1889, flowing water is employed to depress the needle at regular intervals, which can be varied to suit the cements, and the distance through which the needle moves at each stroke is recorded by a pen on a rotating disc. In L. Périn's apparatus (1904), the motive power is clockwork, and the record is taken as a series of arcs on a drum. Both forms have the disadvantage of producing very considerable vibration, and are liable to errors caused by the presence of lumps in the cement paste. A better form is that due to A. Martens (1897). Three needles are placed side by side, and are held up by means of magnets. A cam, moved by clockwork, cuts out the sustaining magnets at intervals, and the needles descend slowly. After half a

---

[1] H. K. G. Bamber, *Trans. Concrete Inst.*, 1909, 1, 106.

minute they are again raised, and the table carrying the cement (mixed in long rectangular moulds) is automatically moved forward through a certain distance. A tracing pen records the vertical movements of the needles. Although this apparatus is greatly superior to the other forms described, the three needles do not, as a rule, give identical results, and it must be admitted that none of the automatic devices hitherto tried are as trustworthy as the needle actuated by hand.[1]

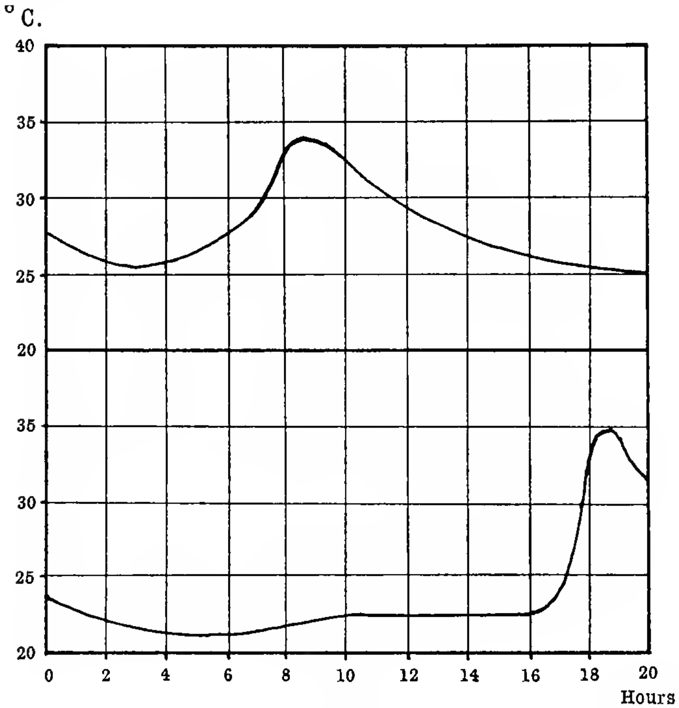


FIG. 12.

Temperature-curves of Cement with Gary's Apparatus.

---

[1] These automatic instruments, as well as the thermal method, are described by M. Gary, *Concrete and Constr. Eng.*, 1907, 1, 350, 431.

An entirely different method of determining the setting time has been employed by Gary, depending on the development of heat during the process of setting.[1] If a thermometer is embedded in the cement paste immediately after gauging, and the containing mould is packed in sawdust to avoid loss of heat, and covered with a perforated wooden lid, the thermometer may be read at intervals, and the readings plotted against the time. A considerable rise of temperature marks the setting. With slow-setting cements there is usually a rapid rise of temperature shortly after mixing, then a fall, and later on a second rise, corresponding with the final set determined by the needle. The lowest point of the curve corresponds with the usual initial set. The apparatus is made self-recording by means of a photographic arrangement, the shadow of the mercury column of the thermometer, thrown by a lamp, being projected on a moving photographic plate. The graduations of the thermometer record themselves on the plate as horizontal lines, and vertical lines representing the time are added by means of a ruled transparent screen during printing from the negative. Two such curves, with most of the ruled lines omitted, are reproduced in Fig. 12. Both refer to slow-setting cements. The thermal and indentation methods in the first case yielded nearly identical results, but in the second a very marked development of heat occurred long after the needle had ceased to make any impression.

Cement.	Time by Thermometer.		Time by Needle.	
	Beginning.	End.	Beginning.	End.
A. . . .	210	510	300	510
B. . . .	285	1100	345	645

---

[1] *Mitt. k. Material-Prüf. Amt.*, 1906, **24**, 225.

The initial set is indicated earlier by the thermal than by the indentation method. This result is of some importance, as the object of determining the initial set is to know when the chemical reaction sets in, a point that is clearly better determined by chemical than by mechanical means. After the first set, caused by the hydration of the aluminates, the mortar loses its perfect plasticity; in the workman's phrase, it is said to be "killed." Killed mortar behaves more like a mud when mixed with water, and if allowed to dry during setting does not harden. There is, therefore, considerable risk in using it in a dry situation. The nature of killed cement, in which the hydration has partially taken place, demands further investigation, but it is a safe rule to avoid its use in practice.[1]

The setting time of a quick-setting cement is practically unaffected by admixture with sand, and is therefore the same in mortar as in "neat" cement paste, but slow-setting cements set more slowly in mortar, the development of heat occurring later and later as the quantity of sand is increased.

The thermal method promises to yield very interesting results when further perfected. The readings, with different quantities of cement, differ considerably, mainly on account of the low conductivity of the material, and hence it has not been widely adopted, but, after being standardised, it may probably come into more general use.

Very careful precautions must be taken to minimise the loss of heat by the mass, especially in the use of slow-setting cements, as small variations of temperature may be entirely masked by the effect of radiation and conduc-

---

[1] A few experiments by H. Burchartz, *Mitt. k. Material-Prüf. Amt.*, 1908, **26**, 192, showed that a slow-setting cement, with final set 6 hours, lost little strength if stored after gauging for periods up to 8 hours, then vigorously re-worked and moulded, being allowed 28 days to harden in water, but that storing beyond 8 hours caused a very rapid fall in strength, reaching zero at 24 hours.

tion of heat to the surroundings. When special arrangements are made to avoid this error, the curves shown in Fig. 12 become somewhat modified, the fall of temperature after the initial set disappearing, so that the curve indicates a progressive rise in temperature, which is rapid at first, then slow or stationary, and then, when the further reaction sets in, again very rapid.[1] The results obtained by the thermal method are therefore dependent in a much greater degree on the quantity of material used for a test than are those obtained by a mechanical or indentation method, and it is for this reason that several investigators, after a trial of the thermal test, have abandoned its use.

CONSTANCY OF VOLUME AND SOUNDNESS.

It is highly important that a cement, after gauging with water and setting in place, should not undergo any appreciable change of volume, as shrinkage would lead to the formation of cracks, whilst expansion would lead to deformation and, if considerable, to disruption and disintegration. From what has been said of the behaviour of the colloidal constituents of gauged cement, it is evident that neat cement must contract slightly during the process of setting and hardening in the air. The shrinkage of a colloidal substance during drying is much lessened by mixing with an inert material, such as sand, and hence cement-sand mortars, if properly mixed from good material, should not crack. When the proportion of cement in the mortar is high, however, a slight contraction becomes apparent, so that rich mortars used for facing purposes very commonly exhibit minute "hair-cracks" after exposure to the air. These very fine cracks are simply a consequence of the desiccation of the cement colloids, and are in no way an indication of defects in the

[1] *Tonind. Zeit.*, 1910, 34.

cement. They can only be avoided by using mortar less rich in cement, the colour being corrected by the use of marble dust or other suitable material to give a satisfactory finish.

Excessive contraction is not observed in cements. On the other hand, expansion after setting is one of the most usual defects of inferior cements, and one of the most serious, involving as it does the risk of destruction of the buildings or structures in which it is used. A minute expansion takes place during setting under water, amounting in normal cements to about 0·3 per cent. of the initial volume. It is doubtful whether this is due to real expansion of the cement, or to a thrusting apart of the gelatinous particles, producing an increased porosity of the mass. The latter explanation appears more probable. When the cement is mixed with an inert substance, as in mortar, such expansion becomes altogether negligible.

A defective cement expands *after* setting, sometimes after a period of weeks or months have elapsed. The expansion, which produces cracks, is often known as "blowing." A pat of defective cement shows after hardening a network of fine cracks or, if of very bad quality, portions of the surface may detach themselves and fragments may break away from the edges. The addition of sand does not prevent blowing.

The expansion of defective cement is attributed to the hydration of certain of its constituents. The phenomenon very closely resembles the slaking of lime, differing from it only in the slowness with which it proceeds. The expansion of the calcium oxide in this reaction is only apparent, as the volume of the slaked lime is actually less than the sum of the volumes of the quicklime and the water from which it is formed, but the mechanical outward thrust produced is very great. It follows that the mass must become porous, the particles being thrust apart. This expansive force of lime during slaking is utilised in the application of lime cartridges to the destruction of walls, &c., the cartridge acting as a wedge when wetted. The cracking of cement pats, and the destruction of mortar or concrete by expansion, are due to an action of precisely the same kind.

Blowing cannot be attributed to the hydration of quicklime in the physical condition in which it is best known to us, of a loose, friable solid, for such lime would undergo hydration immediately on contact with the water used in gauging, and would be rendered harmless before the setting process began. Crystallised lime, however, as is mentioned on p. 53, only becomes hydrated after long exposure to water, and then exhibits expansion in a very marked degree. In accordance with this fact, cements prepared at a high temperature in the laboratory, and containing so large a proportion of lime as to show crystals of calcium oxide in a microscopic section, "blow" after setting. This condition is rare, but lime occurring in a less distinctly crystalline form has very similar properties when brought into contact with water. Actually, three errors in composition are known which may give rise to expansion or blowing:

1. An excess of lime above the quantity capable of being held in combination or solid solution in normal alite;
2. An excessive proportion of magnesia;
3. An excessive proportion of sulphates.

Expansion caused by the action of salt solutions on hardened cement is considered later, in connection with the action of sea water on mortar or concrete.

The most frequent cause of expansion is the presence of lime in an unsuitable condition. The quantity of lime that can be retained in a safe condition by a cement depends, not only on the proportions of the other constituents, but also on the process of manufacture. The higher the temperature of burning, the larger is the quantity of lime capable of being held in solution, so that cement made in a modern rotary kiln may safely contain a larger proportion of lime than cement made in one of the old-fashioned intermittent kilns.

Even although the original mixture may have been correctly proportioned, there are two ways in which the product may come to contain uncombined lime. The materials may have been insufficiently mixed in the grinding process, with the result that some parts of the mixture will contain relatively too much lime and other parts too little. When ground after burning, the over-limed clinker will render the whole of the product unsound.

Inequalities in the burning may also occur. When stationary kilns are used, some parts of the kiln never attain the full burning temperature, owing to inequalities of draught, &c., and the clinker when removed always contains some underburnt portions, which are picked out by hand and rejected. If the hand-picking is insufficiently careful, or if the underburnt portions are not readily detected in a large mass of clinker, the same result may be brought about, namely, the presence of uncombined lime in the finished cement. This defect is much less likely to occur where rotary kilns are used, the burning in this type of kiln being more uniform and complete. In order to guard against expansion of a cement owing to the presence of an excess of lime, it is therefore necessary that the mixture should be correctly proportioned, that the grinding and mixing of the materials should be very thorough, and that the burning should be sufficiently uniform and at a sufficiently high temperature.

Expansion due to magnesia does not show itself, in many cases, until after a much longer period, as strongly heated magnesia often remains inert for a long time before undergoing hydration. Expansion due to this cause was first observed in 1884, when, almost simultaneously, attention was called in France to the destruction, two years after erection, of a number of railway bridges and viaducts, and in Germany to the cracking of the town hall of Cassel, which it became necessary to rebuild.[1] Both cements were found to contain much magnesia, the French from 16 to 30 per cent., and the German 27 per cent., as they were prepared from dolomitic limestone. The expansion was not found to take place in dry air, but only where exposed to rain or otherwise in contact with water. The result of a long series of investigations proved that magnesia was not only dangerous when by its presence it raised the ratio of bases to acids above the safe limit, but also when it merely replaced a part of the lime in a sound cement. The mechanical addition of light calcined magnesia was found to be without influence, whilst strongly calcined magnesia produced enormous expansion. It is still uncertain how far combined magnesia plays a part in the change, and further experiments are needed in this direction. The lightly-burnt natural cements of the United States, which contain large quantities of magnesia, are often perfectly sound, the magnesia then being in a hydraulic condition, and having a certain, although small, cementitious value. In strongly burnt Portland cement, however, magnesia in more than small quantities is always dangerous to soundness. The upper limit is fixed by the British Specification at 3 per cent. and by the German at 4 per cent.

The third compound liable to cause expansion is calcium sulphate. The increase of volume is not due in this case to the hydration of the sulphate, as the hydrated salt, gypsum, produces the same effect if added to the cement in more than a small quantity. The expansion is attributed to the formation of calcium

---

[1] See H. Le Chatelier, *Mortiers hydrauliques*, p. 142.

sulpho-aluminate,[1] which is only dangerous in large quantities. The effect of gypsum in causing expansion therefore stands in relation to the alumina contents of the cement. In accordance with this conclusion, iron-ore cement, in which the alumina is mostly replaced by ferric oxide, is remarkably little affected by the addition of gypsum, as much as 29 per cent. having been added without producing unsoundness when the pats of cement were stored in either fresh or sea water.[2] This point requires further investigation, on account of the somewhat surprising nature of the results hitherto published.

The British Specification fixes a maximum of 2·75 per cent. SO_3, and the German 2·5 per cent., in Portland cement.

Expansion may show itself soon after setting, or may not develop until after a considerable interval. The examination of ordinary test-pieces is therefore insufficient as a means of detecting unsoundness, as the defect may not become visible until so long after mixing that the cement has been taken into use and made into mortar. For this reason accelerated tests have been devised, based on the fact that the changes occurring during the setting and hardening of cement proceed more rapidly when the temperature is raised. Several methods of carrying out the "boiling" test have been proposed, and only the most important of them will be described here.

The simple cold-water test for soundness is performed by mixing cement with water to form a paste of "normal" consistence, moulding into a thin disc on a glass plate, and after 24 hours in moist air, keeping the disc in air or in water. At the ordinary temperature no cracks or blisters should appear within 28 days, and the disc should not separate from the glass.

The most important of the accelerated tests is that due to Le Chatelier. The gauged cement is filled into a small

---

[1] E. Candlot. See p. 125.

[2] *Cement and Engin. News*, 1908, **20**, 112.

brass cylinder, split longitudinally and provided with two needles, the ends of which diverge if the cylinder is forced open by the expansion of the material contained in it.

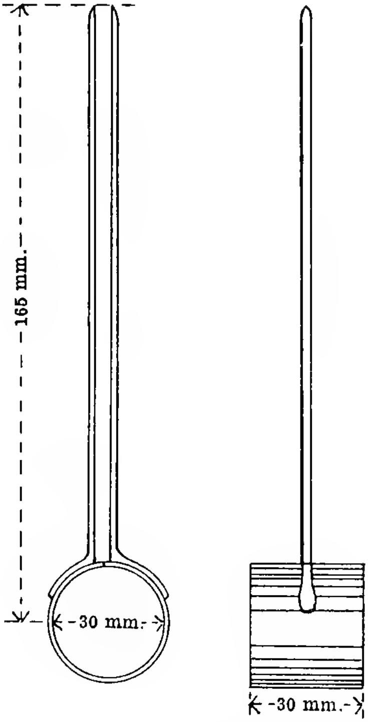


FIG. 13.

Le Chatelier's Apparatus for the Measurement of Expansion.

The form and dimensions of the apparatus are shown in Fig. 13. The performance of the test is best described in the terms of a recommendation of the Committee on Accelerated Tests of the International Association for Testing Materials, presented to the Copenhagen Congress in 1909.[1]

---

[1] *Concrete and Constr. Eng.*, 1909, **4**, 349.

"The cement is gauged and filled into the mould on a plate of glass, the edges of the mould being held together. When the mould has been filled it is covered with a plate of glass held down by a small weight, and the whole is immersed in water at 15° for 24 hours. Any tie or band which has been used to keep the edges of the mould together during setting is then removed. The distance between the indicator needles is then measured and the mould is placed in cold water which is raised to 100° in the course of half an hour and is kept boiling for 6 hours. The mould is removed from the water, and after it has cooled the distance between the indicator needles is again measured. The difference between the two measurements represents the expansion of the cement. This must not exceed 10 mm. when the cement has been aerated for 24 hours, and 5 mm. when the cement has been aerated for 7 days."

A large copper water-bath, with constant level supply, is used for immersing the apparatus, and is made of sufficient capacity to accommodate a number of the brass cylinders.

This test has not been universally adopted. In some laboratories the practice is followed of making a pat of cement on glass covered with blotting paper, allowing to set and removing from the paper and then, after allowing it to remain for 24 hours in a moist atmosphere, heating for 3 hours, or until no more water vapour is evolved, in a steam oven at 100°. This is the German "Darrprobe." Another form of the test, due to Michaëlis, consists in mixing a pat in the form of a disc, 1 cm. thick in the centre and thinning towards the edges. After this disc has remained in a moist chamber for 24 hours, it is immersed in cold water, which is then heated slowly to boiling and maintained at the boiling temperature for 3 hours. Unsoundness is shown in either of these tests by warping of the thin pat or, in serious cases, by cracking or crumbling.

Faija's test, formerly much used, consisted in heating a pat of cement in water-vapour at about 40° for 6–7 hours and then in water at 48° for the remainder of the 24 hours, a jacketed steam bath being used as the heating vessel. It is therefore less severe than the boiling test. On the other hand, Erdmenger's test aims at still greater severity, the test-pieces being heated in an autoclave under a pressure of 40 atmospheres. This test may well be set aside as being unnaturally severe.

There has been much controversy as to the relative advantages of the various accelerated tests for constancy of volume. As has been mentioned above, the committee of the International Congress appointed to deal with this subject has decided in favour of Le Chatelier's test. A comparison of 5 sound samples, 5 doubtful samples, and 4 unsound samples showed that the cold-water test at 28 days was quite inadequate to detect with certainty doubtful cements or even some cements known to be unsound. The tests at 50° sufficed to detect thoroughly unsound cements, but could not be relied on to detect doubtful samples. Tests by Le Chatelier's method were entirely trustworthy.

The British Standard Specification requires that the expansion, measured in the manner described, shall not produce a separation of the points of the needles by more than 10 mm. after the cement has remained 24 hours in the air, or of 5 mm. after 7 days in air.

Many forms of apparatus have been devised for measuring more accurately the expansion of a cement. The best-known test is that due to Bauschinger. The test-pieces are rectangular prisms, 10 cm. long by 5 cm.^{2} in cross section. Small hollows are left at each end of the prism, in which small, conical pieces of brass or agate are cemented. The instrument used is a special form of micrometer callipers, between the jaws of which the prism is brought, so that the points of the callipers touch the two smooth surfaces of the embedded cones. The pressure is regulated by a spring indicator, and the reading of the head of the micrometer is then taken. Some skill in making instrumental measurements is required with such an apparatus, and the cones are very liable to suffer displacement if special precautions are not taken. For this reason the Bauschinger micrometer is not to be recommended for routine tests in the laboratory, although it is very suitable for accurate determinations of expansion in the course of a research.

In another method of measurement, two metal pins are inserted vertically in the test-piece before it is completely set, and the distance between them is measured immediately after setting and after definite intervals, either by a wedge-shaped plate with graduated edges (Le Chatelier) or by a lever arrangement which greatly magnifies the displacement.[1] All such devices depend for their trustworthiness on the immobility of the metal pins, a condition which it is difficult to secure. The simple split cylinder is free from these disadvantages, and fulfils the requirements of a convenient and trustworthy testing appliance. The test is to be preferred to the simple observation of pats or cakes without measurement, as it may happen, especially with cements containing magnesia, that expansion of volume takes place smoothly without producing distortion, so that no warping or cracks are observed. Thus Le Chatelier found that pats of a finely ground mixture of Portland cement and strongly calcined magnesia expanded to the extent of 30 per cent. of their linear dimensions in two years, without any appearance of cracks. Similar results are obtained when unsound cements are heated in steam.

The exact change in dimensions undergone by normal mortar during setting is of importance in connection with the calculation of stresses in structures composed wholly

---

[1] A. Martens, *Mitt. k. Material-Prüf. Amt.*, 1905, **23**, 203.

or partly of these materials, as if hindered by external forces from expanding or contracting freely, internal stresses are set up, and modify the distribution of stress within the structure when a load is applied. In the series of experiments collected in Table XXI.,[1] the measurements were made by means of reading microscopes, the datum marks being engraved on embedded glass rods, as described above. The alterations in length are given in millimetres per metre.

TABLE XXI.

Mortar.	In Air.			In Water.		
	28 Days.	2 Years.	Increase	28 Days.	2 Years.	Increase.
Portland cem. neat	−3·02	−4·70	−1·68	+0·53	+1·33	+0·80
,, ,, 1:3	−1·28	−1·76	−0·48	+0·09	+0·21	+0·12
Slag[2] ,, neat	−2·72	−4·33	−1·61	+0·09	+0·38	+0·29
,, ,, 1:3	−1·60	−2·06	−0·46	+0·05	+0·13	+0·08
Roman ,, neat	−3·08	−5·00	−1·98	+0·38	+0·87	+0·49
,, ,, 1:3	−0·65	−1·17	−0·52	+0·05	+0·11	+0·06
Hydraulic lime neat	−2·43	−2·60	−0·17	+0·07	+0·25	+0·21
,, ,, 1:3	−0·70	−0·86	−0·16	+3·08	+0·07	+0·15

All the methods described above measure the linear expansion. Mention should also be made of the method,[3] better suited to research than to routine work, of determining the volume-expansion directly in a volume-dilatometer, the volume of mercury displaced by a small cylinder of cement being measured. The linear expansion is practically one-third of the volume-expansion, and may thus be calculated. Table XXII. gives the relation between the expansions measured in this way, and by means of the split cylinder.

For small expansions, therefore, the reading given by Le Chatelier's apparatus is proportional to the linear

---

[1] F. Schüle, *Mitt. eidg. Material-Prüf. Amt. Zürich*, 1909, xiii.

[2] Mixture of granulated slag and lime.

[3] F. G. Donnan and G. T. Barker, *J. Soc. Chem. Ind.*, 1906, **25**, 726.

expansion. The displacements of 10 mm. and 5 mm. in the Standard Specification correspond fairly closely with 4 per cent. and 0·35 per cent. by volume respectively.

A test occasionally applied is that of immersion, immediately after mixing in cold water, known as the "plunge test." A pat, mixed on glass, or occasionally a ball, of cement, is used for the purpose. Slow-setting cements are naturally the most liable to disintegrate under such treatment, and the test is not a fair one for detecting unsoundness.[1]

TABLE XXII.

A = Linear Expansion from Dilatometer Reading.	B = Displacement of Needles in Le Chatelier Test.	$\frac{A}{B}$
Per cent.	Mm.	
0·075	3·0	0 025
0·073	3·5	0·021
0·113	4·6	0·025
0·127	5·4	0·023
1·32	16·4	0·081
1·927	14·5	0·133
4·83	35·6	0 136

As a precaution against subsequent expansion, the aeration of cement has been very generally practised. The cement being spread out in a thin layer and turned over several times, the particles are brought into contact with air, necessarily containing moisture and carbon dioxide, and particles of lime have an opportunity of becoming slaked and rendered inert. It was formerly, and is still very frequently, the practice to insert in building and engineering specifications the requirement that the cement should be aerated for a definite period, usually twenty-eight days. There are several reasons why such a

---

[1] See A. C. Davis, *Proc. Inst. Civ. Eng.*, 1909, **177**, 193.

requirement has become unnecessary at the present day. In the first place, the finer grinding of the cement has increased its soundness, the particles of lime or insufficiently burnt material inside the grains being very largely responsible for unsoundness. The more uniform burning obtained in the rotary kiln also reduces the risk of underburnt particles. The process of applying steam during the final grinding in the tube-mills, described on p. 126, supersedes aeration, by hydrating the substances causing unsoundness, and so rendering them innocuous. Any aeration of a cement treated in this manner is superfluous, and even causes deterioration, owing to the inevitable formation of the inert carbonate by the action of carbon dioxide. Where the steaming process is not applied, aeration, by turning the cement out on to a floor in a dry store, should be resorted to, but it is now quite possible for manufacturers to supply a Portland cement which is ready for immediate use, without any danger of subsequent expansion.

CHAPTER VII

THE MECHANICAL PROPERTIES OF CEMENT. CONCRETE AND ARTIFICIAL STONE

THE value of cement, when employed as a structural material, depends primarily on its mechanical strength in the set and hardened condition, a strength due to the cohesion of the particles of the cement, and to their adhesion, firstly to the grains of sand with which they are mixed, and secondly to the surfaces of the stone or brick. On the hypothesis as to the nature of hardened cement adopted in this work, the cause of the mechanical resistance resides in the desiccated gel which constitutes the active mass of the cement after hardening.

Mechanical tests therefore play a most important part in determining the quality of a cement, and every specification requires a certain minimum strength that must be attained by the material under given conditions. The hardening being a very complex process, the strength is in a high degree dependent on the conditions of mixing and testing, and it is therefore necessary to prescribe the exact manner of testing in order to obtain comparable results.

Two forms of stress may be applied, the specimens being loaded in tension or in compression. It is the compressive strength of mortar and concrete which is of principal importance in construction, but tests in tension are more conveniently applied, and are more readily standardised, than tests in compression, and therefore at present constitute the bulk of the ordinary routine tests. The compressive strength bears a fairly constant relation to the tensile under standard conditions, and may therefore be calculated from the latter with an accuracy which is sufficient for most practical purposes. The general practice has been to make tensile tests of "neat" cement, that is, of cement gauged with water alone, without the addition of sand. This practice is unfortunate. An essential quality of the cement, its power of adhesion to the surfaces of foreign particles or masses, is not brought into play in such a method of testing. That the results are apt to be misleading is shown by the fact that if an ordinary cement is re-ground so as to give a greatly increased proportion of the finest flour, the strength of neat specimens is actually reduced, whilst that of the mortar is very considerably increased. Tests on neat specimens alone would lead to the conclusion that very fine grinding is disadvantageous, which is the contrary of the truth. It is therefore very desirable that tensile tests of mortar should replace those of neat cement, the mortar being prepared under standard conditions, with a standard sand. Only in this way can really representative tests of the quality of the cement be obtained. A method of testing, which consists in the application of a bending stress to prisms of mortar, followed by compression of the broken portions, is described below, and appears likely to supplant the older method, or at least to assume an equal importance with it, in the near future, on account of its greater uniformity under standard conditions of working.

The results of mechanical tests depend on a number of factors, including the quantity and temperature of the water used in gauging, the manner of mixing with water and of filling the moulds, the temperature and degree of moistness of the air in which setting takes place, the time which elapses between gauging and testing, and, in the case of cement-sand mortars, the form and grading of the particles of sand. It is therefore essential that these conditions should be maintained constant throughout any series of tests, in order that the results obtained may be comparable with one another.

The quantity of water used in gauging affects the results considerably, the tensile strength increasing with the percentage of water, until a maximum is reached, and then diminishing rapidly. For example, a cement-sand mortar mixed under exactly uniform conditions with varying percentages of water gave the following tensile strengths after twenty-eight days:[1]

Per cent. Water.	Kg./cm.².	Lb./in.².
7	20·7	296
8	22·4	320
9	23·2	331
10	22·3	319
12	19·1	272

the best result being obtained with 9 per cent. of water. A rather dry mixture (7 per cent. of water), heavily rammed in the moulds, gives high results, but it is very difficult to ensure uniformity under such conditions, and a more plastic mortar is now generally preferred. Different cements require different proportions of water to attain the same plasticity.

The temperature of the water used in mixing is also of importance, an increase of temperature hastening the setting, and at the same time reducing the tensile strength. The same cement as in the last example, mixed at different temperatures, gave the following tensile strengths after twenty-eight days:

Temp.	Kg./cm.².	Lb./in.².
14° C.	23 5	336
16	23·1	330
17	22·5	321
19	20·5	293
20	20·2	288
22	19·5	278
24	18·9	270

---

[1] These and the following figures are given by P. Steinbrück, Address to the *Polytechn. Verein München*, January 1901.

Within certain limits, the strength of the mortar increases with the time during which mixing is continued, provided that the moment of the initial set is not reached. The same cement, worked vigorously for different periods, gave the following strengths after twenty-eight days:

Time.	Kg./cm.².	Lb /in.².
Minutes.		
1·5	19·3	276
3	21·1	301
5	22·5	321
7	23·1	330
9	23·4	334

the strength increasing rapidly up to five minutes and very little afterwards.

Another factor which influences the strength of the mortar is the amount of moisture in the atmosphere in which setting takes place. A decrease in the relative saturation of the air from 80 per cent. to 50 per cent. lowered the strength from 22·6 to 20 kilograms. Setting should therefore always proceed in an atmosphere maintained artificially in a moist condition. The state of the atmosphere is determined by means of a Saussure's hair hygrometer.

The mortar for neat briquettes is gauged up by hand and mechanical treatment is inapplicable, but cement-sand mortar may be filled into the mould and consolidated by mechanical ramming. The advantage is gained by this treatment of ensuring uniform density. If the mortars to be compared are mixed to an equal consistence with water, and rammed with an equal number of blows of given force, briquettes are obtained which may be fairly compared with one another, whilst no proper comparison is possible between briquettes consolidated under an undetermined pressure.

If the mortar is mixed by hand, a copper bowl is a convenient mixing vessel, the mortar being thoroughly turned over and worked with a small trowel. The working should be continued for a fixed time, usually three minutes for slow-setting cements, the time being conveniently indicated by a sand-glass. In the hands of an expert laboratory assistant, mortar of very uniform quality may be prepared in this way, the results being quite as satisfactory as when a machine is used. It is often preferred, however, to mix the mortar mechanically, and the machine designed by Steinbrück and Schmelzer is then almost always employed. This machine is a single edge-runner, the heavy roller, mounted on a horizontal axis, moving in an annular trough, which rotates about a vertical axis. The roller and trough turn in the same direction, but with different velocities, and the mortar, continually worked and turned over by the action of the roller and of two curved scrapers, is rendered smooth and uniform. The moving parts are carried on a hinged arm, and can be turned out of the way for cleaning. The mortar, after being roughly mixed by hand, is transferred to the machine, which is set in motion, and stopped after twenty rotations of the pan, occupying 2½ minutes.

The standard form of briquette is shown in Fig. 14. The briquette moulds are of brass, accurately cut, and divided longitudinally, the two halves being clamped together with screws. The pattern shown on the left of Fig. 15, in which a spring takes the place of the screws, is less convenient. For hand filling, the mould, which has been previously slightly oiled, is laid on a thick glass plate, filled with mortar, and the contents pressed in with an iron spatula until quite plastic, when water exudes from the surface. The mortar is then carefully levelled, and the mould is set aside in the moist chamber until the contents have set, so that the screws may be released and the mould removed.

For machine ramming, the moulds are of cast iron, and are more massive in construction, having the halves tightly clamped together. An iron piston slides closely inside the moulds, which rest on a cast-iron base, solidly supported in its turn on a brick or concrete pillar. The blows required to consolidate the mass are applied by means of a mechanical hammer. In Boehme's machine, the most generally employed for this purpose, the action of the hammer is precisely that of the old-fashioned tilt-hammer used in the manufacture of wrought iron. The hammer-head forms the end of the long arm of a lever, and the short arm is periodically depressed by a projecting tooth on the rim of a wheel. When depressed to the

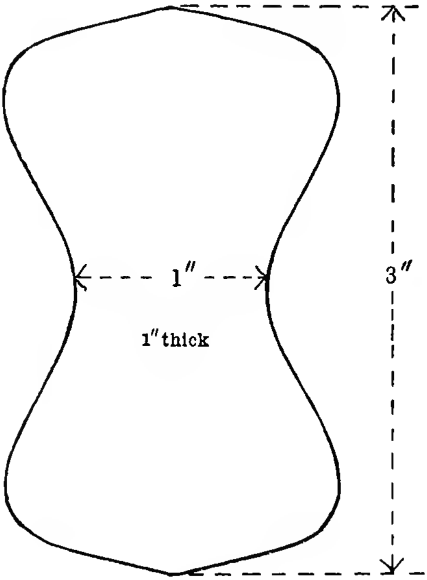


FIG. 14.

Standard Form of Briquette for Tensile Tests.

fullest extent, so that the hammer is at the top of its stroke, the short arm slips from the tooth, and the head falls by its own weight on to the piston of the mould. The wheel has nine such teeth, and revolves at such a rate that one blow is delivered every second. After 150 blows the gearing is automatically disconnected, so that the blows cease. The moulds should then be removed and transferred to the moist chamber.

Boehme's machine has certain disadvantages, as the blow of the hammer is not delivered vertically, but with an inclination to one end of the mould. Another type of machine, proposed by Tetmajer and designed by Klebe, is constructed on the principle of the pile-driver, and delivers a perfectly vertical blow. The ramming head falls between two vertical guides, and is raised by a wooden lath, which is gripped between two wheels, and released at the top of its stroke, and then falls freely. In ramming briquettes for tensile tests, a weight of 2 kilograms is allowed to fall through 25 cm., the apparatus stopping automatically after 120 blows. This pattern of machine is prescribed by the Austrian and Swiss regulations, the German regulations prescribing Boehme's machine, whilst the British Standard Specification requires the tests to be made with briquettes filled into the moulds without ramming by hand or by machinery. Tests of briquettes prepared by the three different methods must not be compared together, as the energy of the blows delivered by Boehme's and Klebe's machines is not the same, whilst filling by hand yields results differing from those obtained with either machine. An increase in the number of blows causes an increase in the strength of the test-pieces, the effect being more marked in compressive than in tensile tests.

In America, the Olsen press has been used to a small extent. This machine is a small hydraulic press, by means of which pressure is gradually applied, instead of suddenly as in machines using hammers. The results obtained with the Olsen press are much lower than with a hammer, and the machine has no special advantages.

The freshly made briquettes are at once transferred to a moist chamber, consisting in its simplest form of a wooden box lined with zinc, having a lid covered on the inside with thick flannel, which is kept thoroughly moist during use. The moulds rest on a floor of wooden laths. The box is kept in a place free from vibration, at a constant temperature of 16°, or as near to it as is practicable.

After twenty-four hours the briquettes are taken out of the moist chamber, the halves of the moulds separated and removed, and the specimens transferred to a shallow tank, lined with zinc, and containing water at 16°. The laboratory should have a number of these tanks, which may be conveniently arranged in tiers one above another. The water must be kept clean, being changed once a week, or at more frequent intervals if necessary. The briquettes remain in these tanks until required for testing, each briquette bearing a reference number and a system of arrangement being adopted by which any specimen can be found when required. The briquettes should not be removed from the tank more than half an hour before being broken in the testing machine.

The simple steelyards formerly used for breaking briquettes under tensile stress have now been almost universally superseded by compound lever machines, which have the great advantage of compactness, occupying little room on a laboratory bench. The usual form of machine is shown in Fig. 15. The briquette *i* is held in the accurately shaped clips *d* and *e*. The lower lever has a ratio of 5 to 1 between its arms and the upper one of 10 to 1, so that the combined leverage is 50 to 1, and the load on the briquette is 50 times the weight of the loaded bucket *c*. The hand wheel below the lower clip *e* is used to adjust the position of the briquette, and the machine is also furnished with a sliding weight at *b* as a means of bringing the levers to an initial state of equilibrium. All the bearings are knife-edges of hardened steel.

The load is applied in the form of small lead shot, which may be poured at a uniform rate into a suspended bucket. The shot are stored in a vessel *g*, and escape through a spout *o*. The size of the apparatus is so arranged that the load is nominally applied at the rate of 400 lb. per minute in British tests, or of 60 kg. per minute in Continental tests. When the briquette breaks, the pan falls, and striking the lever *n*, at once cuts off the supply of shot. The pan is then transferred, with its contents, to the spring balance, the dial of which usually bears, in

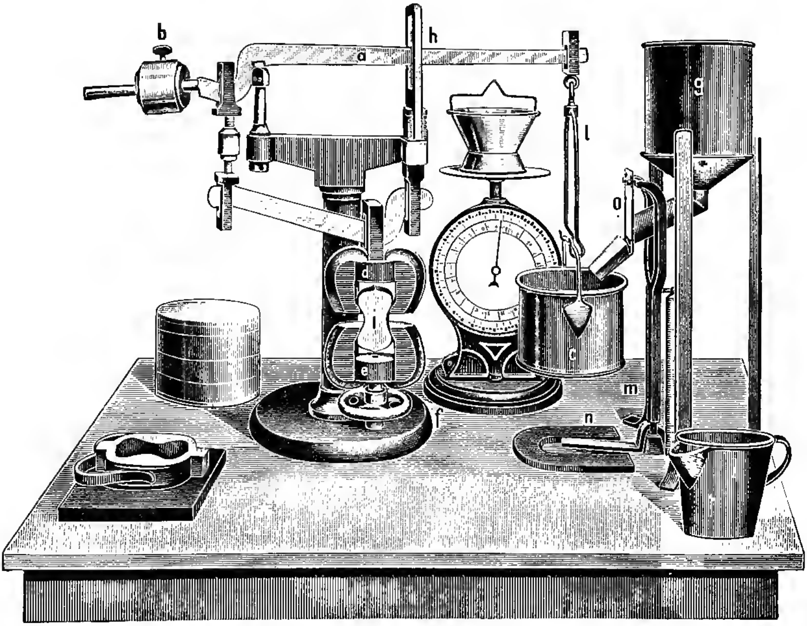


FIG. 15.

Briquette-testing Machine.

addition to the ordinary scales of pounds and kilograms (actual weight), a special scale multiplying the load by 50, and therefore giving directly the load in pounds per square inch on the briquette. The height through which the pan may fall should be less than is represented in the figure, in order to avoid undue shock, and a soft felt pad should be provided to break the fall.

Tests under compressive stress are made in a hydraulic press, cubes being used as test-pieces. Any of the hydraulic testing machines usually found in engineering laboratories may be used for this purpose, but the small vertical presses, in which the ram works in a cylinder filled with oil, are most convenient. The pressure is applied gradually, and is determined by means of a gauge. In Amsler and Laffon's press, the gauge is a column of mercury, communicating with a pressure-reducing cylinder. The pressure is then measured by the height of the column. In a later form of the same machine, the pressure of the oil in the cylinder raises a heavy pendulum, the movements of which are registered on a dial.

The test-pieces are in the form of cubes, and are prepared in iron moulds, the sides of which can be separated. The mixing, ramming, storage in the moist chamber and in water are conducted in the same manner as in the preparation of briquettes for the tensile test. The usual Continental form of cube has a side of 70·7 mm., so that the area of each face is 50 sq. cm. The same form is often used in England, being roughly $2\frac{3}{4}$-inch side, but 3-inch cubes are also used. Fracture should take place in such a way that the two largest fragments produced are pyramids, of which the bases are in contact with the surfaces of the press, and the apices meet at the centre of the cube.

A method of testing cement-sand mortars by the application of bending and compressive stresses, excluding simple tension, has been devised, and now forms the object of numerous researches in other laboratories. With a view to securing uniformity in the testing of mortars, Feret proposed the preparation of rectangular prisms, the consistence of the mortar being more plastic than in the usual method of testing, so that light ramming by hand is sufficient for its consolidation. The principal difficulty in the application of the test lies in the determination of the proper quantity of water to be used in gauging. As the result of a large number of experiments, the provisional conclusion has been reached[1] that comparative results are best obtained by using the same weight of water for each sample. As the same weights of cement, sand, and water are taken for each test, the weight of a given volume of the freshly gauged and rammed mortar is in each case the same. Changes in specific gravity during setting are neglected.

The quantities required for a series of six prisms, each 16 × 4 × 4 cm., are, if German standard sand is used: 2340 grams of sand, 780 grams of cement, and 10 per cent., or 312 grams, of water. The cement and sand are mixed dry by hand, and the water is added in two portions, being thoroughly worked by hand until it is as plastic as possible. One-sixth of the quantity is then weighed out, and rammed into one of the moulds with an iron rammer weighing 1 kilogram, and having a stamping surface 3 × 3 cm. The ramming is not completed until all six moulds have been filled. Water should not escape to more than a very slight extent from the bottom of the mould. After 48 hours in the moist chamber, the moulds are removed and the prisms are placed in water until required for testing, as in the usual laboratory method. Slightly different proportions are necessary if a different sand be used.

---

[1] Report of the Committee No. 42 of the International Congress for Testing Materials (President F. Schüle) presented to the Copenhagen Congress. See *Concrete and Constr. Eng.*, 1909, **4**, 483.

Each prism of the form described furnishes one bending test and two compressive tests. A greater weight than usual is therefore assigned, in this method of testing, to the determination of the strength in compression, which is the most important property of mortar from a practical point of view. The bending strength bears a fairly constant relation to the tensile strength, and is determined in this case from the same prism as the compressive strength, the two broken portions being utilised for the tests in compression. The variations of individual tests from the mean value are less than in the customary methods of testing.

The testing machine in general use for tensile tests (p. 173) may be conveniently adapted for the purpose of bending, the grips only being altered. The upper horseshoe clip carries two transverse knife-edges, 10 cm. apart, directed upwards, on which the prism rests symmetrically. A third transverse knife-edge, directed downwards, is attached to the lower clip, and rests on the prism at the middle of its length. The load is applied in the same way as when ordinary briquettes are being tested, and fracture should take place at or near the middle point. The two fragments are tested in compression without trimming to cubical shape, by the device of placing steel plates, 4 cm. wide, above and below the half-prism. The plates are laid transversely, the one exactly above the other, so that the mass of mortar enclosed between them and subjected to the load is exactly a 4-cm. cube, the portions projecting beyond the area of the plates being without influence on the result.

Table XXIII. gives the results obtained with six prisms, from experiments made by Frey, of Luterbach. The "apparent specific gravity" of the prisms was accurately determined by weighing and measuring the volume of the prisms in a volumenometer, after twenty-eight days' immersion in water. All six prisms were rammed to the same extent. The strength is expressed in kilograms per sq. cm.:

TABLE XXIII.

No. of Prism.	Apparent Specific Gravity.	Bending Strength Kg./cm.^{2}.	Compressive strength. Kg./cm.^{2}.		
			Halves of Prism.		Mean.
1	2·195	39·8	201·5	204	202·75
2	2·195	38·1	204	183·5	(193·75)
3	2·186	(33·4)	170·5	212	(191·25)
4	2·194	(37·5)	198	199·5	198·75
5	2·197	38·7	185·5	208	196·75
6	2·198	44·0	214	207	210·5
Mean	2·194	38·6	199·0		...
Mean of 4 highest	...	40·1	...		202·2

Tests to determine the adhesion of a cement to a given surface are occasionally made. The only surface which has been found to be satisfactory for this purpose is one of hardened cement, although tests with bricks and natural stones have often been made for special purposes. A rectangular block, provided with a groove for the attachment of the grip, is prepared and allowed to harden for a sufficient time in water. The flat upper surface is then rubbed with emery paper, and the second cement block is moulded upon it in a suitable iron mould, the size of which increases upwards. After setting and hardening for a specified time, the load required to separate the two blocks in an ordinary tensile testing machine is determined. This test must now be regarded as superfluous, the adhesive power of the cement being tested in a far more satisfactory manner by bending or tensile tests of cement-sand mortars. It has indeed been urged by several workers that the adhesive qualities of cement would be even better tested by adopting a less rich mixture (1 cement : 4 sand in place of 1 : 3) for briquettes, and it is possible that this may be one of the directions in which the present method of testing may be modified in the future.

The strength of cement and mortar briquettes and test-pieces increases with time, rapidly at first, then more slowly, the curve becoming asymptotic, but the maximum strength is not attained until after an interval of several years. W. C. Unwin[1] has concluded that the increase takes place according to the equation

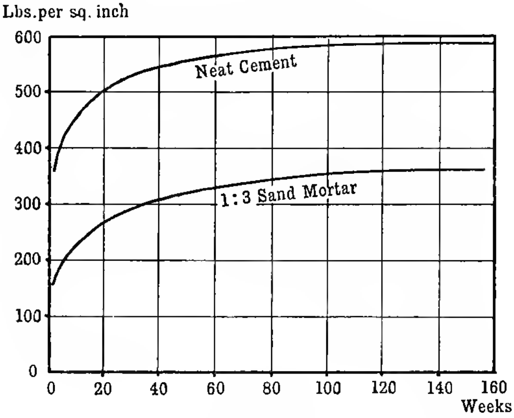


FIG. 16.

Increase of Tensile Strength of Cement with Time.

$$y = a + b(x - 1)\tfrac{1}{3},$$

in which y is the strength at any given time, x the number of weeks that have elapsed since setting, a is the strength one week after setting, and b is a constant, depending on the material. Two of Unwin's curves are shown in Fig. 16. The equation given is empirical, but represents

---

[1] *J. Soc. Chem. Ind.*, 1886, **5**, 188.

with fair accuracy the course of the hardening process. Another series of figures from tensile tests is given in Table XXIV.[1]

TABLE XXIV.

Age.	Neat Cement.		1 : 3 Mortar.	
	Kg./cm.^{2}.	Lb./in.^{2}	Kg./cm.^{2}.	Lb./in.^{2}.
7 days	39	555	16	228
28 ,,	45	640	21	298
90 ,,	54	768	25	356
1 year	66	939	30	426
2 years	72	1023	34	484
3 ,,	75	1067	36	514

The resistance to compression is at first eight to ten times the resistance to tension, but the ratio increases with age, so that old mortars may have as high a ratio of compressive to tensile strength as 12 or 16.

The necessity of waiting at least 28 days after gauging a mortar before obtaining results as to the strength of a cement being tested has led several workers to attempt the artificial "ageing" of the briquettes by heat. The briquettes, after remaining as usual for 24 hours in a moist chamber, are immersed in cold water, which is then gradually raised to boiling, and the heating is continued for 6 days. The tensile strength of the briquettes thus treated is supposed to represent that attained after hardening for 28 days at the ordinary temperature. Although a few experts have pronounced in favour of this test, the opinion of the majority is unfavourable.[2] Experiments are still in progress, with the object of establishing a definite relation between the strengths

---

[1] All these data refer to Portland cement.

[2] See reports to the Copenhagen Congress, 1909, by F. Berger, L. Deval, and A. Greil.

attained under the two conditions. A remarkably severe test is in use in Denmark, in which the briquettes are subjected to heating in water under pressure in an autoclave before testing. In so far as the accelerated strength test merely indicates the degree of unsoundness of the cement, it has no advantage over the usual hot tests for constancy of volume.

The requirements of the British Standard Specification in respect to strength are as follows: Briquettes of neat cement, kept in a damp atmosphere for 24 hours and in water for 6 days, must have a tensile strength of not less than 400 lb. per square inch (28 kg./cm.^{2}) and of not less than 500 lb. per square inch (35 kg./cm.^{2}) after 28 days. The increase in strength from 7 to 28 days must not be less than

25 per cent. if the 7-day test is between 400 and 450 lb.
20 ,, ,, ,, 450 ,, 500 ,,
15 ,, ,, ,, 500 ,, 550 ,,
10 ,, ,, ,, 550 ,, 600 ,,
5 ,, ,, ,, over 600 lb.

Mortar made with 3 parts of standard (Leighton Buzzard) sand and 1 part of cement must have a tensile strength of 150 lb. per square inch (10·5 kg./cm.^{2}) after 7 days, and 250 lb. per square inch (17·5 kg./cm.^{2}) after 28 days, the conditions of storage being the same as for neat briquettes. The increase of strength from 7 to 28 days must not be less than 20 per cent.[1] There is, unfortunately, no provision for compressive tests.

These standard figures are much lower than those given by the best brands of British cement on the market. For instance, the average of a large number of tests of different British Portland cements in the last few years gives the tensile strengths shown in Table XXV., whilst several brands are regularly delivered with still greater strength. One firm of contractors, using cement for reinforced concrete work, specifies that all cement supplied shall have

---

[1] See Appendix I.

a tensile strength, in the form of 1 : 3 briquettes, of not less than 250 lb. per square inch after 7 days and 325 lb. after 28 days. The compressive strength should be about 10 times as great, increasing to 11 times after 28 days.

TABLE XXV.

	7 Days.		28 Days.	
	Lb./in.².	Kg./cm.².	Lb./in.².	Kg./cm.².
Neat cement . .	656	46	808	56·7
1 : 3 mortar (standard sand) . . .	267	18·7	329	23

The German standard requires a tensile strength, for 1 : 3 sand briquettes, of 16 kg./cm.² (228 lb./in.²) after 28 days, and a compressive strength of 160 kg./cm.² (2280 lb./in.²) under the same conditions. Provision is also made for a test with 1 : 3 mortar, allowed to remain 24 hours in moist air, 6 days in water, and 21 days in air, the tensile and compressive strengths should then reach

TABLE XXVI.

	Tension.		Compression.	
	Kg./cm.².	Lb./in.².	Kg./cm.².	Lb./in.².
Light hydraulic limes .	6	86	30	426
Heavy ,, ,, .	8	114	50	712
Roman cement . .	10	142	80	1140
Quick-setting Portland .	14	200	130	1850
Slow ,, ,,	16	228	160	2280
Slag cement . .	16	228	160	2280

20 and 200 kg./cm.^{2} respectively. Such a test as this is of value in view of the fact that a very large part of the cement consumed is employed in the construction of buildings above ground. Quick-setting cements are not expected to reach so high a standard, a condition which is also provided for in the Austrian and Swiss Specifications. Tests with neat cement are not recognised.

Much less regularity exists in the specifications for cements other than Portland. The Swiss Standard Specification requires the following tensile and compressive strengths for normal (1 : 3) mortars of different materials after 28 days' hardening as described above (Table XXVI.).

The "slag cement" in the above table refers to the mixture of lime and granulated slag often sold under that name. Cement made by granulating basic slag, without the addition of lime, should give as high results as Portland cement. The figures given by one cement of this class are for 1 : 3 mortar:

7 days,	16·7 kg./cm.^{2}	(240 lb./in.^{2})
28 „	28 „	(400 „)

The mechanical strength of mortars prepared from lime, hydraulic lime, or other materials is tested in exactly the same way as cement mortars, but different methods of gauging have to be adopted according to the nature of the cementing material. Lime, after slaking, is usually made into a paste by working with water until it contains 43–46 per cent. of water. A definite quantity of this paste is taken for the preparation of mortars. It is also used for the testing of pozzolanic materials. As an example, the method recommended for the testing of volcanic trass[1] may be mentioned. A mixture of 1 vol. of trass, 1 vol. of standard lime paste, and 1 vol. of standard sand is thoroughly worked in a kneading

---

[1] M. Gary, *Mitt. k. Material-Prüf. Amt.*, 1910, **28**, 155.

machine, and is then rammed into the moulds in an "earth-moist" condition by means of a Boehme hammer. Briquettes thus prepared should be capable of resisting 14 kg./cm.^{2} (200 lb./in.^{2}) after being allowed to harden for 3 days in moist air and 25 days in water.

Mixtures of lime and cement may also be employed in making mortar. The addition of a small proportion of Portland cement to lime mortar is practised, particularly on the Continent, as a means of increasing the strength without unduly increasing the cost. The converse practice, of adding slaked lime to an ordinary cement mortar, has been frequently recommended as a means of rendering the mortar more plastic, and therefore more easily worked in laying bricks, whilst it has also been considered to improve the quality of mortar intended to harden in a moist situation. The addition is of no advantage when the hardening takes place in air. In Table XXVII. the quantity of lime powder or paste is expressed as a percentage of the weight of

TABLE XXVII.

Per cent. Lime.	Tensile Strength after 6 Months in Water.	
	Kg./cm.^{2}.	Lb./in.^{2}.
0	26·8	382
10 Paste	29·8	426
20 „	31·6	450
30 „	32·4	462
40 „	27·0	384
0	26·0	371
7 Powder	31·0	443
14 „	31·7	451
21 „	30·3	431
28 „	30·9	440

cement used, the weight of sand being in all cases three times that of the Portland cement.[1]

A study of the behaviour of such mixtures under different external conditions would be of interest. The extra mechanical strength given by the addition of lime must be the result of the formation of a mechanically resistant colloid, but it might be expected that the product would be more readily attacked by external agents than a pure cement mortar, on account of the large excess of lime. It must be remembered that the practice of adding trass or pozzolana to cement mortar required to resist water has precisely the opposite object, namely, that of diminishing the quantity of free lime in the hardened mortar by combining with it to form silicates.

The nature of the sand used for the preparation of mortars has a very marked effect on their strength, and it is therefore necessary to fix a "standard sand." The British standard sand is obtained from Leighton Buzzard, and consists of clean quartz grains. It is required to pass through a sieve having 20 meshes per linear inch and to be retained on one having 30 meshes per inch, the diameters of the wires being 0·0164 and 0·0108 inch respectively. The sand is therefore of very uniform grain. Greater strength is given by a graded sand, containing a proper proportion of coarse and fine particles, but it is very difficult to standardise a natural sand of this type, or to prepare a sufficiently regular artificial mixture. The German standard sand is obtained from Freienwald, and must pass through a brass plate 0·25 mm. thick, perforated with circular holes 1·350 mm. in diameter, and be retained by a similar plate having holes 0·775 mm. in diameter. The American, Austrian, French, and Swiss standard sands are of the same fineness as the British, whilst the

---

[1] Calculated from results given by L. C. Sabin, *Cement and Concrete*, London, 1905.

Russian sand is a mixture of equal parts of sand of this fineness with sand retained between sieves having respectively 30 and 37 meshes per linear inch. The question of the possibility of obtaining an international standard sand is at present under the consideration of a committee of the International Association for Testing Materials, and comparative experiments are also being made to determine the influence of different sands on tests performed under otherwise identical conditions.[1]

The effect of clayey matter or dirt, which is commonly present to a greater or less extent in the sand as received, is variously estimated by different authorities. It is frequently made a condition in specifications that all sand intended for use in mortar shall be thoroughly washed to free it from clay and dirt, but this precaution is regarded by some as superfluous. The presence of organic matter, the so-called "humic acids" of surface soil, is undoubtedly deleterious, but it is not certain that the presence of finely-divided clay, loam, or earth of a purely mineral character, is in any respect harmful. Experiments with mixtures of sand and fine dry loam, free from coarse particles, showed that the strength of the mortar was increased by the use of sand containing loam when the latter was not in excess of 10 per cent., and that washing a sand containing this quantity of clean earthy matter would even diminish its value as a constituent of mortar.[2]

The proportion of clay or loam in a sample of sand may be estimated by transferring a known weight of the dried material to a dish or basin, washing in a stream of water until all the lighter particles have been carried away, and drying and weighing the residue.

---

[1] The strength of mortars prepared from a large number of different sands has been studied by R. L. Humphrey and W. Jordan, *Bull. U.S. Geol. Survey*, 1908, No. 331.

[2] H. Germer, *Mörteluntersuchungen*, p. 41 (Berlin, 1910). This work contains a valuable series of curves illustrating the effect of different factors on the mechanical properties of cement mortar.

It is often desirable to determine the degree of compactness of a mortar after setting and hardening. The direct measurement of the porosity by determining the amount of water absorbed is impracticable, and the best method is that of determining the weight and volume of a briquette or other test-piece. The "apparent specific gravity" thus obtained is a measure of the compactness. The most convenient apparatus for the purpose is known as Ludwig's volumenometer. It consists of a glass cylinder, provided with tap a little above the foot, and having a ground flange at the top, on to which a conical lid fits, terminating in a narrow neck and funnel. The apparatus is first filled with water as far as the mark engraved on the neck. Water is then run out from the tap into a tarred beaker, until the level has fallen sufficiently far below the flange to allow the introduction of the specimen of mortar. The specimen is lowered into the vessel, the lid is replaced, and water is poured back from the beaker until the original level is again reached. The weight of water remaining in the beaker (in grams) gives the volume of the test-piece (in cubic centimetres). The weight of the test-piece, divided by the volume, gives the apparent specific gravity.

TABLE XXVIII.

Mortar.	Per cent. Water.	Apparent Specific Gravity.		
		24 Hours.	7 Days.	28 Days.
Neat cement	19·0	2·101	2·149	2·175
1:1	10·5	2·279	2·299	2·256
1:3	8·5	2·223	2·251	2·268
1:5	7·0	1·994	2·079	2·104
1:7	5·75	1·896	1·986	2·017

Prisms prepared without ramming, in the manner described above, from 1 part of cement and 3 parts of German standard sand, using 10 per cent. of water for mixing, have an initial apparent density of 2·234. A few figures are given in Table XXVIII. to illustrate the change taking place during the storage of test-pieces in water. The figures refer to cubes prepared for compression tests, with German standard sand, rammed with Boehme's hammer.[1]

The 1:1 mixture is denser than neat cement, but further additions of sand reduce the apparent specific gravity. The test-pieces become denser with increasing age.

PLASTERS.

Little has yet been done to standardise the methods of testing plasters. The fineness and apparent density are determined in the usual manner, and mechanical tests, so far as they have been made, have generally followed the lines of those employed for cements. When tensile tests are made, the plaster is gauged with 30–35 per cent. of water, filled by hand into ordinary briquette moulds, and allowed a few hours to set. Wall plasters reach their full strength at the end of a week, and it is therefore useless to prolong the tests to 28 days. The strength diminishes if the specimens are kept in moist air. The strength of neat plaster briquettes amounts to 21–28 kg./cm.^{2} (300–400 lb./in.^{2}), becoming as high as 32 kg./cm.^{2} (461 lb./in.^{2}) in the case of an exceptionally finely ground plaster.[2] The compressive strength is about three times as great, and is diminished by the addition of gelatinous substances as retarders.

Tests of the adhesion of plaster to surfaces of brick, stone, cement or other material are also made, the arrangement of the experiment being generally such that an ordinary table machine for tensile tests may be used. It

---

[1] M. Gary, *Mitt. k. Material-Prüf. Amt.*, 1904, **22**, 81.

[2] A. Marston, *Rep. Iowa Geol. Survey*, 1901, **12**, 224.

is convenient to arrange the two materials in such a way that the test-pieces may be held by tensile clips of the usual form.

The hard, slow-setting forms of gypsum may be mixed with sand, and develop sufficient mechanical strength in the process of setting to serve as mortars. The following tensile strengths have been obtained from mixtures of Estrich gypsum with German standard sand:[1]—

TABLE XXIX.

	7 Days.		28 Days.	
	Kg./cm.^{2}.	Lb./in.^{2}.	Kg./cm.^{2}.	Lb./in.^{2}.
1 : 1	20	286	23	328
1 : 2	16	228	24	343
1 : 3	13	186	15	214

It is a common practice, in making tests of the mechanical strength of cements and mortars, to prepare six briquettes from each consignment, and to take the average of the four highest results obtained, or the best six if ten are made. This procedure is to be deprecated. Exceptionally high results are as likely to be due to accidental causes as those which are exceptionally low, and the only fair method is that of averaging *all* the results obtained, rejecting only those briquettes which are clearly seen, before testing, to be cracked or otherwise damaged.

CONCRETE.

In concrete, a fragmentary material known as the "aggregate," and consisting either of natural gravel or of artificially broken stone, brick, or other hard substance, is used, the spaces which are formed on packing or piling such a material being filled with a matrix or mortar, composed of sand mixed with lime or cement. Although

---

[1] O. Frey, *Tonind. Zeit.*, 1910, **34**, 170.

the materials named, together with water, are the only essential constituents, others may be added, such as fine clay for the purpose of filling voids and producing greater compactness, and pozzolanic substances for the purpose of increasing the hardness of the mortar.

The strength of concrete depends on that of the aggregate, and on the proportions of mixing, the best proportions being those which result in exactly filling the voids of the aggregate with mortar, so as to avoid porosity on the one hand, and separation of stones by intervening mortar on the other. It is evident that such a result is more readily accomplished by using a graded aggregate, containing masses and particles of various sizes, than by having all the component stones of uniform size.

The voids in any given aggregate may be determined by the aid of water. The material is filled into a vessel of known capacity until just level with the top, and the amount of water which it will then hold exactly is measured. For example, a vessel is taken, the capacity of which is found by measurement of the water required to fill it to be 10 litres. It is then emptied, and filled with the aggregate to be tested, for example, broken granite. The quantity of water now required to fill the vessel is found to be, say, 4·75 litres, the aggregate is then said to have 47·5 per cent. of voids. This simple procedure is inapplicable if the aggregate is porous, as a quantity of water is then absorbed, in addition to that required to fill the voids. This error is eliminated by soaking the aggregate before the determination in order to saturate it fully. Very loosely porous aggregates, such as pumice or coke, are even then liable to an error, as the water used to saturate them largely runs out of the pores when decanted, thus causing the measurement of the voids to be too high. It may be said that the error is of no consequence, as the mortar will enter into the pores in the same way as the water employed in the determination, but this is only true if a very liquid mortar is used, as a thicker mortar is not sufficiently fluid to enter into the fine pores. Measurements may be made in a glass cylinder with mercury, the coke being prevented from floating up by a wooden cover. Mercury does not wet the surfaces, and therefore does not penetrate into the coke. This method is troublesome, and is fortunately rarely necessary.

The percentage of voids in an aggregate composed of fragments of varying sizes is less than in one composed of uniform fragments. That this is so is readily seen if we assume, for the sake of simplicity, that all the fragments are spherical. A vessel filled to the brim with cannon balls is capable of taking up a large quantity of marbles, and the vessel, now apparently full, is still able to receive a quantity of small shot, the smaller spheres coming to occupy the interstices between the larger ones. The voids are not completely abolished by the addition of shot, so that it is still possible to introduce water. Evidently, the more perfectly the aggregate approaches in character such an arrangement of spheres of varying sizes, the less is the quantity of cement required to fill the voids, and the denser the resulting concrete is likely to be. For material broken to pass the same screen, the percentage of voids is smaller in rounded than in angular material. That is to say, if both materials are of the same specified size, rounded gravel requires less mortar to form a dense concrete than does broken stone.

If we suppose the stone used to have 40 per cent. of voids, this number represents the volume of sand which must be added. If the sand has also 40 per cent. of voids, as is frequently the case, the quantity of cement which has to be added is $\frac{40 \times 40}{100} = 16$ per cent. by volume. The relative volumes actually occupied by cement, sand, and stone respectively in the finished concrete are therefore 16 : 24 : 100, or $1 : 1\frac{1}{2} : 6\frac{1}{4}$. The volume allotted to the cement is, however, that occupied by the colloidal products of hydration after setting, and not that of the original dry cement. We are unable to calculate the weight of cement to be used from the above data without some assumption as to the volume occupied by a given weight of dry cement after gauging and setting. A method of determining this volume has already been given on p. 187. If the volume occupied by 1 kilogram of the original cement after it has set and hardened for 28 days under water be v c.c., it will require $\frac{1000}{v}$ grams of cement to yield 1 c.c. of hardened colloid after 28 days. The mortar is to consist of 100 vols. aggregate, 40 vols. sand, and 16 vols. cement, and as it requires $\frac{16 \times 1000}{v}$ grams of dry cement to yield 16 c.c. of colloid, or $\frac{16 \times 1000}{v}$ kilograms to yield 16 litres, the weight of cement to be used in preparing a mixture may be used in place of the volume, provided that v is known. Further experiments are, however, required to determine the value of v in most cases.

It will be seen that the weight of cement to be used could not have been calculated from the specific gravity, or from the apparent density, both of which refer to the dry cement before hydration. The weight of a given volume of hardened mortar is not difficult to determine, and gives us an accurate knowledge of the volume a given weight of cement will occupy after being made into mortar or concrete.

However the calculation be made, the proportion of cement to be used in concrete should always be specified by weight and not by volume, as it is impossible to fill a measure satisfactorily with such a fine substance as cement, whilst weighing is easy. As cement is commonly sent out by the manufacturers in bags containing a fixed weight, usually 100 lb., it is a good plan to have measures made for the sand and stone or gravel capable of holding the exact volumes required to mix with one bag of cement. The trouble of weighing is thus avoided.

AGGREGATES.

A great variety of materials may be employed as coarse aggregates in making concrete, including both natural rocks and artificially burnt products. The choice of an aggregate in any given case is determined by a number of considerations, including the purposes to which the concrete is destined to be put, and the cost and local availability of the material. Further research is necessary to determine the relative value of different aggregates for particular classes of work, but the choice is often severely restricted by local conditions.[1]

Natural aggregates may be already fragmentary, as gravel, or may require to be broken before use, as granite or limestone. Natural gravels, particularly certain kinds of river ballast, have the advantage of being composed of pebbles of varying sizes, passing insensibly into sand, so that a dense concrete is more readily obtained by their use than by mixing fragments of approximately equal size with sand. Thames ballast is one of the best known materials of this kind. The adhesion of the mortar to smooth, rounded pebbles is less than to rough broken stone, but this difference is not serious, in view of the fact that the resistance of concrete to tensile stresses is not taken into account in reinforced concrete, and in

---

[1] A special commission was appointed by the British Fire Prevention Committee in 1907 to examine the question of concrete aggregates. The author was chemist to this commission, which issued an interim report in 1908 (see *Concrete and Constr. Eng.*, 1909, 3, 454). The elaborate series of tests proposed will necessarily extend over a long period.

mass concrete the tensile stress is never sufficient to test the adhesion very severely. A more serious objection to ballast is the liability of the flints of which it is composed to fly to pieces under the influence of heat. Ballast concrete is therefore unsatisfactory as a fire-resisting material in buildings, although perfectly satisfactory in foundations, embankments, retaining walls, &c. Fire tests, in which the concrete, in the form of slabs or vaults, is exposed to the action of a fierce fire, followed by the application of a jet of water, show that flint pebbles crack freely if the temperature reaches 1000°.[1] For reinforced concrete the ballast should always be crushed before use.

It is a general rule that the best fire-resisting aggregates are those which have been previously subjected to the action of great heat, that is, igneous rocks among natural, and burnt brick, &c., among artificial materials. To take the natural aggregates first, the denser varieties, such as basalts, traps, and dense lavas, are admirably suited for the purpose, the principal objection to their use being their high specific gravity (3·02 for Rhenish basalt, 2·72 to 2·94 for British dolerites and similar rocks). The more porous lavas and other volcanic materials are naturally lighter, the lightest being pumice, which has a low crushing strength, but is very suitable for concrete partitions and similar work in which lightness and high fire-resisting qualities are desirable. Granite (specific gravity about 2·7) is an excellent material, and yields sharp, angular fragments when crushed, from which a dense concrete may be prepared for use with steel reinforcement. The granite must be free from decomposed material.

Amongst sedimentary rocks, the limestones are the most important as aggregates. A dense and uniform limestone, such as Portland stone, of specific gravity about

---

[1] *Fire Tests with Floors*, Report No. 101 of British Fire Prevention Committee, London, 1905.

2·7, breaks into angular fragments with a rough surface, to which the mortar adheres very firmly. For such purposes as the construction of bridges, limestone is found to give unsurpassed results, especially if sand made from the crushed stone be employed in place of the usual siliceous sand. Concrete made in this way is less heavy than that prepared from ballast, and is also more homogeneous. When broken in a crushing test, the fracture is found to pass through aggregate and mortar, without any separation of the stone from the matrix. A further advantage is that Portland stone concrete may be dressed to produce an attractive surface, the constituents being of similar hardness and appearance.[1] Limestone concrete should not be used for internal work intended to be fire-resisting, as the low temperature of decomposition of calcium carbonate causes the limestone to "burn" and fall to powder when exposed to flame, bringing about a rapid collapse of the concrete.

Little has yet been done to determine the suitability of different sandstones, quartzites, and similar rocks for use as aggregates. Micaceous sandstones, however, should be as a rule avoided, on account of the flat shape of the fragments into which they break on crushing. The same objection applies to other rocks, either sedimentary or metamorphic, which have a schistose or a slaty structure, as the thin, flat fragments do not pack together in a compact manner, but form bridges, and therefore cavities, in the concrete.[2]

The most generally useful artificial aggregates are broken brick and burnt clay ballast, both of which have rough surfaces giving good adhesion. The bricks should be hard and well burnt, and all dirt should be removed before crushing. Clay ballast must be well burnt, and

---

[1] E. P. Wells, *Trans. Concrete Inst.*, 1909, **1**, 65.

[2] Notes on the general properties of aggregates are given by J. S. Owens, *Concrete and Constr. Eng.*, 1909, **4**, 40.

must be able to bear immersion in cold water for a considerable time without disintegration. Terra-cotta and similar materials may be used in the same way as brick. Clinker from furnaces, if thoroughly burnt and free from dust, yields good concrete, but is liable to contain sulphur, as described below.

Two artificial aggregates remain, as to the merits of which there has been much controversy, namely, coke-breeze and blast-furnace slag. Clean coke breeze, free from sulphur, is undoubtedly a useful material where great strength is not required; it is very light, adheres well to the mortar, and resists great heat, resembling in these respects natural pumice. Most coal, however, contains sulphur generally in the form of iron pyrites, and the greater part of this sulphur remains in the coke after the process of distillation, as iron sulphide, a compound which is readily oxidisable in the presence of moisture. Should air and moisture gain entrance to the interior of the mass, a process which occurs with ease in so porous a material as coke-breeze concrete, oxidation takes place, accompanied by a considerable increase of volume, which may result in the complete disruption of the concrete. Many instances are known in which fire-proof floors have expanded from this cause, and have cracked and bulged with sufficient force to lift up and break an overlying layer of asphalt. Experiments are needed to determine the permissible limit of sulphur, and the conditions under which oxidation takes place; in the meantime, it is advisable to regard coke-breeze concrete as a material to be employed only with the utmost caution, or, better, to be avoided altogether.

Blast-furnace slag, if dense and of suitable composition, forms an excellent fire-resisting aggregate, to which the mortar adheres well. The presence of sulphides is an objectionable feature, as tending to form iron sulphide, which may subsequently cause expansion by its oxidation, although the calcium sulphide, in which form the sulphur is originally present, is not in itself deleterious. It is very desirable that systematic investigations should be made to determine the requirements of a slag suitable for use in concrete. The claim has been made,[1] that all blast-furnace slags, including those which disintegrate in course of time on exposure to air, yield sound concretes, and the claim is supported by tests on concrete, up to an age of six months, showing a steady increase of strength, even in the case of unstable slags. This rather remarkable result is explained by the protective action of the mortar in preserving the masses of slag from exposure to the air. However this may be, it is obviously undesirable that an unstable material should be used, liable to disintegration whenever air gains access to the interior or when, by cutting or drilling, new surfaces are produced. At the same time, it is certain that many blast-furnace slags are capable of yielding sound concrete, and in view of the enormous accumulations of this waste product, obtainable at low cost, its utilisation in this way is a question of great technical importance. The same remarks apply to the use of granulated acid slag in place of ordinary sand, a practice which is now frequently adopted where suitable material is available. Concrete has even been prepared[2] in which all the constituents are derived from blast-furnace slag, the aggregate being broken slag, mixed with slag sand, and the cement being of the kind known as "Iron-Portland." Evidently many further tests are necessary before such a material can be employed without serious risk.

REINFORCED CONCRETE.

In reinforced concrete structures steel is embedded in the concrete in such a way that tensile stresses are taken,

---

[1] H. Passow, *Stahl und Eisen*, 1910, **30**, 829.

[2] A. Knaff, *ibid.*, 827.

as far as possible, by the steel, whilst the compressive stresses are taken by the concrete. The efficiency of this form of construction depends on the proper proportioning and arrangement of the steel reinforcement, on the quality of the concrete, and on the adhesion between the steel and concrete. The first of these conditions is entirely a matter for the engineer, but the second and third call for some notice here.

Portland cement concrete is the only material suitable for reinforced construction, on account of its high strength, and it is necessary that the quality of the cement shall be fully equal to the standard, especially in respect to soundness. Unsound cement may produce the most disastrous results in this class of work. The aggregate may be of any of the kinds enumerated above, according to circumstances. It must be much more thoroughly broken than is necessary for mass concrete work, a good rule being that the whole should pass through a screen having meshes $\frac{3}{4}$ inch (19 mm.) square. The proportion of voids in the sand and aggregate should be accurately determined, and the ingredients should then be employed in such proportions as to yield a thoroughly dense concrete. It is obviously useless to prescribe fixed proportions, since the best quantities of the respective ingredients have to be determined in every case by direct measurement. The practice of using fixed proportions, irrespective of the grading of the aggregate, is to be condemned, but, as an indication of the quantities used in a particular case, it may be mentioned that one firm conducting much work of this kind uses the following quantities when suitable material is available:—

Gravel, containing stones of all sizes between a $\frac{3}{4}$ inch (19 mm.) and $\frac{1}{8}$ inch (3 mm.) mesh, but free from larger stones and from sand, 20 cubic feet; sharp sand, 10 cubic feet; cement, 500 lb.

The concrete may be mixed by hand or by means of a machine. Where skilled men are employed, hand mixing gives results which are not to be excelled by work with any form of machine, but care must be taken that the ingredients are very thoroughly mixed by being turned over not less than three times in the dry state and three times after the addition of water. If mechanical mixing be employed, the machine should be one in which there is no tendency to bring about separation of the ingredients. Those forms of machine in which the materials fall from a height on to baffle plates, water being added in the course of the fall, almost inevitably produce a separation of the heavier and lighter particles, especially if the concrete be very wet.

There is some difference of opinion as to the best consistence of concrete for reinforced work. Concrete containing a comparatively low proportion of water may be more strongly rammed than one which is more liquid, and attains a higher strength after setting. A mixture which is too dry is unsafe to use, as it is impossible to ensure its compactness, hollows tending to form under the reinforcing rods owing to the lack of plasticity of the mass. On the other hand, a fairly liquid concrete enters readily into all the recesses of the work, and although it cannot be rammed heavily, this is not really a disadvantage, as heavy ramming is very likely to cause displacement of the reinforcing metal, especially when loose "stirrups" or connecting pieces are used. On the whole, the best results are obtained by the use of a fairly plastic concrete, which can be tamped into position without heavy ramming, the slight loss of strength, as compared with a drier mixture, being amply compensated for by the greater certainty that no cavities will remain between and under the reinforcing rods. Concrete which is too liquid has little strength, and is apt to settle, the coarser particles falling to the bottom. The practice, adopted in some places, of using concrete which flows like a thick soup, is entirely to be condemned.

The adhesion of good concrete to steel is remarkably perfect. It is facilitated by coating the steel before use with a thin liquid cement grout, a procedure which preserves the rods from rusting. Loose rust should be removed by brushing or scraping, but it is not at all necessary that the surface of the steel should be perfectly bright, a firmly adhering, thin film of rust having no evil effect. Many means have been adopted of increasing the adhesion by artificial means, by employing corrugated, indented, or other forms of bars in place of smooth cylindrical rods, but the relative advantages of the two methods are still the subject of discussion and experiment.

Tests of Concrete.

The quality of concrete may be determined in the laboratory by compressive tests on 6-inch or 4-inch cubes. It is useless to perform tests on cubes smaller than those named, as in small test-pieces the dimensions of the particles of aggregate are too large in comparison with those of the cube, and the results are influenced too greatly by merely accidental circumstances. The concrete may be mixed by hand or in a laboratory mixer, but is always rammed by hand, using a heavy iron pestle, which is raised and allowed to fall by its own weight until a sufficient degree of compactness is obtained. The square base of the pestle fits loosely into the iron mould. The conditions of setting and hardening are the same as in the testing of mortar, and the testing press is of the same kind, a very heavy machine being of course necessary for crushing the larger cubes.

The strength of concrete, like that of mortar, increases with time. Fig. 17 shows the rate of increase of strength of a concrete prepared from 1 vol. cement, 1¾ vols. sand, and 3¼ vols. gravel, the latter passing a ¾-inch sieve and being retained on a ¼-inch sieve. A 12-inch cube was used for each test, and the results are expressed in tons per square foot. The cubes, after being once hardened, are kept in water or in air until tested, according to the nature of the work for which the concrete is to be employed.

Tests of blocks prepared in the laboratory, although indicating the strength which may be attained by the concrete mixture in question under favourable circumstances, are not an accurate indication of the strength of a structure composed of the same concrete, as the conditions of mixing and ramming are less favourable in the work of actual construction than in the careful procedure of the laboratory. The necessity of taking specimens from the structure after erection may therefore sometimes arise, and provision is made in many building regulations for the purpose. A mass of concrete which has been removed from a wall or embankment may be trimmed to the form of a cube for a compression test by using a machine saw, consisting of a thin steel blade without

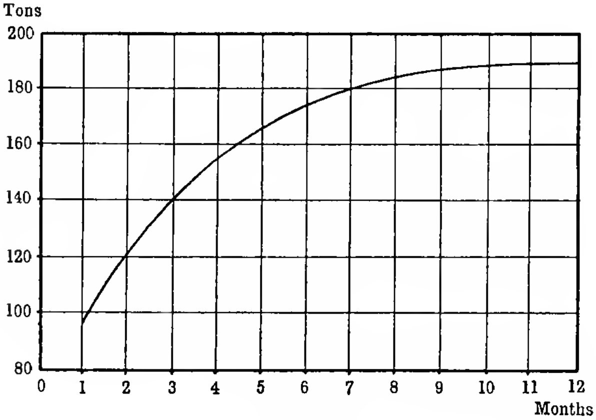


Fig 17.

Increase of Compressive Strength of Concrete Cubes with Time.

teeth, the cutting being effected by feeding a continuous stream of sharp sand and water on to the part being cut. Cubes thus prepared are crushed in a press in the ordinary manner.

Tests of reinforced concrete are necessarily carried out on a large scale. It is impossible to form any opinion as to the strength of structural members from small laboratory prisms, and the usual method of testing, by bending beams, is only applicable to specimens from 1 to 2 metres in length, the value of the test increasing with the size of the test-piece. Experiments of this kind may be performed in a laboratory provided with one of the modern forms of hydraulic machine, but the conduct of such tests lies outside the scope of this work.

Tests of the adhesion of concrete to steel, a quality which is intimately connected with the chemical properties of mortar, may be usefully made in the laboratory. In the usual method of conducting the tests, rectangular prisms of the concrete are prepared, in each of which a single steel rod is embedded in an axial position. The hardened prism is held in the testing machine by a plate pressing against one of the end faces, and the force required to pull out the rod is measured. The effect of varying the density of the mortar, the nature of the aggregate, the surface condition of the steel reinforcement, &c., may be conveniently determined in this manner. The effect of mechanical devices for preventing slipping between the steel and the concrete, such as twisting or indenting the bars, turning up or splitting their ends, &c., is best determined by the observation of specially prepared beams under the bending test.

Artificial Stone.

Artificial stone is a material similar in character to concrete, and composed of chips of natural stone (the refuse obtained in quarrying and shaping blocks) cemented together by a suitable matrix. It is usually cast in moulds, allowed sufficient time to set and harden, and employed in the same way as blocks of natural stone.

In the older forms, the sand or stone chips were mixed with sodium silicate solution, in a wet mill, and cast in moulds. After turning out, the blocks were immersed in a solution of calcium chloride, at first cold and then hot, sometimes even under pressure. The reaction between sodium silicate and calcium chloride approximately follows the course of the equation

$$Na_2SiO_3 + CaCl_2 = CaSiO_3 + 2NaCl,$$

but the calcium metasilicate thus produced is not crystalline, but colloidal. The matrix of the stone is therefore, as in the case of cement mortar or concrete, a colloidal calcium silicate. It is necessary to remove the other product of the reaction, common salt, by very thorough washing, as otherwise its crystallisation weakens the mass and the appearance of salt crystals as a surface efflorescence disfigures the stone.

The method described being a troublesome and comparatively costly one, has been generally superseded by the simpler process of mixing stone chips with Portland cement, and allowing the mixture to set. Nearly all artificial stones are now made in this way.[1] The matrix is, as before, mainly a colloidal calcium silicate, but it is more easily obtained. In the best qualities, granite chips are used, from 2·5 to 4 parts of chips being used to one part of Portland cement. After being moulded to shape, generally under pressure, the moulds being provided with rams, and allowed to set, the blocks or slabs may be merely stored in air or in water until the hardening has proceeded

---

[1] The composition of the different commercial brands of artificial stone is given in *Concrete and Constr. Eng.*, 1907, **2**, 60. A much longer list, with numerous tests, is given by H. Burchartz, *Mitt. k. Material-Prüf. Amt.*, 1905, **23**, 97.

sufficiently far, but in many varieties a further treatment is applied, consisting in the immersion of the stone in a solution of sodium silicate, which converts the lime of the cement, liberated in setting, into calcium silicate. The action is mainly confined to the surface of the blocks, although by prolonged steeping the silicate may be made to penetrate to a considerable depth. In most cases, however, the action of the silicate is limited to the formation of a hard outer layer, capable of resisting weathering, and of protecting the interior during the slow hardening of the cement. The quality of the stone evidently depends on the quality of the cement and aggregate employed in its manufacture, on the proper proportioning of the mixture to produce a minimum of voids, and on the time allowed for increase of strength by hardening. Mineral colouring matters are sometimes incorporated with the mortar in order to produce an approximation to the colour of some natural stone.

SAND-LIME BRICKS.

An artificial material which has now assumed some industrial importance and stands in chemical relationship to the calcareous cements, in spite of its different method of production, is that known in Germany as "Kalksandstein" (lime-sandstone) and in this country as sand-lime bricks.[1] The preparation of this material depends on the fact that crystalline silica is largely converted into the soluble form when heated with steam under pressure, especially in the presence of bases with which it can combine to form silicates. In the process of manufacture, sharp sand is mixed with a small quantity of powdered slaked lime, the mixture moulded into blocks in a brickmaking press, and the bricks thus obtained subjected to the action of steam under high pressure. The grains

---

[1] First prepared by W. Michaëlis in 1880.

of sand are superficially converted into the soluble modification, which combines with the lime, forming a cement of hydrated calcium silicate uniting the grains together to form a coherent mass. Most writers on sand-lime bricks represent the cementing material by the formula CaH_2SiO_4, with a greater or less number of molecules of water of crystallisation. On the view here taken of the nature of hardened Portland and other cements, we must regard this substance as consisting of colloidal calcium silicate, to which it is useless to assign a definite formula. The soluble silica formed by the action of steam on sand is itself a colloidal substance, and we should therefore expect that it would react with the lime in immediate contact with it, without giving rise to the production of any crystalline substance. In the finished product there should therefore be a continuous variation of composition, from pure silica at the unaltered centre of the sand grains, through colloidal layers becoming richer in lime as they are farther removed from the centre.

In the actual process of manufacture, the quantity of lime used is only 5–10 per cent., according to the nature of the sand used. Felspar sand, which already contains 5–7 per cent. of soluble silica, gives the best results. The addition of kaolin to the mixture lowers the tensile strength of the product. After moulding into blocks, hardening is performed by heating for about eight hours under a steam-pressure of 8–12 atmospheres.[1] It is possible to obtain still more complete combination, and therefore to incorporate a larger proportion of lime, by heating under 200 atmospheres in the laboratory, but no advantage is gained by increasing the pressure within the limits which are practicable on the large scale.[2] Dolomitic lime may be

---

[1] S. V. Peppel, *Tonind. Zeit.*, 1903, **27**, 2204; 1904, **28**, 23; H. Schön, *Chem. Ind.*, 1903, **26**, 621; R. Seldis, *Zeitsch. angew. Chem.*, 1906, **19**, 181; H. Steffens, *Rep. intern. Congr. appl. Chem.*, Berlin, 1908, i. 699.

[2] E. Tischler, *Oesterr. Chem. Zeit.*, 1905, **8**, 145; M. Glasenapp, *Tonind. Zeit.*, 1905, **29**, 689.

used with success, as silica combines with magnesia under the same conditions as with lime, but it has not been found possible to incorporate alumina in the same manner, although, when kaolin is used as one of the ingredients, alumina is found as a constituent of the cementing material.

The strength of sand-lime bricks, properly hardened, so that the whole of the lime is converted into silicate, is considerable, amounting to 300–400 kg./cm.^{2} (4270–5690 lb. per square inch) in compression. The strength increases in some cases after storage in water, but this statement probably only applies to material in which the reaction has not been carried to completion in the hardening vessel. Bricks composed only of sand and lime resist a temperature of 1250° without losing their shape or strength, but those containing kaolin are apt to crack and explode under such conditions.[1]

The following books may be referred to on the subjects of concrete and reinforced concrete, and of methods of testing. The literature dealing with these materials is now very extensive.

C. F. Marsh and W. Dunn, *Reinforced Concrete*, 2nd edn. London, 1908.

R. Feret, *Étude Expérimentale du Ciment Armé.* Paris, 1906.

F. von Emperger, Editor, *Handbuch der Eisenbetonbau*, Berlin, 1907 onwards. A very comprehensive work, extending to many volumes.

G. Revere, *Le Construzioni in Cemento Armato.* Milan, 1910.

W. C. Unwin, *The Testing of Materials of Construction*, 3rd edn. London, 1910.

---

[1] H. Gerlings, *J. Chem. Metall. Soc. S. Africa*, 1905, **5**, 229.

CHAPTER VIII

THE RESISTANCE OF CEMENT AND CONCRETE TO DESTRUCTIVE AGENTS

STRUCTURES composed of concrete, or into the composition of which cement enters, although primarily designed from the point of view of mechanical strength, are generally exposed to destructive influences of quite another order. Alternations of high and low atmospheric temperature tend to produce cracks in the material, whilst exposure to frost, even for short periods, may bring about rapid disintegration under certain conditions. The solvent action of rain or of pure water is comparatively unimportant, but water containing mineral salts in solution is exceedingly destructive, and the problem of preparing concrete having a high degree of resistance to the disintegration of sea-water is one of the most serious with which the engineer has to deal, whilst the action of peaty water, of sewage, and of waste water from factories introduces further special difficulties. The more important of these influences may be considered in order.

The effect of **alternations of temperature** varies with the dimensions of the structure. Unlike metals, cement and concrete have a low conductivity for heat, and the temperature of a mass is only very slowly equalised. In consequence of this low conductivity, the outer surface of a mass of concrete exposed to hot sunshine by day and to a much lower temperature at night, is first hotter and then colder than the mass at a small depth below the surface, the temperature of which remains practically constant. Stresses are thus produced which may result in the formation of cracks. The effect only becomes serious in the case of large surfaces exposed to direct sunshine, and is even then less than is generally supposed, being insufficient to cause cracking if the structure is properly proportioned, and sufficient elasticity is present at such points as the abutments of large arches. Exaggerated estimates of the stresses produced by changes of temperature have often been made, especially in dealing with bridges.[1]

The effect of **great heat,** as in a conflagration, is partly physical, to produce expansion, and partly chemical, to cause dehydration of the cement. The value of reinforced concrete in fire-resisting construction is largely due to the fact that steel and dense concrete have practically the same coefficient of expansion. A well constructed building, therefore, in which the concrete and steel are continuous throughout, so that the structure may be described as monolithic, is highly resistant to fire, but its good qualities are entirely dependent on the good proportioning and mixing of its ingredients, and the care taken to ensure a sufficient thickness of concrete as a protecting layer of low conductivity around the steel. If the steel be exposed at any point, or so thinly covered as to become heated rapidly, its high conductivity for heat causes its temperature to rise far above that of the surrounding concrete, so that it expands excessively, and severe internal stresses are produced in the reinforced members. The influence of the character of the aggregate on the resistance to fire has already been referred to (p. 194).

However good the quality of the concrete may be, disintegration sets in when a temperature of 300° is reached, owing to the expulsion of water from the cement by heat. The desiccated gel being destroyed, the cement

---

[1] F. von Emperger, *Concrete and Constr. Eng.*, 1909, **4**, 87.

crumbles to dust, with complete loss of mechanical strength. This action is unavoidable, but if the concrete be hard, and the aggregate be a suitable one, the disintegration is confined to a thin surface layer, the conductivity being too low to allow the heat to penetrate deeply in any but prolonged conflagrations.[1]

The next destructive agent to be considered is **frost.** Water expands considerably in its passage from the liquid to the solid state, so that water enclosed in the pores of a mass of concrete, if allowed to freeze, forces the particles of mortar apart, or at least sets up severe internal stresses. The effect becomes intensified by repetitions of the processes of freezing and thawing. The first freezing develops minute internal cracks, which subsequently become filled with water. At the second exposure to frost, the water enclosed in the cracks also freezes, producing further disruption of the concrete, until after several repetitions the whole mass becomes fissured. The first appearance is usually that of the separation of flakes of mortar from the surface, the water penetrating most readily into the superficial layers, and exerting its greatest influence there. The denser the concrete, and the less permeable it is to water, the better it is able to resist the action of frost.

Several of the larger testing laboratories, notably those of Zürich and Rome, are provided with freezing machines for the purpose of making comparative tests of the resistance of different concrete mixtures to frost. The specimens may be placed in a vessel of water, surrounded by brine cooled by the expansion of carbon dioxide or ammonia. Immersion of concrete blocks in the apparatus until frozen, followed by thawing and drying in air, the process being repeated several times, is an exceedingly severe test of the density of the concrete. The production of cold being an operation requiring special apparatus, the

---

[1] For notes on the requirements of fire-resisting construction, see J. Sheppard, *Concrete and Constr. Eng.*, 1907, **2**, 13.

plan has been adopted in some laboratories of immersing the blocks to be tested in a warm solution of sodium thiosulphate, and allowing the salt to crystallise in the pores of the mass as it cools. The outward thrust exerted by the crystals as the solution solidifies closely simulates the disruptive thrust due to the expansion of water in freezing. Tiles are sometimes disintegrated by the disruptive force of salts taken up from a solution in contact with them, and crystallising in their pores.[1] Quantitative comparisons between the effects of frost and the crystallisation of salts do not appear to have been made.

It is not easy to explain the apparent expansion of a salt at the moment of crystallisation. Actual measurement shows that the passage of a supersaturated solution from the liquid state to that of a mixture of crystals and another liquid is accompanied, in the case of such salts as sodium thiosulphate, by a diminution, and not by an increase of volume. The same statement holds good of the solidification of many substances on cooling from the molten state. Water, as is well known, expands at the moment of freezing, and there is therefore no reason to seek further for an explanation of the disruptive effect which it exerts when enclosed in the pores of a mass of stone, brick, or concrete, but many metals and alloys, which undergo an actual contraction during freezing, nevertheless exert a considerable outward thrust when crystallising from the molten state. This thrust can only be attributed to the axial growth of the crystals. Crystals of some salts, growing in their aqueous solution, have been observed to exert a thrust in the direction of their principal axes, amounting to several kilograms for a single crystal. This "crystallising force," whatever may be its physical nature, is responsible for the disruptive effects of crystallising salts.

---

[1] J. W. Cobb, *J. Soc. Chem. Ind.*, 1907, **26**, 390; *Trans. Amer. Ceram. Soc.*, 1909, 11, 64.

Mortar is generally considered to be seriously injured by freezing after mixing and before use. Careful experiments indicate, however, that the injury is less than is commonly supposed.[1] Mortar frozen by cooling to −10°, and then broken up and thawed before setting in place, is very little injured, even when it has remained in a frozen state for a whole day, although freezing for several days results in a marked diminution of strength. Much depends on the consistence of the mortar, a "wet" mortar being much less weakened by freezing than one which has been gauged with the minimum quantity of water. This influence is particularly marked in the case of concrete, the strength of a very dry concrete being reduced, in one instance, to 14 per cent. of its normal value by freezing for three days, whilst a wet concrete only had its strength reduced to 67 per cent.

It is particularly necessary to guard against damage by frost during the setting of cement in position. In the erection of ordinary brickwork or masonry, such damage may be avoided by covering up the work with sacking and boards as soon as laid, but special precautions have to be taken in the erection of concrete structures, including the erection of canvas screens around the part of the building under construction. When it is necessary, owing to lack of time, to continue work during severe frost, the plan has even been adopted of heating the bins in which the materials are stored, and of blowing steam through the water used for mixing.

Impermeability to water is required of much of the concrete used in building, but is of the first importance in concrete employed for the construction of reservoirs, aqueducts, conduits, gasholder tanks, sewers, &c. The difficulty of obtaining an impermeable mass is often overcome or evaded by coating the surface in contact with water with a layer of impermeable material, such as a

---

[1] H. Burchartz, *Mitt. k. Material-Prüf. Amt.*, 1910, **28**, 276.

dense mortar, but it is nevertheless desirable to obtain a concrete offering the greatest possible resistance to the passage of water through its mass.

Much difference of opinion exists as to the relative advantages of different calcareous cements in situations exposed to the direct contact of water, and although Portland cement is commonly preferred, and is often regarded as the only suitable material, there are not wanting engineers who employ by preference lime concrete, using a hydraulic lime of good quality, generally in conjunction with trass or some other material having pozzolanic properties, with or without the addition of a certain proportion of Portland cement. Such methods of construction assume, from the nature of the case, greater importance in Continental countries than in Great Britain.

Several methods have been proposed for lessening the permeability of mortar and concrete for water, depending, as a rule, on the filling of the pores with an insoluble and water-repelling substance. Such a filling may be distributed throughout the mass, by mixing with the mortar before setting in place, or it may be confined to a layer at the surface, being applied externally after the cement has set. Again, the fillings may be classified as (1) those of an organic character, which coat the particles of the mortar without uniting chemically with them, (2) inert particles of inorganic matter, and (3) those which produce increased hardness and impermeability by the formation of an insoluble inorganic compound.

The device of mixing a fatty or albuminous substance with the mortar is very old. Vitruvius and Pliny mention the use of milk, blood, and lard as additions to the mixture of slaked lime and powdered marble composing their stucco, and later examples of the use of oils are known.

Modern "waterproofing" materials, intended for addition to the mortar or concrete at the time of mixing, very commonly consist of mixtures forming an insoluble soap, that is, a salt, generally a calcium or aluminium salt, of stearic and other fatty acids.[1] Mixtures of lime and tallow, or of soap and alum, are the most usual preparations of this kind. They are sometimes supplied in the form of powder, to be mixed with the cement before gauging, or they may be produced at the moment of gauging by mixing the two solutions, so that a finely divided precipitate of the insoluble soap is obtained. If alum be mixed with an alkali instead of with soap, the precipitate is composed of aluminium hydroxide in a colloidal condition, which fills the pores mechanically, but does not possess water-repelling properties.

More recently, American experiments have shown that oil may be mixed with the constituents of concrete.[2] A mineral oil must be used, on account of the chemical inertness of the hydrocarbons of which it is composed, as animal and vegetable oils inevitably give rise to the formation of organic acids in course of time. A viscous oil is to be preferred, and it must be thoroughly mixed with the wet mortar or concrete, so that the oil and water form an emulsion. Setting takes place without change of volume, and the resulting mass is impervious to water. In other preparations on the market the oil is made into an emulsion before mixing with the mortar.

Assuming that impermeability is really attained by the addition of oily substances or insoluble soaps to the mortar, it is natural to inquire what effect is produced on the mechanical strength. Whilst it is claimed that the strength is not reduced by such treatment, general experience goes to show that a reduction of as much as 30 per cent. results. The emulsified oil or soap forms a coating round the particles of cement, each of which is already

---

[1] The composition of a number of patented and proprietary mixtures of this class is given by W. L. Gadd, *Concrete and Constr. Eng.*, 1908, **3**, 154.

[2] See A. Moyer, *Concrete and Constr. Eng.*, 1910, **5**, 166.

surrounded by a thin shell of water. Within the sphere thus formed the chemical reactions proceed in a normal manner, the velocity of setting being somewhat reduced, but without interfering with the hydration and formation of the gel. Hardening in air may therefore even be facilitated, the layer of oil preventing loss of water by evaporation and consequent shrinkage, thus ensuring freedom from cracks. The strength of a mortar depends, however, on the continuity of the colloidal mass between the cement particles, and if anything occurs to interrupt this continuity, the cohesion of the cement is lessened, and the strength is reduced. It is possible that suitable oily materials may be absorbed by the desiccated gel as hardening proceeds, so that the separating layers of oil gradually disappear and continuity is not destroyed, but there is no direct proof of such an effect. On the other hand, soaps are very unlikely to be absorbed in this way, and it would seem inevitable that soapy materials should diminish the strength. The importance of improving the watertight qualities of concrete is so great that further direct experiments in this direction are greatly to be desired.

Greater compactness may be given to concrete by the addition of very finely divided filling material of an inorganic and chemically inert nature. Clay has been largely used for this purpose, and still finds defenders, but there can be no doubt that it is inferior to a dense mortar prepared with sand without the addition of loading material. The most watertight mortar is that prepared by mixing proper proportions of mortar and aggregate, so as to reduce the porosity to a minimum. The advantages of adding pozzolanic materials or of using cement containing little or no alumina, in the preparation of concrete intended to resist water, are discussed on pp. 221 and 224.

The plan may also be adopted of coating that surface of the concrete which is to be in contact with water with a preparation intended to form an impervious external layer. It is not essential that penetration to any great depth should take place, provided that the surface layer is completely impervious and adherent, so that flakes will not become detached. Leaving aside the plan of coating the surface with asphalt or tar, which affords a mechanical protection independently of the concrete, most of the preparations employed deposit an insoluble precipitate, either of an inorganic or of an organic character, in the previously existing pores of the concrete surface. Sometimes the concrete is given a preliminary coating with a thin mixture of cement and sand, with or without the addition of lime. After the application of this coating the surface is brushed with solution of alum and sodium hydroxide, applied alternately, and a fine, gelatinous precipitate of alumina is thus produced. Another method consists in brushing alternately with solutions of soap and alum, time being allowed for drying after each coat. The precipitate in this case is the insoluble and water-repelling aluminium soap. A solution of paraffin wax in light petroleum, well brushed into the dry surface, penetrates well into the concrete, and produces a very impervious coating.

The conversion of the lime at the surface into an insoluble calcium compound, by brushing with solutions of sodium silicate or silicofluoride, is also very effectual as a means of lessening the permeability. In a few instances oxalic acid has been used, as the calcium oxalate formed is not decomposed by carbon dioxide or by dilute organic acids.

Special reference may be made to the treatment of cement and concrete surfaces with soluble silicofluorides, as the object of such an application is not merely an increase of the water-resisting properties of the mass, but an increase in the hardness and durability. The silicofluorides of aluminium, magnesium, and zinc are employed for this purpose, and are brought into commerce under the designation of "fluates." The following results were obtained by immersing cubes of 1:3 Portland cement-sand mortar two or three days after setting, in a bath of dilute silicofluoride solution for two to five hours:[1]—

TABLE XXX.

	7 Days.		28 Days.	
	Kg./cm.^{2}.	Lb./in.^{2}.	Kg./cm.^{2}.	Lb./in.^{2}.
Untreated . .	81	1150	87	1340
Fluated . . .	125	1780	120	1710

The resistance to the influence of frost was also found to be increased by 50 per cent. or more, whilst blocks subjected to abrasion tests, which indicate the condition of the external layers, gave as much as ten times greater resistance when treated than when untreated.

As regards the best means of preparing concrete for use in situations in which impermeability to water is an essential quality, as in tanks and reservoirs, it must be remembered that the closeness of texture of the concrete is all-important. It may be possible to exclude water more perfectly by special treatment, whether of the ingredients at the time of mixing, or of the surface after hardening, but the permanent value of such methods has not yet been satisfactorily demonstrated, whilst it is certain that concrete composed of well-graded aggregate, the voids of which are completely filled with mortar prepared with fine sand, may be entirely watertight. An excess of water must be avoided in mixing, being liable to cause shrinkage

---

[1] M. Merkuloff, *Tonind. Zeit.*, 1909, **33**, 871, from the Russian *Ingenieur*, 1909, **28**, 114.

during setting, and precautions must of course be taken to prevent drying by evaporation, as well as frost, shock, and other disturbing influences tending to produce cracks. Even very fine cracks, ramifying in the interior of the mass, increase the permeability to a remarkable extent.

Tests of the permeability of mortar and concrete are made in the laboratory by measuring the volume of water which passes through a slab of the material in a given time under a fixed constant pressure. The apparatus required is comparatively simple. Mortars are moulded in the form of circular discs, which are held by means of packing at the upper part of a steel cylinder, to which pressure can be applied by a pump, so that water is forced through the specimen from below. The water collects above the specimen in a graduated tube. A similar apparatus is used for testing concrete, the cylindrical blocks being larger than the discs of mortar, and the water passing through being collected in a circular channel, from which it runs into a measuring vessel. Although it is possible to compare different mixtures from the point of view of permeability by such means, the results do not give more than an approximate idea of the water-resisting power on the large scale, owing to the difference in the conditions of mixing and setting. A larger apparatus, capable of accommodating specimens a foot square, consists of a heavily ribbed iron chest, connected with a hydraulic accumulator. For testing concrete mixtures, the chest is filled to a depth of 9 inches with non-absorbent stones, the concrete is then laid above this to a depth of 3 inches, and the upper surface is trowelled or finished in the manner intended to be adopted on the large scale. Slabs of artificial stone or concrete blocks may be tested in the same apparatus, if accurately bedded and cemented in with a sufficiently strong mortar. It is also possible to test the effect of sea-waters, sewage, beer, naphtha, oil, or other liquids in this apparatus.[1]

It is useless to test concrete under a pressure much greater than that to which it is to be subjected in practice, as the increased flow of water causes solution to proceed so rapidly that the permeability is increased. The pressure in harbours, docks, and reservoirs rarely exceeds 40 feet head of water, equivalent to 17¼ lb. per square inch (1·2 kg./cm.^{2}). It is, of course, sometimes much greater in dams and aqueducts for water supplies. In good concrete work the permeability is found to decrease gradually owing to the solution of some of the constituents and their re-deposition in the voids of the concrete. It is, therefore, not uncommon for the "weeping" observed when a new concrete tank or reservoir is first used to diminish after a few weeks, the structure ultimately becoming perfectly watertight.

Le Chatelier obtained measurements of the permeability of water by immersing the blocks to be tested in a solution of some salt which could be detected by its colour or otherwise, and determining the depths to which penetration took place after a given interval. He found that sodium sulphide was a good reagent for this purpose, as its reaction with the traces of iron always present in the mortar produces a greenish-black stain. When the cubes or prisms are broken through after a sufficiently long immersion, the stain is found to have penetrated to a depth below the surface proportional to the permeability of the mortar. Good mixtures of sand with either cement or hydraulic lime proved to be practically impermeable under such conditions, but porous mortars were very rapidly penetrated. Calcium sulphide is preferable to sodium sulphide.

The gradual removal of lime by the solvent influence of water has been studied by a very similar method, also

---

[1] G. & T. Earle & Co., *Standard Methods of Testing Cement.* Hull, 1904.

employed by Le Chatelier. The specimens are immersed in a solution of mercuric chloride after being broken across. Ordinary cement, rich in lime, is coloured yellow by this reagent, owing to the formation of yellow mercuric hydroxide, but where the lime has been largely removed by the action of percolating water, this reaction does not occur, and a specimen from which lime has been removed therefore shows, on immersion in the reagent, an outer uncoloured zone surrounding a core which is stained yellow.

Water containing much **carbon dioxide** in solution has a much greater solvent action on the constituents of cement than pure water, owing to the formation of the soluble calcium bicarbonate. Marsh and peaty waters are particularly active in removing lime from cement, and waters of this class have proved very troublesome in cases in which concrete aqueducts or conduits pass through marshy ground.[1] The effect of the continued removal of lime and of calcium carbonate is to loosen the texture of the mortar and to increase its permeability, so that the action tends to proceed at an increasing rate. Waters containing ferrous carbonate are destructive, because in contact with air ferric hydroxide is formed, and carbon dioxide is set free. Waters containing sulphates are also destructive, but for a different reason, their action resembling that of sea-water.

The destructive action of **sea-water** on concrete is far greater than that of ordinary fresh water, and is of greater importance to the engineer on account of the very extensive application of concrete in the construction of harbours, docks, marine embankments, breakwaters, &c. It is necessary to distinguish between the strictly chemical action of the dissolved salts, and the physical and mechanical influences which are also present in situations

---

[1] E. Stephan, *Arm. Beton.*, 1909, 95.

of this kind, such as the impact of waves, often carrying sand and shingle, the alternate exposure to water and to air of work between tide-marks, the occasional freezing at low tide, followed by thaw, and other influences of the same kind. The tests commonly made on a small scale, consisting in the immersion of concrete blocks in tanks containing sea-water at a constant level, only indicate the effect of the chemical action, and do not take into account the other factors enumerated, which, as will be shown immediately, are of even greater practical importance.

The approximate composition of sea-water, in grams per litre, from two different regions, is shown in Table XXXI.:[1]—

TABLE XXXI.

	Mediterranean.	Atlantic.
Na . .	11·56	9·95
K .	0·42	0·33
Mg .	1·78	1·50
Ca .	0·47	0·41
Cl . .	21·38	17·83
Br . . .	0·07	0·06
SO_3 .	2·55	2·12

In addition, sea-water contains a variable quantity of carbon dioxide, in the form of bicarbonates, oceanic water containing more than that of partly enclosed seas, whilst a marked increase is observable near to the mouths of rivers, owing to the bicarbonates brought down by the river water.[2] Of the salts present in solution, the alkali chlorides, which constitute the major portion of the saline constituents, are comparatively inactive. A some-

---

[1] T. Schloesing, *Compt. rend.*, 1906, **142**, 320 (recalculated).

[2] E. Ruppin, *Zeitsch. anorg. Chem.*, 1910, **66**, 122.

what porous concrete, on analysis after prolonged immersion in sea-water, is often found to contain a considerable quantity of chlorides, but this result is due to mechanical absorption, and not to a chemical reaction with the constituents of the concrete.[1] On the other hand, sulphates exert a direct chemical action. Calcium sulphate reacts with the calcium aluminate in the cement, forming the calcium sulpho-aluminate already referred to (p. 158) as the cause of expansion in cements containing gypsum. The formation of this compound is accompanied by expansion, and the altered superficial layer of the concrete rapidly cracks and separates in scales, exposing a fresh surface to attack. The extent to which this reaction proceeds depends on the proportion of aluminates in the cement, hence it has been found that special cements containing little or no alumina, such as the hydraulic lime of Teil or the cement prepared by burning the "grappiers" occurring in some hydraulic limes, are very resistant to the action of sulphates. The good qualities of sidero-cement (p. 34) also depend on the practical absence of alumina. Where concrete work has to be carried out in soil containing bands of gypsum, so that the ground water contains much calcium sulphate, a mixture of such a cement, almost free from alumina, with finely ground dehydrated clay is found to give the best results.[2]

Magnesium sulphate is even more active than the calcium salt, and magnesium chloride also exerts a destructive influence, both salts decomposing the cement, forming soluble calcium sulphate and chloride. An examination of small cylinders of different mortars, immersed

---

[1] W. Michaëlis considers, however (*Tonind. Zeit.*, 1909, **33**, 1308), that the chlorine is sometimes retained as calcium chloro-aluminate, whilst the sodium has entered into combination with lime, silica, and alumina to form a compound of the class of zeolites.

[2] J. Bied, *Intern. Congr. Applied Chem.*, London, 1909.

in sea-water, has shown[1] that no known mixture is capable of resisting the destructive action for any length of time. The time required in the experiments to destroy completely cylinders 2 cm. in diameter was found to vary from 25 to 2000 days, quick-setting cements offering a remarkably high resistance. Teil hydraulic lime gave a better result than Portland cement, and all the mortars were greatly improved by the addition of pozzolanic materials, either natural or artificial.

Le Chatelier's experiments are open to the objection that they were performed upon unduly small specimens. The natural conclusion to be drawn from them would be that it is impossible to construct durable concrete work in contact with sea-water, whilst the experience of engineers proves the contrary, many works executed in concrete having resisted the action of the sea for many years without injury. Numerous local experiments have been made to determine the most suitable mixtures for use in work intended to be executed, but only experiments on a large scale, and continued for long periods under carefully observed conditions, can yield decisive information on this point. Two important series of experiments are now in progress, and statements have recently been made respecting the results so far obtained.[2] The most valuable experiments are those conducted by the Scandinavian Association, on account of the completeness of the scheme, which includes the testing of a large number of mortars and concretes under a variety of conditions. Three positions were selected for immersing blocks of mortar, one being in the southern part of Denmark, one within the Arctic Circle, and the third in the Baltic, at a point where the salinity is only one-seventh of that

---

[1] H. Le Chatelier, *Intern. Congr. Applied Chem.*, London, 1909.

[2] A. Poulsen, *Report of the Scandinavian Portland Cement Manufacturers' Committee*, Copenhagen, 1909; M. Gary and C. Schneider, *Mitt. k. Material-Prüf. Amt.*, 1909, **27**. See summary of both papers by the author, *Concrete and Constr. Eng.*, 1910, **5**, 23.

of the North Sea. Further, the sets of test-pieces were duplicated, one set being immersed below low tide-mark, and the other being placed between tide-marks, so as to be alternately submerged and exposed. The concrete blocks were built into a groyne, and removed in turn for examination. The German experiments also involved the use of an experimental concrete groyne, but the mortar blocks were merely immersed in tanks of sea-water, and not exposed to the tides. The Scandinavian experiments are planned to continue for a period of thirty years. The principal conclusions that may be drawn from the examination of the test-pieces already taken up are the following :—

1. The main agency in the destruction of mortar and concrete in marine embankments, harbour works, groynes, &c., is not chemical action, but the successions of saturation, drying in the sun, freezing, &c., due to alternate exposure and covering by the rise and fall of the tide. Destruction takes place by cracking or scaling, the latter effect being produced especially by frost. The pounding action of the waves, and the abrasive action of sand, are also important factors.

2. Good Portland cements, such as are obtainable in most countries, are chemically very resistant to the action of sea-water. No marked difference in the behaviour of cements of different composition has been found, except that a high proportion of aluminates tends to cause disintegration. Teil hydraulic lime, which is much used for marine work in the non-tidal Mediterranean, is greatly inferior to Portland cement in northern seas, mortar prepared from it having little power to resist the physical influences enumerated above.

3. In a dense concrete, the chemical action is confined to an outer layer of small depth, further action being checked by the slowness of diffusion. A porous concrete admits salt water to the interior, and the expansion produced frequently causes cracking.

4. The denser the mortar used as matrix the better. One part of cement to 3 of sand is too poor. An admixture of fine sand with ordinary sand increases the compactness of the concrete, and a well-graded aggregate is advantageous for the same reason.

5. The addition of finely ground trass or other pozzolanic material appears to have some advantage in the case of the weaker mortars, but it is very doubtful whether anything is gained by adding pozzolana to rich mortars, although such additions have the general reputation of being advantageous.

6. As long a period as is practicable should be allowed for the hardening of concrete blocks before they are placed in the sea. The German recommendation of one year in moist sand before setting in place is probably impracticable in most instances, but should be approached as nearly as possible.

7. Tests by mere immersion in stationary sea-water are of little value.

8. The behaviour of test specimens for the first twelve months is irregular, and definite conclusions can only be drawn from the results of long-period tests.

These conclusions, although in some respects contrary to generally received opinions, are quite consistent with the observed behaviour of large marine works in concrete.

The effect of sea-water on iron-ore cement is seen in Table XXXII., which shows the effect of immersing blocks of 1:3 cement-sand mortar in sea-water immediately after gauging.[1]

The loss at 100° may be regarded as a measure of the porosity of the mortar, and is seen to undergo little or no variation. The very small increase of magnesia, sodium chloride, and sulphates is an indication that the cement has been little affected by the chemical action of the sea-water. This is partly to be attributed to the small propor-

---

[1] E. Maynard, *Tonind. Zeit.*, 1910, **34**, 651.

tion of aluminates, perhaps also in part to the comparatively low proportion of lime, which renders the cement less reactive towards magnesium salts than a fully-limed Portland cement. The resisting qualities which cement prepared by the granulation of blast-furnace slag is stated to possess are sometimes attributed to the latter cause, although experience with Portland cements goes to show that those rich in lime are the most resistant.[1]

The prolonged action of water capable of exercising a destructive influence on concrete sometimes results in the formation of stalactitic outgrowths. Thus, blocks of mortar composed of cement, sand, and trass, immersed in stationary sea-water for only 28 days, have been observed to form stalactites 20–40 cm. long, consisting of calcium and magnesium carbonates.[2] The explanation in this case appears to be that the blocks had been prepared at too low a temperature, so that setting was not complete when they were immersed in the tanks. Similar growths have been observed on the concrete surfaces of harbour works. In one case[3] the floor of a dock was covered after 4 weeks with stalagmites 10–20 cm. long, which increased after 18 months to a metre. Chemical analysis showed

TABLE XXXII.

	1 Day.	1 Month.	1 Year.	$5\frac{1}{2}$ Years.
	Per cent.	Per cent.	Per cent.	Per cent.
Loss at 100° . .	8·54	6·14	7·35	8·35
„ on ignition .	10·24	5·16	5·18	5·96
Lime .	12·80	14·41	13·62	13·42
Magnesia . .	0·27	0·33	0·37	0·40
NaCl	0·21	0·59	0·65	0·58
SO_3	0·65	0·58	0·82	0·78

---

[1] A. Dyckerhoff, *Chem. Zeit.*, 1910, **34**, 419.

[2] M. Gary, *Mitt. k. Material-Prüf. Amt.*, 1905, **23**, 66.

[3] *Ibid.*, 1906, **24**, 273.

them to consist of calcium and magnesium carbonate. The concrete was composed of lime, sand, trass, and gravel, and did not contain cement. No information is given regarding the conditions of mixing and setting. Somewhat similar outgrowths, consisting in this case of practically pure calcium carbonate, were observed in a fresh-water canal (constructed with cement concrete) after 2 years' use. It is certain that in all these instances, the original concrete must have been insufficiently dense, and that a similar occurrence is not to be feared in the case of thoroughly sound and well-made concrete.

Concrete also finds extensive application in the construction of sewers and of tanks for the treatment of **sewage.** General experience shows that well-made concrete is highly resistant under such conditions, and that failures may usually be traced to the insufficient compactness of the mixture used. In this case, as in that of marine work, concrete with a minimum proportion of voids is essential to the durability of the structure. A few exceptional cases may be mentioned. The discharge of acids, such as the waste liquors from dye-works or other places in which acids are used, is fatal to concrete in the neighbourhood of the point of discharge, the cement being completely eaten away, thus reducing the concrete to the condition of loose gravel. A preservative coating of tar or of Angus Smith's composition has been found useful in such cases, but there can be no doubt that the entire prohibition of the discharge of acid waste liquors without neutralisation is the only practicable solution, such discharge of corrosive liquids, whether into common sewers or directly into natural water-courses, being a danger as well as a nuisance to the community.

Instances of the corrosion of concrete by ordinary domestic sewage have only been noticed occasionally. Some of these have been in tropical climates, where the high temperature of the liquids, and the humidity of the atmosphere, probably combined with the initial porosity of the concrete, sufficiently explain the effect. In a few cases, whilst the concrete below the usual level of the stream of sewage has remained perfectly sound, the portion exposed to the moist atmosphere above it has disintegrated, whilst a zone alternately covered and exposed by fluctuations in the level of the sewage has been very deeply corroded and destroyed.[1] This effect has been observed in plant for the treatment of very concentrated and putrid sewage, where the plan has been adopted of drawing a large volume of air through the pipes and tanks for the purpose of diluting the offensive gases. A principal constituent of such gases is hydrogen sulphide, which is readily oxidised in presence of an excess of moist air. A part of the hydrogen sulphide is thus converted into sulphur dioxide, which reacts with a further quantity of the same gas, depositing sulphur:

$$2H_2S + SO_2 = 2H_2O + 3S.$$

That this reaction takes place is proved by the formation of a loose, solid deposit of sulphur on the exposed surface of the concrete. At the surface of the liquid, a part of the hydrogen sulphide is oxidised to sulphuric acid, which rapidly attacks the matrix of the concrete. It was, in fact, observed that the lime contained in the cement in the instance quoted had been completely converted into calcium sulphate. Corrosion is inevitable under such conditions, and it is evidently necessary to avoid the presence of a large excess of air in tanks and vessels in which concentrated and putrid sewage is under treatment.

Liquids containing organic acids attack cement, but if the acid is not too concentrated, the surface of concrete may be sufficiently protected against attack from this cause by treatment with a solution of sodium silicate. Wine musts and similar liquids are almost without action

---

[1] S. H. Chambers, *Trans. Concrete Inst.*, 1910, **2**, April 21.

on cement, but beer, owing to the organic acids present and to the large proportion of carbon dioxide in the solution, which removes lime from the surface in the form of bicarbonate, cannot be stored in concrete vessels unless the surfaces are treated with some preparation for the purpose of rendering them resistant.[1]

The employment of concrete with steel reinforcement brings with it the necessity of protecting the steel against corrosion by chemical agents, such as percolating water, acid fumes, and the carbon dioxide of the air. All these are capable of setting up corrosion if they reach the steel, and the formation of **iron rust** having once begun, continues at an increasing rate, as the expansion due to rusting causes disintegration of the concrete. Here, as in all the cases considered above, the security of the structure depends chiefly on the compactness of the concrete. A dense concrete thoroughly protects the enclosed iron from rusting, and when it has been found necessary to destroy old reinforced concrete work of good quality in the course of alterations, the steel reinforcement has always been found in a clean state, free from rust, even when the situation is one involving the constant wetting of the concrete with sea-water. The presence of lime and basic lime compounds in the mortar hinders the access of carbon dioxide or acid fumes to the steel, but if water can gain entrance through the pores of the concrete, rusting may take place, even though the liquid in contact with the steel remain alkaline.[2] An insufficiently dense concrete, moreover, by allowing water and corrosive solvents to enter its pores, tends to become more and more porous, until the action results in the complete destruction of both the concrete and the reinforcement.

Much attention has also been given to the question of

---

[1] P. Rohland, *Zeitsch. ges. Brauw.*, 1906, **29**, 704.

[2] J. N. Friend, unpublished experiments.

the influence of sulphides in concrete on the rusting of reinforcing metal. Certain materials often employed in the preparation of concrete for floors, vaults, partitions, &c., such as coke breeze, some forms of clinker, and blast-furnace slag, contain notable quantities of sulphides, either originally in the form of iron sulphide, or yielding iron sulphide by their reaction with the iron compounds which are always present to a greater or less extent. Moist air gaining access to the interior of the mass, oxidises the sulphide, expansion taking place at the same time. Sulphuric acid may be formed under these conditions, and rusting may thus be produced. Experiments with furnace ashes containing sulphides showed[1] that the corrosion of iron by moist air is increased from ten to thirty times when the iron is embedded in a mass of moist ashes. On the other hand, concrete made with this material and Portland cement was found to protect the iron from corrosion. The protection must be purely mechanical in character, by preventing the access of air. It is not due to the alkaline nature of the cement, for the ash has itself an alkaline reaction. Other experiments have shown that well-mixed concrete, the constituents of which contain a considerable proportion of sulphides, affords perfect protection to iron rods embedded in it, even after exposure to water for twelve months, and to steam and acid fumes for some time.[2] It must not be inferred from these results, however, that materials containing oxidisable sulphides may be safely employed for reinforced concrete work, for although the sulphides may remain entirely inert so long as the concrete remains sound, the formation even of a small crack may start chemical action, which will then proceed at an increasing rate, probably ending in the complete destruction of the member.

---

[1] F. W. Hinrichsen, *Mitt k. Material-Prüf. Amt.*, 1907, **25**, 321.

[2] R. T. Surtees, *Concrete and Constr. Eng.*, 1907, **2**, 43.

CHAPTER IX

THE CHEMICAL ANALYSIS OF CEMENTS

THE discussion of the constitution of cements in Chapter IV. has sufficiently shown that the properties of a cement are not an immediate function of its ultimate chemical composition. That is to say, two cements which yield exactly the same results on ultimate analysis—the same percentages of calcium, of silicon, of oxygen, of sulphur, &c.—may prove to be entirely dissimilar in their properties. If we possessed a means of determining their *proximate* composition—the percentages of each calcium silicate and aluminate, &c.—we should probably be in a position to predict the properties of the cements. A knowledge of the proximate composition and microscopic structure would certainly suffice for such a prediction. Unfortunately, however, the proximate analysis of products of this kind is entirely beyond our present powers. It has been shown (p. 95) that the methods proposed for the estimation of "free lime" in a cement are entirely untrustworthy, and that the quantity of lime indicated by them is merely the resultant of a series of complex reactions between the solutions employed in testing and certain of the constituents of the cement. Even greater difficulties are met with in attempting to determine the proportions in which more complex compounds are present. Microscopical examination reveals the form in which the constituents are mechanically arranged, but, owing to the property which the silicates and aluminates possess, of forming solid solutions with one another, it does not give direct information as to the chemical composition. We are therefore restricted to ultimate chemical analysis, that is, to the estimation of the elements composing the cement, leaving to the microscopical method and to the determination of physical properties the task of distinguishing between the different modes of combination of the ultimate components.

The complete chemical analysis of a cement requires considerable manipulative skill and experience. Shortened and approximate methods are much employed in industrial routine work, and the full analysis is only resorted to occasionally as a means of control, or in the course of a scientific investigation. In view of the fact that cements having the same ultimate composition may differ widely in properties, chemical analysis is of comparatively little worth as a means of valuation. On the other hand, in a works, in which the conditions of manufacture are maintained as far as possible constant, variations in the chemical composition indicate variations in the quality. For example, if the best results in a certain works are found to be obtained from a cement containing 62·5 per cent. of lime, a charge containing 63·5 per cent. of lime is very likely to prove unsound; whilst in another works, where the conditions of manufacture are different, the second percentage may still be within the safe limit. It is in such a manner that the chemical analysis of cement finds its principal application, the buying and selling of cement according to its analysis having been abandoned. The estimation of certain chemical components, however, forms a part of the ordinary routine of examination, most specifications of cements fixing an upper limit to the permissible quantity of sulphuric acid, magnesia, and insoluble residue.

We may consider the complete analysis of Portland cement first, as being the most representative material of the class. Subsequent notes deal with the modified methods required in dealing with other cements, and with the raw materials of manufacture.

On account of the extremely fine grinding of modern Portland cements, it is not difficult to obtain a satisfactory sample, either from a single bag, or selected from a number of bags to represent a whole consignment, the usual precautions being of course observed in sampling. It is unnecessary to grind the cement any further before treating it with reagents, as was formerly the case with coarsely ground products. Moreover, in one respect at least, a subsequent grinding of the sample produces an error in the analysis. This is in the estimation of the "insoluble residue." Experiment shows that the term "insoluble residue" is only a relative one, the quantity of matter unattacked by acids depending on the state of division of the material. By fine grinding in the laboratory the insoluble residue may be reduced to an insignificant fraction, and the usefulness of the estimation, as indicating the proportion of matter devoid of cementitious value, is destroyed. For similar reasons, the cement should not be specially dried before analysis.

The following methods fairly represent modern practice in the analysis of Portland and other similar cements.[1] All estimations should be performed in duplicate.

SILICA, SESQUIOXIDES, LIME, AND MAGNESIA.

A quantity of 0·5 gram of cement is placed in a porcelain or platinum dish, and thoroughly mixed with water. Ten c.c. of hydrochloric acid are added, and the whole is evaporated to dryness. After adding 5 c.c. of

---

[1] See C. Richardson, *J. Soc. Chem. Ind.*, 1902, **21**, 12 (report of committee); W. H. Stanger and B. Blount, *ibid.*, 1902, **21**, 1216; O. H. Klein and S. F. Peckham, *ibid.*, 1900, **19**, 644; 1901, **20**, 539; R. F. Young and B. F. Baker, *Chem. News*, 1902, **86**, 148; B. Enright, *J. Amer. Chem. Soc.*, 1904, **26**, 1003. The method here described follows that of Stanger and Blount in most respects, but that of the American committee has been preferred in a few details.

hydrochloric acid, the liquid is diluted and heated for ten minutes, and then filtered. The filtrate and washings are evaporated to dryness, and after again adding hydrochloric acid, the small quantity of silica thus obtained is added to the original residue, which contains the whole of the silica and the insoluble residue. It is dried and ignited in a platinum crucible for twenty minutes over a blowpipe, or for an hour in a hot muffle. The weight, after subtracting the insoluble residue, estimated as described below, represents the silica, SiO_2.

Stanger and Blount state that the silica can be rendered perfectly insoluble after the first evaporation by baking in a shallow dish at 200° for an hour. The second evaporation described above is, however, a simple operation, and will be generally preferred, since it errs, if at all, on the side of safety.

The filtrate is rendered strongly ammoniacal, and boiled until only a slight smell of ammonia remains, and the precipitate formed is collected and washed. On account of the obstinate retention of lime by this precipitate, it is advisable to re-dissolve it in hydrochloric acid and to repeat the precipitation. The two filtrates are then mixed. The precipitate is washed, dried, ignited, and weighed. It represents the two sesquioxides, $Al_2O_3 + Fe_2O_3$. Should it be necessary to determine the amount of these two oxides separately, the ignited precipitate may be used. It is fused at a low temperature in a platinum crucible with 10 grams of potassium hydrogen sulphate, dissolved in hot water with the aid of dilute sulphuric acid, and reduced by means of hydrogen sulphide. After the removal of this reagent by boiling in a current of carbon dioxide, the ferrous iron in the solution is estimated by titration with a standard solution of potassium permanganate. The proportion of alumina is then obtained by difference.[1]

[1] Titanium may also be present, and may be estimated in this precipitate, by the method described below.

The filtrate from the ferric oxide and alumina contains the lime and magnesia. It is rendered ammoniacal, raised to the boiling-point, and precipitated with 10 c.c. of a saturated solution of ammonium oxalate. After boiling for a few minutes, the liquid is set aside for an hour, and the precipitate of calcium oxalate is then collected, and washed with dilute ammonia. Most European cements contain only a small proportion of magnesia, and in that case a second precipitation of the lime is unnecessary, but when analysing American cements, which usually contain a greater quantity of magnesia, it is advisable to take the precaution of dissolving the precipitate in dilute hydrochloric acid, and re-precipitating with ammonium oxalate. The calcium oxalate is dried and ignited over the blowpipe or in a muffle. It is then weighed directly as lime, CaO.

The filtrate from the calcium oxalate (or the united filtrates, if double precipitation has been resorted to) must be freed from the greater part of the accumulated ammonium salts before a satisfactory precipitation of the magnesia is possible. The most convenient method of removing ammonium salts consists in evaporating in a porcelain basin until the residue becomes pasty, and adding a large quantity (40 to 50 c.c.) of concentrated nitric acid. The ammonium compounds are now readily decomposed and volatilised by heating gently.

In accurate work, the residue is dissolved in a small quantity of dilute hydrochloric acid, and ammonia and ammonium oxalate are added in slight excess. The precipitate consists mostly of impurities derived from the reagents and vessels, and is best neglected. Magnesia is precipitated by adding ammonia and sodium phosphate, and the solution is set aside in a warm place for several hours (preferably overnight) until the magnesium ammonium phosphate has separated in a thoroughly crystalline form. The precipitate is ignited (previous drying of the filter-paper being unnecessary) and is weighed as magnesium pyrophosphate, $Mg_2P_2O_7$.

ALKALIES.

One gram of the cement should be taken. Silica, sesquioxides, and lime are removed as above, and after destruction of the ammonium salts by means of nitric acid, barium hydroxide is added, followed by ammonium carbonate. After removal of the barium carbonate by filtration, hydrochloric acid is added, and the solution is evaporated to dryness in a platinum basin, and ignited gently. The residue consists of sodium and potassium chlorides, $NaCl+KCl$. Should separate estimations of the two alkalies be required, the potassium is precipitated in the form of its platinichloride, and weighed.

Many chemists, however, prefer to estimate alkalies by Lawrence Smith's method. One gram of the sample is finely ground with its own weight of ammonium chloride and six times its weight of pure calcium carbonate. The mixture is heated to redness in a closed platinum crucible for an hour, and is then boiled out with water. The whole is then evaporated once or twice with ammonium carbonate and filtered. The filtrate contains the alkalies in the form of chlorides. It is evaporated to dryness in a platinum basin, ignited to remove ammonium chloride, and weighed.

TITANIUM.

An estimation of titanium is not often required. As it is generally present in clays to a small extent, however, and as the study of elements present only in small proportion may prove, as in other departments of inorganic chemistry, to have some importance, a method of estimation may be briefly described. The material is decomposed by heating with concentrated sulphuric acid in a platinum capsule, extracted with dilute sulphuric acid, and the filtrate is then oxidised by means of hydrogen peroxide. The yellow coloration thus produced is compared with that given by a standard solution of titanium, prepared by decomposing pure potassium titanifluoride with strong sulphuric acid, dissolving in dilute sulphuric acid, and diluting until each c.c. contains 0·002 gram of titanium, weaker solutions being obtained by further dilution.

INSOLUBLE RESIDUE AND SULPHATES.

A further quantity of 1 gram of cement is mixed with water, 20 c.c. of hydrochloric acid are added, and evaporated to dryness. The residue is treated with 10 c.c. of hydrochloric acid and filtered. After washing the silica on the filter-paper back into the dish, an excess of sodium carbonate solution is added, and the vessel warmed until all gelatinous silica is dissolved. The liquid is filtered, and the residue is thoroughly washed until free from soluble salts, dried, ignited, and weighed.

The first (acid) filtrate is precipitated while hot with barium chloride solution, and the barium sulphate, $BaSO_4$, is ignited and weighed in the usual manner.

LOSS ON IGNITION.

Half a gram of cement is heated in a platinum crucible, preferably in a muffle. The temperature should not exceed 900°, as otherwise some of the calcium sulphate may be decomposed. The loss represents water and carbon dioxide, and it is, as a rule, unnecessary to estimate these constituents separately. Carbon dioxide may, however, be estimated as described below.

The best German filter papers, freed from ash by extractions with hydrochloric and hydrofluoric acids, should be used for cement analysis, and only the purest obtainable acids should be used as reagents.

Materials other than Portland cement are analysed by methods resembling the above as closely as possible. Manganese is present in Roman cements, and in some cements prepared from blast-furnace slag. Manganese may be brought down together with iron and alumina by adding a little bromine at the time of precipitating. The manganese may be estimated separately if iron and aluminium be first precipitated as basic acetates.

SULPHIDES.

Cements prepared from slag almost always contain an appreciable quantity of sulphides. In one method of analysis, the sulphur present as sulphates is estimated as described above, after dissolving the cement in hydrochloric acid, the sulphur present as sulphides escaping in the form of gaseous hydrogen sulphide. Another portion of the same cement is dissolved in hydrochloric acid and bromine water, thereby oxidising the sulphides to sulphates. The difference between the "total sulphur" thus obtained and the "sulphate sulphur" gives the amount of sulphur present as sulphides. Another method consists in dissolving the cement in hydrochloric acid and passing the gases evolved into an absorbing vessel, in which the hydrogen sulphide is either precipitated by means of a cadmium salt, or oxidised to sulphuric acid and precipitated as barium sulphate. In either case, there is some danger of loss of sulphide owing to the presence of ferric compounds in the cement, which causes oxidation. This error is avoided by the addition of a small quantity of a reducing agent during solution, and stannous chloride has proved itself the most suitable reagent for this purpose.[1] The cement is dissolved in 50 c.c. of hydrochloric acid, to which 10 c.c. of a 20 per cent. solution of stannous chloride has been added, in a glass generating flask with ground-in funnel and exit tube. The escaping gases pass into an

---

[1] F. W. Hinrichsen, *Mitt. k. Material-Prüf. Amt.*, 1907, **25**, 321.

absorbing apparatus consisting of a row of bulbs containing hydrochloric acid saturated with bromine. At the conclusion of the experiment, the contents of the bulbs are washed out into a beaker, and the sulphur is precipitated by means of barium chloride. This method also serves conveniently for the estimation of sulphides in aggregates and in slag sand, the material being first ground to a sufficient degree of fineness.

Sulphides may also be estimated very accurately by the following method:[1]—

Five grams of slag are mixed in a flask with 1 0 c.c. of an arsenious solution, prepared by dissolving 3 grams of arsenious oxide in 300 c.c. of concentrated hydrochloric acid and diluting to a litre with water. The mixture is then diluted with water to 500 c.c., shaken vigorously and filtered. The sulphur is thus precipitated in the form of arsenious sulphide, and may be estimated indirectly by determining the quantity of arsenic remaining in the filtrate. For this purpose, 250 c.c. of the filtrate are taken, and precipitated by hydrogen sulphide. The precipitate is washed with water containing hydrogen sulphide, and is then dissolved in ammonia and evaporated to dryness, the residue being heated with sulphuric acid on a sand bath until white fumes are freely evolved. After cooling, the mass is dissolved in water, evaporated to 30 c.c., cooled and filtered. The filtrate, after the addition of sodium bicarbonate, is titrated with iodine in the usual manner.

Analysis of Raw Materials.

Such raw materials as chalk, limestone, clay, marl, &c., always contain more or less moisture, the proportion being very variable. As a rule, an approximate estimation of the moisture is sufficient, 100 grams or more of the crushed sample being taken, and spread in a thin layer

---

[1] J. and H. S. Pattinson, *J. Soc. Chem. Ind.*, 1898, **17**, 211, modified by W. Fresenius.

over the surface of a large dish, and then dried at a temperature not exceeding 110°. If the sample is already in a finely powdered state, a smaller quantity, such as 5 or 10 grams, may be dried in a steam oven at the same temperature.

Chalk or limestone may be analysed in the same way as cement, a larger quantity (5 to 10 grams) being taken in order to secure sufficient accuracy in the estimation of silica, alumina, &c. The more clayey the limestone, the smaller is the quantity that will suffice for the analysis. Clayey limestones should always be strongly ignited before dissolving in hydrochloric acid.

The quantity of calcium carbonate in raw materials is most generally determined by estimating the proportion of carbon dioxide evolved when the sample is treated with a dilute acid. This may be done, in the case of carbonates which are decomposable in the cold (that is, of all but dolomitic or magnesian limestones) by means of any of the usual compact laboratory forms of carbon dioxide apparatus, consisting of a small evolution flask provided with attached drying tubes through which the escaping gas has to pass, the loss in weight, after adding the acid to the sample, giving the weight of carbon dioxide. The most rapid and convenient method of conducting the estimation is, however, by measuring the volume of carbon dioxide by means of a special apparatus, the calcimeter, of which several modifications exist. Fig. 18 represents Clarke's calcimeter, in which the whole of the parts are enclosed in a large water jacket in order to maintain a constant temperature. The graduated tube A, open below, is enclosed in an outer tube B, connected with a rubber bulb F, containing water. The weighed quantity of slurry or other moist material is placed in the bottle J, together with a tube K containing 10 c.c. of concentrated hydrochloric acid (drawn from the burette C), the bottle is then corked and is placed in the gauze cage M to assume the temperature of the jacket. The tap N is opened, and the water in A and B is brought to the zero level by compressing the bulb F with the screw H. The tap is then closed, the bottle is removed from its cage, and the acid is brought into contact with the sample by tilting. At the same time, the screw H is gradually turned so that the levels of the water in A and B descend at equal rates. After shaking the generating bottle to complete the action, it is replaced in the cage, and the apparatus is left to itself for two minutes in order to equalise the temperature. The water level is finally adjusted until it is the same in A and B, and the reading in A is then taken. A correction, taken from a table, is made for the absorption of carbon dioxide by water. The quantity of material to be taken varies with the temperature and atmospheric pressure, and is determined before the experiment by reference to a table furnished with the instrument. Other forms of calcimeter are the same in principle, and only differ in detail.

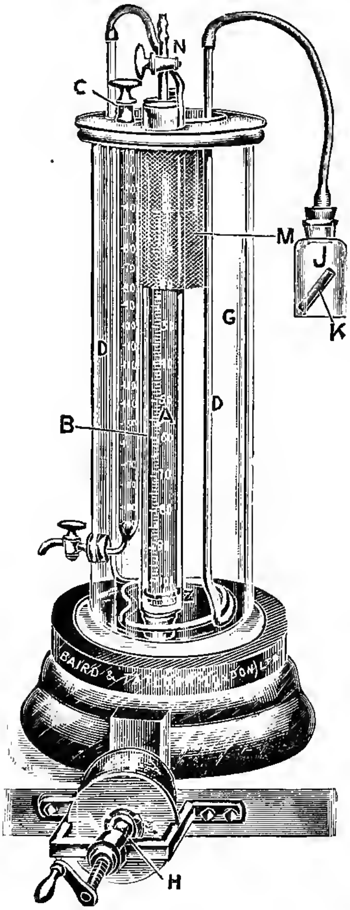


Fig. 18.

Clarke's Calcimeter.

More accurate estimations of carbon dioxide may be made by decomposing the material in a small flask provided with a tap-funnel through which the acid is admitted. The gas evolved passes into a series of absorbing tubes, of which the first contains pumice moistened with concentrated sulphuric acid, to remove moisture whilst the two following tubes contain soda-lime. When the evolution of gas is complete, a current of air, dried and purified by passing through vessels containing sulphuric acid and soda-lime respectively, is drawn through the whole apparatus by means of an aspirator, in order to sweep the last traces of carbon dioxide into the absorbing tubes. The increase in weight of the latter gives the weight of carbon dioxide. This form of apparatus is to be used when the material to be tested does not contain sufficient carbonate to give satisfactory results in the calcimeter, or when it contains carbonates, such as dolomite, which are not decomposed by cold dilute acids. In this case the contents of the flask may be heated by means of a small flame.

In the analysis of mixtures of raw materials for the preparation of cement, whether intended for the dry or the wet process, the best results are obtained by heating the mixture strongly in a platinum crucible in a muffle or over the blast for forty-five minutes. A product resembling cement is thus obtained, and may be analysed by the usual methods. The preliminary heating has the advantage that the silicates are thus converted into the soluble form, so that special methods of bringing the material into solution are unnecessary. The moisture is estimated by drying a fairly large quantity in an air oven at 120°, 100 grams being taken if the material is fairly dry, or 200 grams in the case of slurry. The same method is applicable to the analysis of natural cement rock, or to those marls which yield products approaching Portland cement in composition after ignition.

Clays may be brought into solution by prolonged heating with concentrated sulphuric acid at a moderate temperature, afterwards heating sufficiently to expel the excess of acid. The residue is then extracted with a sufficient quantity of hydrochloric acid, leaving the silica and insoluble matter in the residue. The subsequent procedure is similar to that adopted in the analysis of cement. This method of attack is generally preferable to fusion with a mixture of sodium and potassium carbonates.

BLAST-FURNACE SLAG.

The silica in slags may be estimated as described under cement. The powdered slag should be first boiled with water, the hydrochloric acid being then added at such a rate as not to check the boiling. In this way the formation of an adherent layer of gelatinous silica is avoided. Nitric acid is added towards the end of the evaporation.

The filtrate from the silica is used for the estimation of the usual bases in the same manner as in the analysis of cement.

Manganese is always present in slags, and it is often desirable to estimate it, although its quantity in Portland cement and in ordinary raw materials is usually negligible.

For the determination of manganese, one gram of the powdered slag is heated with 20 c.c. of water and 10 c.c. of concentrated nitric acid, a small quantity of hydrofluoric acid being added if necessary. The filtrate is taken, and after removal of the iron by precipitation with acetate, the manganese is estimated by precipitation with bromine and ammonia, the precipitate being ignited and weighed as Mn_3O_4.

Sulphur, being mostly present as calcium sulphide, may be estimated as previously described, by expelling the hydrogen sulphide and collecting it by means of a suitable reagent. The total sulphur may be estimated by heating 1 gram of slag with 2 c.c. of bromine and 10 c.c. of hydrochloric acid, boiling and filtering. After adding sufficient ammonia to the filtrate to render it nearly neutral, barium chloride solution is added, and the precipitate of barium sulphate is weighed in the usual way.

The Detection of Slag in Portland Cement.

The problem of detecting blast-furnace slag when added to Portland cement has attracted more attention in Germany than in England, but a short reference may be made in this place to the methods proposed. Other adulterants are, as a rule, easily detected by differences of specific gravity, colour, or other physical properties, but such tests have proved insufficient for the recognition of slag, and chemical methods are therefore necessary.[1] The ordinary chemical analysis only reveals the adulteration when a considerable proportion of an acid slag has been added, by which the percentage of lime is greatly reduced, and does not detect the addition of basic slag. The principal chemical difference between Portland cement and slag is in the proportion of sulphides. Hence it was formerly the practice to treat the sample with potassium permanganate in acid solution, and to regard the quantity of permanganate reduced as a measure of the sulphides present, other reducing substances being neglected. This method was satisfactory in dealing with the older Portland cements, the safe upper limit being fixed at 2·8 milligrams of $KMnO_4$ per gram of cement. With the introduction of the rotary kiln, however, the reducing power of cement towards permanganate was found to increase, although there was no increase in the proportion of sulphur.[2] This

---

[1] Many chemists have attempted a preliminary separation of the specifically lighter slag by suspending in methylene iodide and benzene, but the method is troublesome and uncertain. See M. Gary and J. von Wrochem, *Mitt. k. Material-Prüf. Amt.*, 1905, **23**, 1.

[2] W. Fresenius, *Rep. Intern. Congr. Appl. Chem.*, Berlin, 1908, i. 394.

effect was explained by the greater reducing activity of the fuel in the rotary kiln, leading to the reduction of a larger quantity of the iron compounds to the ferrous state.

The direct titration of the cement with permanganate is unsatisfactory, on account of the irregularity of the action, and Fresenius found the following procedure to give the best results: One gram of the cement, ground to pass the 180 sieve (4900 meshes/cm.^{2}), is mixed with 30 c.c. of water in a flask, and 150 c.c. of sulphuric acid, (1 vol. concentrated acid + 3 vols. water) are added, immediately followed by 20 c.c. of a solution containing 5 grams of potassium permanganate per litre. Should this be completely decolorised, a further quantity of 20 c.c. is added. After five minutes, the flask being shaken occasionally, the liquid is decolorised by the addition of a solution containing 66 grams of ferrous ammonium sulphate per litre from a burette, and the slight excess is titrated back with permanganate. The direct estimation of sulphides by the arsenic method confirms the trustworthiness of the process. Table XXXIII. indicates the nature of the results obtained:[1]—

TABLE XXXIII.

Material Examined.		$KMnO_4$ Reduced by 1 Gram.
		Milligrams.
Portland cement A.	Stationary kiln	1·84
„ „	Laboratory furnace	trace
„ „	Rotary kiln	21·51
„ „	30 per cent. slag added before burning	43·7
„ „	„ „	48·8
„ „	„ after „	41·1
„ „	40 per cent. „ „	55·9
Iron-Portland cement		35·0
„ „		44·6
Blast-furnace slag		145·5

---

[1] Gary and von Wrochem, *loc. cit.*

PLASTER.

The principal estimation required in the analysis of plaster is that of the sulphate present. A quantity of 1–2 grams of the sample is dissolved by warming with 100 c.c. of hydrochloric acid (1 : 2) and is made up to 200 c.c. after filtering off undissolved impurities. A fraction of this, say 25 c.c., is precipitated while boiling with barium chloride solution, and the precipitate is collected, dried, and ignited in the usual way.

When such varieties of gypsum cement as flooring plaster are being dealt with, it is sometimes necessary to determine the relative proportions of the different modifications of gypsum present in a given specimen. This is a problem of considerable difficulty, and is only capable at present of a partial solution.[1]

The hemihydrate, $CaSO_4,\frac{1}{2}H_2O$, is estimated by determining the quantity of water taken up at the ordinary temperature and retained at 60°. Five grams of the plaster are spread in a thin layer over a porcelain basin, and just covered with water from a wash-bottle. After 30 minutes the basin is transferred to a drying cupboard at 60°, and is kept at that temperature until the weight is constant. If the weight of water taken up be a, the weight of hemihydrate is:

$$y = 5{\cdot}37a \qquad \text{I.}$$

unless soluble anhydrite be also present, in which case its weight z (see III. below) must be taken into account:

$$y = 5{\cdot}37(a - 0{\cdot}26z). \qquad \text{II.}$$

Soluble anhydrite is estimated by exposing 5 grams of plaster in a thin layer to water vapour at the ordinary temperature for 7 days under a bell-jar. The whole of the soluble anhydrite is thus converted into the hemi-

---

[1] O. Frey, *Tonind. Zeit.*, 1909, **33**, 1229.

hydrate, and, if b be the increase of weight after drying at 60–70°:

$$z = 15{\cdot}11b. \qquad \text{III.}$$

In order to decide whether soluble anhydrite is present, a portion of the plaster is sifted into a small cylinder containing 200 c.c. of water, in which a sensitive thermometer is immersed. Should soluble anhydrite be present, the temperature rises almost at once, and continues to do so for 2 minutes, whilst the rise of temperature due to hydration of the hemihydrate only begins after 5 minutes, and continues for 15–25 minutes.

The "Estrich gypsum" which forms the principal constituent of flooring plaster, but is only present in ordinary plaster when the burning has been conducted at too high a temperature, is estimated by wetting 5 grams as in I., and allowing it to remain for 7 days in a moist atmosphere, finally drying at 60°. If c be the increase in weight and e the quantity of Estrich gypsum:

$$e = 3{\cdot}78(c - a). \qquad \text{IV.}$$

The constituents named above are all active, that is, capable of hydration. In addition to these, the plaster may contain unburnt gypsum, dead-burnt plaster, natural anhydrite, and impurities (clay, sand, &c.). The unburnt gypsum is estimated by determining the loss of weight on ignition. If the loss be v, the weight r of unburnt gypsum is

$$r = 4{\cdot}78(v - 0{\cdot}062y). \qquad \text{V.}$$

The total calcium sulphate, as determined by estimating the sulphate present, is G. The weight of natural anhydrite and dead-burnt plaster is then

$$t = G - (0{\cdot}93y + z + e + 0{\cdot}79r). \qquad \text{VI.}$$

The impurities (sand and clay) may be estimated by difference.

CHAPTER X

CONCLUSION

The rapidly increasing production of calcareous cements is chiefly due to the increasing employment of concrete in building and engineering construction. The plastic character of concrete, which enables it to be moulded to any form, and the monolithic nature of concrete structures even of a complex form, sufficiently explain the tendency to make use of that material for the most diverse purposes. Experience has shown that concrete of good quality possesses a highly satisfactory power of resistance to atmospheric and other destructive influences, whilst its resistance to fire has been one of the principal causes of its general adoption as a building material. Mass concrete finds its principal application in the construction of embankments, dock and harbour works, reservoirs, dams, retaining walls, and foundations, whilst concrete reinforced with steel has shown its suitability to the construction of bridges, and also of factories, warehouses, and business premises. The remarkable property of reinforced concrete structures, of retaining their monolithic character even when exposed to the most extreme changes of temperature, gives them a great advantage over the alternative type of steel-framed structure, in which the thrust due to the expansion of horizontal members has repeatedly proved to be a source of danger in a conflagration. The monolithic character of reinforced concrete is also its recommendation in districts subjected to earthquake shocks, which prove so destructive to buildings of brickwork or masonry.

It is also in great part owing to the increased use of concrete, and to the introduction of reinforced construction, that Portland cement has assumed so great an importance relatively to the older calcareous cements. A far higher mechanical strength is now demanded of cements than was formerly the case, and Portland cement has shown itself to be the only material capable of meeting the increasingly severe requirements of the constructional engineer. The demand for a better material has been met by the manufacturers, and its results have been seen in the remarkable improvement in the quality of Portland cement during recent years, and there is no reason to suppose that the limit of improvement has yet been reached. An examination of the progress which has now been made yields some indications of the direction in which further changes may occur. An increase in the temperature of burning would render the reaction between the components more complete, and would thereby increase the homogeneity of the product. This might be expected to yield a cement of greater strength and also of greater regularity in respect to setting. The recently introduced methods of controlling setting by partial hydration of the more reactive constituents during the process of manufacture point to the ultimate possibility of dispensing with all additions of catalytic agents after grinding—a change which would be of the utmost advantage in increasing the stability and soundness of the material. It is possible, also, that a greater variety of raw materials may be employed under certain conditions.

The various types of "natural" cements are likely to diminish steadily in commercial importance, whilst the same may even be said of hydraulic limes, as the limestones from which they are obtained will probably be employed in future as ingredients of artificial cements rather than as the sources of products of inferior strength. The future of cements derived from blast-furnace slag is less easy to predict, but it is probable that the difficulties connected with its utilisation will be overcome, and that means will be found of so regulating the chemical and physical characters of the slag as to ensure the stability of the product.

There is still room for great improvement in the methods of preparing cement concrete. In the foregoing discussions of the properties of concrete, one property has been insisted on as being of supreme importance, namely, the compactness, or absence of porosity. The mechanical strength, the impermeability to water, the power of resisting the destructive action of sea-water, acids, and other corrosive substances, and the degree of protection afforded to steel when embedded in the concrete, all depend in the first place on its compactness. A concrete is thoroughly compact, and is therefore likely to be satisfactory from the above points of view, when the voids of the aggregate are completely filled with a dense mortar, and every particle of sand and aggregate is completely coated with cement. Several factors demand special attention if these conditions are to be fulfilled. A knowledge of the actual proportion of voids in the materials used is essential, and a preliminary determination of this proportion will certainly be indispensable in future work in concrete. Again, a thorough grading of the aggregate is necessary, and it may even prove advantageous, in spite of the increased expense entailed thereby, to prepare artificially graded materials rather than to use ballast, &c., in a natural or in a roughly screened state. Further research is required to determine the most favourable grading of the sand and aggregate, and the best proportions of water to be used in mixing. Emphasis should be laid on the importance of good workmanship in the mixing, laying, and ramming of concrete, operations which are too often entrusted to unskilled workmen, whilst they imperatively demand a high degree of skill. The remarkable qualities of some of the ancient mortars and concretes, which have led to the popular belief that the ancient builders possessed some secret, now lost, for their composition, are undoubtedly due in reality to the care and skill expended on their preparation. Especially in the erection of reinforced concrete buildings and bridges, a great responsibility rests on those who are charged with the preparation and setting in place of the concrete, as errors are scarcely to be detected after the work is completed unless by the failure of some part of the structure. Public attention has been directed on several occasions to the disastrous collapse of reinforced concrete buildings, and although in one or two instances the original design was shown to be defective, it is safe to say that the principal fault in every case lay in the concrete. Mixing the ingredients in unsuitable proportions, using a quantity of water so large as to prevent proper setting or so small as to render efficient tamping impossible, carelessness in filling the moulds, neglect to provide a proper connection between layers filled in at different times, and removal of centring before sufficient time has been allowed for setting, are amongst the commonest errors, and any one of these may lead to disaster. Special stress should be laid on the last-mentioned error, the premature removal of centring. The precaution should always be taken of determining the time taken by a concrete mixture to attain a sufficient degree of strength. The time depends, as has been shown above, on the quantity of water used in mixing, and on the temperature and atmospheric conditions during erection, as well as on the setting time of the cement employed. A sufficient margin of time should then be allowed before removing any of the temporary supports. Undue haste in construction is a prolific cause of disaster. It must be repeated that the mechanical properties of Portland cement concrete depend on a number of complex physical and chemical changes which demand time for their completion and are influenced in a high degree by external physical conditions. If correctly prepared, it gains in strength with age, the gain being the more marked the better the concrete.

The steady improvement in the quality of commercial Portland cements renders an increase in the stringency of the present standard specifications inevitable. The entire abolition of tests with neat cement is one of the most urgent reforms in connection with the testing of cements, whilst it is also very necessary that the exact conditions thould be determined under which the most concordant results may be obtained with cement-sand mortars. The method of mixing and of filling the moulds, and the quantity of water to be used in gauging, require to be determined in such a manner that experimenters working in different laboratories shall be able, with reasonable care, to obtain practically identical results when testing the same cement. It is almost unnecessary to add that the method adopted must be an international one, the testing of materials being one of the subjects most urgently demanding the co-operation of workers in different countries.

It is probable that the system of testing briquettes in tension will in future be relegated to a secondary position, and that the chief weight will be laid on tests consisting in the application of a bending stress to prisms of mortar, followed by the crushing of the two broken portions under a compressive load. Such a method gives promise of yielding concordant results, and has the advantage of bearing a direct relation to the forms of loading which occur in the actual use of the mortar. It is possible, but by no means certain, that a method of conducting accelerated tests of strength may be devised, thus obviating the necessity of waiting twenty-eight days for the result of the test. Our knowledge of the general behaviour of colloids, however, makes it appear very doubtful whether such artificial "ageing" can produce the same effect as slow hardening at the atmospheric temperature, although it may be possible to establish a relation between the mechanical strengths at high and low temperatures respectively.

In the determination of soundness, on the other hand, accelerated tests have fully established their utility, the object in this case being to reveal latent defects. The objection that the hot test is unduly severe is without force, in view of the fact that the best qualities of commercial cement withstand the test in its most severe form. Unsoundness in a cement is so dangerous a defect that it is well that any test should err, if at all, on the side of stringency.

A better definition of the setting time is needed, whilst the exact method of gauging is as much in need of regulation as the mixing of mortars for strength tests. It is possible that the determination of the heat development during setting may find a place among the routine tests of the laboratory, although not in any of the forms hitherto devised, and it is not unlikely that automatically recording apparatus may be adopted as a means of lessening the laboriousness of such tests.

The question of the chemical constitution of cements (as distinguished from the ultimate *composition*) is sometimes regarded as having merely academic interest. This view is certainly a mistaken one. The valuable properties of cements can only be utilised to the full by taking into account their entire chemical behaviour. The remarkable alterations in the rapidity of setting which take place during storage, for instance, are due to the presence of components in a state of unstable equilibrium, which can only be investigated by chemical methods. The complexity of the chemical systems constituted by the silicates and similar inorganic substances is even greater than that exhibited by metallic alloys, as has been abundantly shown by the few accurate investigations in this department which we already possess. The progress of the metallurgy of alloys has been closely linked throughout with their metallographic study, and most valuable results may be confidently expected from the application of similar methods to the study of cements. Of the two most important methods of metallographic investigation, the thermal and the microscopical, the first has received little attention from chemists investigating cement, whilst the second is still in the initial stages of its development. Just as the microscopical examination of metals and alloys now forms a part of the routine work of foundries, mills, and engineering works, so we may expect that the examination of clinker and finished cement will, in course of time, find its way into cement laboratories as an indispensable adjunct of the ordinary methods of testing. Before this practice can become general, however, much further research will be needed to establish with sufficient certainty the connection between structure and properties, and to correlate their variations.

Turning from the practical to the more purely scientific aspect of the chemistry of cement, the investigation of the silicates and similar systems throws light on the problem of reactions between components differing little in electro-chemical behaviour, and suggests, if it does not solve, most interesting problems relating to the valency of the metallic elements, and to the nature of atomic linking in inorganic molecules. The study of colloidal substances has opened up new fields of research, and the apparent absence of the usual regularity of composition which characterises crystalline chemical substances, whilst introducing difficulties and complications into their study, is compensated for by the highly interesting chemical and physical relations which they present. The recognition of the setting and hardening of cements as processes occurring in a colloidal medium brings their chemistry into close relation with that of the clays and other materials of mineralogical and geological interest. No one who attempts the study of these substances can fail to be struck by the multitude of unsolved problems which they present when regarded from the chemical or the microscopical point of view. It will be long before these departments of chemistry and physics attain the certainty and systematic character of those dealing with the metals and the crystalline compounds, or still less of organic chemistry, but there is every prospect that researches in this direction, apart from their great technical importance, will yield results of the highest scientific interest.

APPENDIX I

THE REVISED BRITISH STANDARD SPECIFICATION

THE Engineering Standards Committee has recently (August 1910) issued a second revision of the Standard Specification for Portland Cement, and it therefore becomes necessary to note certain points in respect to which the new specification differs from that of 1907, to which reference is made in the foregoing pages. The following extracts from the preface will indicate the nature of the principal changes.

1.[1] "Since the issue of the first revision of the Specification the Committee has continued its investigation into the determination of the initial setting time of cement. It was found that while the final setting times determined by the British Standard and Vicat needles approximated very closely, the initial setting time as determined by the British Standard needle differed considerably from that given by the Vicat needle which is in general use, and also from that obtained by the rough and ready test of the finger-nail.

2. "It was considered preferable that one instrument only should be specified for determining the initial and final setting times of cement, and the Vicat needle has been adopted for that purpose.

3. "The Committee has also considered the question of inserting a clause in the Standard Specification to provide against the expansion of cement in cold water, but as the result of experimental investigation, they recommend that no test of the plunging type be inserted, as it depends upon the setting time of the cement rather than upon its soundness.

4. "In regard to chemical composition, a minimum lime content has been inserted with a view of excluding cements other

---

[1] The numbers have been added for convenience of reference. For permission to publish the above extracts the Author is indebted to the Engineering Standards Committee.

than Portland cements, the total loss on ignition has been specified to provide an additional criterion of the quality of the cement and to restrict the amount of water present, and provision is now made for limiting the total amount of sulphur present in the cement, whether in the form of sulphides or of sulphates.

5. "The instructions for gauging cement have been slightly modified with a view of removing as far as practicable any ambiguity as to the actual consistency of cement which may have existed under the previous instructions, and the growth of tensile strength of cement and sand briquettes has been graded in a similar manner to that of neat cement briquettes."

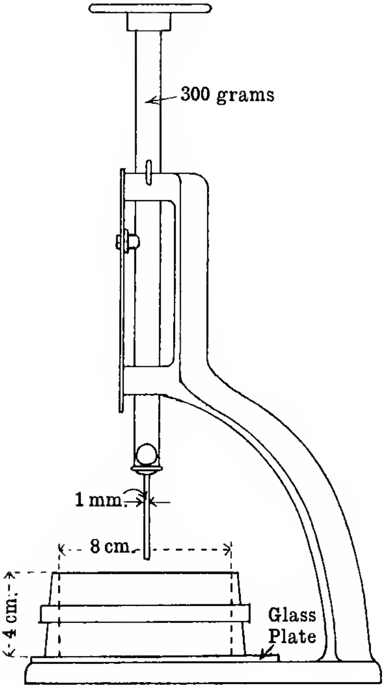


Fig. 19.

Standard Vicat Needle, 1910.

The other changes that have been made in the Specification are mainly verbal alterations intended to give greater clearness. For the rules as to sampling, reference should be made to the published Specification.[1]

In regard to the determination of setting time (paragraphs 1 and 2), the heavy needle described on p. 148 is now abandoned, and a return is made to the older Vicat needle of 300 grams weight only. The dimensions of the standard form of Vicat needle are shown in Fig. 19. The consistence is only specified by the provision that "the cement shall be mixed with such a proportion of water that the mixture shall be plastic when filled into the Vicat mould. The gauging shall be completed before signs of setting occur." Permission is given to use Vicat needles provided with a dash-pot or other mechanical appliance for ensuring a steady and gentle application of the point of the needle to the surface of the pat. Several instruments thus provided are now on the market.

Par. 3. The addition of a plunging test in cold water, advocated by some workers (p. 164), has been rejected as depending on the setting time rather than on the soundness of the cement. Exception has been taken to this decision, on the ground that the test is valuable as a means of detecting excessive additions of gypsum, and that cements which disintegrate under the test have generally undergone such additions. In the author's opinion, however, the test is rightly rejected, as being unfair to well-prepared slow-setting cements, the use of which, in concrete work, is to be encouraged.

Par. 4. The new requirement as to the proportion of lime fixes a minimum value as well as the maximum previously fixed. It is now required that the value of the ratio $\frac{CaO}{SiO_2 + Al_2O_3}$ (expressed in chemical equivalents, see p. 93) shall lie between 2·85 as a maximum and 2·0 as a minimum. This requirement excludes most cements consisting of granulated blast-furnace slag, in which the proportion of lime is decidedly lower than the above minimum. The same clause fixes the maximum insoluble residue at 1·5 per cent., and the maximum magnesia as 3 per cent. The total loss on ignition (water and carbon dioxide) is not to exceed 2 per cent.

---

[1] Report (No. 12, Revised August 1910) British Standard Specification for Portland Cement.

unless it can be shown that the cement has been ground for more than four weeks. A further new provision is that the total sulphur, calculated as SO_3, shall not exceed 2·75 per cent. As this will include the sulphides present, most cements prepared directly from slag are again excluded. It is right that granulated slag cements should not be classed as Portland cements, their mode of preparation being essentially different. If the manufacture of such novel materials increases, as the author believes will be the case, it will become necessary to prepare a separate standard to which they must conform. Such a procedure is greatly to be preferred to that of widening the definition of Portland cement so as to include them.

Par. 5. The requirements concerning the consistence of the paste to be employed in the mechanical tests now run as follows :—

For neat cement: "The cement shall be mixed with such a proportion of water that after filling into the mould the mixture shall be plastic."

For cement-sand mortars: "The mixture of cement and sand shall be gauged with so much water as to be moist throughout, but no surplus of water shall appear when the mixture is gently beaten with a trowel into the mould. Clean appliances shall be used for gauging, and the temperature of the water and that of the test room at the time the said operations are performed shall be from 58 to 64 degrees Fahrenheit [14–17° C.], and no ingredient other than cement, sand, and clean fresh water shall be introduced in making the test. The mixture gauged as above shall be filled, without mechanical ramming, into moulds. . . ."

It is obvious that such a mode of prescribing the method of operating in making mechanical tests leaves much to the judgment of the individual, and can only be regarded as provisional. It is to be hoped that the investigations to which we have alluded on p. 176 may lead to the establishment of a more rigorous method of testing, from which independent workers may expect to obtain comparable results.

The last alteration to which reference need be made is the provision for fixing the growth in tensile strength of the cement-briquettes, which runs :—

"The average breaking stress of the briquettes twenty-eight days after gauging must not be less than 250 lb. per square inch of section, and the increase in the breaking stress from seven to twenty-eight days must not be less than :—

25	per cent.	when the 7 days' test is above	200 lb.	and not above	250 lb.
15	,,	,,	250 ,,	,,	300 ,,
10	,,	,,	300 ,,	,,	350 ,,
5	,,	,,	350 lb.		

(Compare the figures for neat cement, p. 181.)

APPENDIX II

CHRONOLOGICAL TABLE

	A.D.
Smeaton's researches on hydraulic limes and pozzolanas	1756
Lavoisier's researches on plaster	1765
Higgins' book on cements	1780
Parker's invention of Roman cement and Lesage's invention of Boulogne cement	1796
Vicat's researches on hydraulic limes and artificial cements, from	1818
Aspdin's invention of Portland cement	1824
Fuchs' memoir on constitution of cement	1829
Discovery of cement rock in America	1829
Reinforcement of concrete proposed by J. C. Loudon	1830
Sir C. W. Pasley's book on cements	1838
First German Portland cement works at Stettin	1850
First employment of reinforced concrete	1855
Winkler's theory of hydrolysis of silicates	1856
Hydraulic properties of granulated slag discovered by E. Langen	1862
Zulkowsky's first paper	1863
Michaëlis' first paper	1867
Beginning of controversy regarding addition of slag to Portland cement	1882
Le Chatelier's first paper	1883
Ransome's invention of rotary kiln	1885
Introduction of tube-mills into cement works by F. L. Smidth	1892
Hurry and Seaman's invention of modern form of rotary kiln	1895
Törnebohm's researches on microscopic structure	1897
Newberry's investigations	1897

	A.D.
Passow's first patent for treatment of slag	1901
Richardson's investigations	1903
First British standard specification	1904
Colloseus' first patent for treatment of slag	1905
Bamber's process for hydration in mill	1906
Day, Shepherd, and Wright's memoir	1906
Stern's work on microscopic structure	1908

SUBJECT INDEX

NAME INDEX

THE END

Printed by Ballantyne, Hanson & Co.
Edinburgh & London

Mr. Edward Arnold's List of

Technical & Scientific Publications

Extract from the LIVERPOOL POST of Dec. 4, 1907:

"During recent years Mr. Edward Arnold has placed in the hands of engineers and others interested in applied science a large number of volumes which, independently altogether of their intrinsic merits as scientific works, are very fine examples of the printers' and engravers' art, and from their appearance alone would be an ornament to any scientific student's library. Fortunately for the purchaser, the publisher has shown a wise discrimination in the technical books he has added to his list, with the result that the contents of the volumes are almost without exception as worthy of perusal and study as their appearance is attractive."

The Dynamical Theory of Sound. By HORACE LAMB, D.Sc., LL.D., F.R.S., Professor of Mathematics in the Victoria University of Manchester. viii + 304 pages, 86 Illustrations. Demy 8vo., 12s. 6d. net (inland postage 5d.).

An Introduction to the Theory of Optics. By ARTHUR SCHUSTER, Ph.D., Sc.D., F.R.S., Honorary Professor of Physics at the University of Manchester. Second Edition (Revised). xvi + 352 pages. Demy 8vo., 15s. net (inland postage 5d.).

The Becquerel Rays and the Properties of Radium. By the Hon. R. J. STRUTT, F.R.S., Fellow of Trinity College, Cambridge; Professor of Physics at the Imperial College of Science and Technology. Second Edition (Revised and Enlarged). vi + 215 pages. Demy 8vo., 8s. 6d. net (inland postage 5d.).

An Introduction to Projective Geometry. By L. N. G. FILON, M.A., D.Sc., Fellow and Assistant Professor of University College, London; Examiner in Mathematics to the University of London. Crown 8vo., 7s. 6d.

Advanced Examples in Physics. By A. O. ALLEN, B.A., B.Sc., A.R.C.Sc., Assistant Lecturer in Physics at Leeds University. With Answers. Crown 8vo., 1s. 6d.

A collection of 274 classified examples for advanced students.

Five-Figure Tables of Mathematical Functions. By J. B. DALE, M.A., Assistant Professor of Mathematics, King's College, London. Demy 8vo., 3s. 6d. net.

LONDON: EDWARD ARNOLD, 41 & 43 MADDOX STREET, BOND STREET, W.

Logarithmic and Trigonometric Tables (To Five Places of Decimals). By J. B. Dale, M.A. 2s. net.

Mathematical Drawing. Including the Graphic Solution of Equations. By G. M. Minchin, M.A., F.R.S., Formerly Professor of Applied Mathematics at the Royal Indian Engineering College, Cooper's Hill; and J. B. Dale, M.A. 7s. 6d. net (inland postage 4d.).

Vectors and Rotors (with Applications). By O. Henrici, Ph.D., F.R.S., LL.D., and G. C. Turner, B.Sc. 4s. 6d.

The Strength and Elasticity of Structural Members. By R. J. Woods, M.E., M.Inst.C.E., Fellow and formerly Assistant Professor of Engineering, Royal Indian Engineering College, Cooper's Hill. Second Edition. xii + 310 pages. Demy 8vo., cloth, 10s. 6d. net (inland postage 4d.).

BY THE SAME AUTHOR.

The Theory of Structures. xii + 276 pages. Demy 8vo., 10s. 6d. net (inland postage 4d.).

The Calculus for Engineers. By John Perry, M.E., D.Sc., F.R.S., Professor of Mechanics and Mathematics in the Royal College of Science. With many Diagrams. Crown 8vo., 7s. 6d.

Oblique and Isometric Projection. By John Watson, Lecturer on Mechanical Engineering and Instructor of Manual Training Classes for Teachers for Ayrshire County Committee. 50 pages. Fcap. 4to., 3s. 6d.

The Balancing of Engines. By W. E. Dalby, M.A., B.Sc., M.Inst.C.E., M.I.M.E., Professor of Engineering, City and Guilds of London Central Technical College. Second Edition. xii + 283 pages. Demy 8vo., 10s. 6d. net (inland postage 4d.).

Valves and Valve Gear Mechanisms. By W. E. Dalby, M.A., B.Sc., M.Inst.C.E., M.I.M.E. xviii + 366 pages. Royal 8vo., 21s. net (inland postage 5d.).

The Practical Design of Motor-Cars. By James Gunn, Lecturer on Motor-Car Engineering at the Glasgow and West of Scotland Technical College. Fully Illustrated. Demy 8vo.

Cement. By C. H. Desch, D.Sc., Ph.D., Lecturer in Metallurgical Chemistry in the University of Glasgow. Illustrated. Demy 8vo. [*In preparation.*

Hydraulics. For Engineers and Engineering Students. By F. C. Lea, B.Sc., A.M.Inst.C.E., Senior Whitworth Scholar, A.R.C.S.; Lecturer in Applied Mechanics and Engineering Design, City and Guilds of London Central Technical College, London. xii + 536 pages. Demy 8vo, 15s. net (inland postage 5d.).

Hydraulics. By Raymond Busquet, Professeur à l'École Industrielle de Lyon. Translated by A. H. Peake, M.A. viii + 312 pages. Demy 8vo., 7s. 6d. net (inland postage 5d.).

Power Gas Producers: their Design and Application. By Philip W. Robson, of the National Gas Engine Co., Ltd.; sometime Vice-Principal of the Municipal School of Technology, Manchester. iv + 247 pages. Demy 8vo., 10s. 6d. net (inland postage 4d.).

The Foundations of Alternate Current Theory. By C. V. Drysdale, D.Sc. (Lond.), M.I.E.E. xii + 300 pages. Demy 8vo., 8s. 6d. net (inland postage 4d.).

Electrical Traction. By Ernest Wilson, Whit. Sch., M.I.E.E., Professor of Electrical Engineering in the Siemens Laboratory, King's College, London; and Francis Lydall, B.A., B.Sc. Two volumes, sold separately. Demy 8vo. Vol. I., 475 pages, Direct Current; Vol. II., 328 pages, Alternating Current. 15s. net each volume (inland postage 5d. each).

A Text-Book of Electrical Engineering. By Dr. Adolf Thomälen. Translated by G. W. O. Howe, M.Sc., Whit. Sch., A.M.I.E.E., Assistant Professor in Electrical Engineering at the Central Technical College, South Kensington. Second Edition. viii + 464 pages. Royal 8vo., 15s. net (inland postage 6d.).

Alternating Currents. A Text-Book for Students of Engineering. By C. G. Lamb, M.A., B.Sc., A.M.I.E.E., Clare College, Cambridge; Associate of the City and Guilds of London Institute. viii + 325 pages. Demy 8vo., 10s. 6d. net (inland postage 5d.).

Electric and Magnetic Circuits. By Ellis H. Crapper, M.I.E.E., Head of the Electrical Engineering Department in the University College, Sheffield. viii + 380 pages. Demy 8vo., 10s. 6d. net (inland postage 5d.).

Applied Electricity. A Text-Book of Electrical Engineering for "Second Year" Students. By J. Paley Yorke, Head of the Physics and Electrical Engineering Department at the London County Council School of Engineering and Navigation, Poplar. Second Edition. xii + 420 pages. Cloth, 7s. 6d. (inland postage 4d.).

Physical Chemistry: its Bearing on Biology and Medicine. By J. C. Philip, M.A., Ph.D., B.Sc., Assistant Professor of Chemistry in the Imperial College of Science and Technology. Illustrated. 7s. 6d. net.

Lectures on Theoretical and Physical Chemistry. By Dr. J. H. Van 'T Hoff, Professor of Chemistry at the University of Berlin. Translated by R. A. Lehfeldt, D.Sc.

Part I. Chemical Dynamics. 12s. net.

Part II. Chemical Statics. 8s. 6d. net.

Part III. Relations Between Properties and Composition. 7s. 6d. net.

A Text-Book of Physical Chemistry. By R. A. Lehfeldt, D.Sc., Professor of Physics at the Transvaal University College, Johannesburg. xii + 308 pages. Crown 8vo., 7s. 6d. (inland postage 4d.).

Organic Chemistry for Advanced Students. By Julius B. Cohen, Ph.D., B.Sc., Professor of Organic Chemistry in the University of Leeds, and Associate of Owens College, Manchester. viii + 632 pages. Demy 8vo., 21s. net (inland postage 6d.).

The Chemistry of the Diazo-Compounds. By John Cannell Cain, D.Sc. (Manchester and Tübingen), Editor of the Publications of the Chemical Society. 176 pages. Demy 8vo., 10s. 6d. net (inland postage 4d.).

The Chemical Synthesis of Vital Products and the Inter-relations between Organic Compounds. By Raphael Meldola, F.R.S., V.P.C.S., F.I.C., etc.; Professor of Chemistry in the City and Guilds of London Technical College, Finsbury. Vol. I., xvi + 338 pages. Super royal 8vo., 21s. net (inland postage 5d.).

Elements of Inorganic Chemistry. By the late W. A. Shenstone, F.R.S., Lecturer on Chemistry at Clifton College. New Edition (Enlarged and Revised). xii + 554 pages. Crown 8vo., 4s. 6d.

A Course of Practical Chemistry. Being a Revised Edition of "A Laboratory Companion for Use with Shenstone's 'Inorganic Chemistry.'" By the late W. A. Shenstone, F.R.S. xii + 136 pages. Crown 8vo., cloth, 1s. 6d.

A History of Chemistry. By Dr. Hugo Bauer, Royal Technical Institute, Stuttgart. Translated by R. V. Stanford, B.Sc. (Lond.). Crown 8vo., 3s. 6d. net (inland postage 4d.).

A First Year's Course of Experimental Work in Chemistry. By E. H. Cook, D.Sc., F.I.C., Principal of the Clifton Laboratory, Bristol. viii + 135 pages, with 26 Illustrations. Crown 8vo., cloth, 1s. 6d.

Physical Chemistry for Beginners. By Dr. Ch. M. Van Deventer. With a Preface by Dr. Van 'T Hoff. Translated by R. A. Lehfeldt, D.Sc. xvi + 146 pages, with Diagrams and Tables. Crown 8vo., cloth, 2s. 6d.

Experimental Researches with the Electric Furnace. By Henri Moissan. Translated by A. T. de Mouilpied, M.Sc., Ph.D. xii + 307 pages. Demy 8vo., 10s. 6d. net (inland postage 4d.).

Electrolytic Preparations. Exercises for use in the Laboratory by Chemists and Electro-Chemists. By Dr. Karl Elbs, Professor of Organic and Physical Chemistry at the University of Giessen. Translated by R. S. Hutton, M.Sc. xii + 100 pages. Demy 8vo., 4s. 6d. net (inland postage 4d.).

Introduction to Metallurgical Chemistry for Technical Students. By J. H. Stansbie, B.Sc. (Lond.), F.I.C., Associate of Mason University College and Lecturer in the Birmingham University Technical School. Second Edition. xii + 252 pages. Crown 8vo., 4s. 6d. (inland postage 4d.).

On the Calculation of Thermo-Chemical Constants. By H. Stanley Redgrove, B.Sc. (Lond.), F.C.S. iv + 102 pages. Demy 8vo., 6s. net (inland postage 4d.).

First Steps in Quantitative Analysis. By J. C. Gregory, B.Sc., A.I.C. viii + 136 pages. Crown 8vo., 2s. 6d.

Manual of Alcoholic Fermentation and the Allied Industries. By Charles G. Matthews, F.I.C., F.C.S., etc. xvi + 295 pages. Crown 8vo., 7s. 6d. net (inland postage 4d.).

An Introduction to Bacteriological and Enzyme Chemistry. By Gilbert J. Fowler, D.Sc., Lecturer in Bacteriological Chemistry in the Victoria University of Manchester. Illustrated. Crown 8vo. [*In preparation.*

An Experimental Course of Chemistry for Agricultural Students. By T. S. Dymond, F.I.C., lately Principal Lecturer in the Agricultural Department, County Technical Laboratories, Chelmsford. 192 pages. Crown 8vo., 2s. 6d.

ARNOLD'S GEOLOGICAL SERIES.

General Editor: DR. J. E. MARR, F.R.S.

THE economic aspect of geology is yearly receiving more attention, and the books of this series are designed in the first place for students of economic geology. They will, however, also be found of great use to all who are concerned with the practical applications of the science, whether as surveyor, mining expert, or engineer.

The Geology of Coal and Coal-Mining. By WALCOT GIBSON, D.Sc., F.G.S. 352 pages. With Illustrations. 7s. 6d. net (inland postage 4d.).

The Geology of Ore Deposits. By H. H. THOMAS and D. A. MACALISTER, of the Geological Survey of Great Britain. Illustrated. 7s. 6d. net (inland postage 4d.).

The Geology of Building Stones. By J. ALLEN HOWE, B.Sc., Curator of the Museum of Practical Geology. Illustrated. 7s. 6d. net (inland postage 4d.).

The Geology of Water Supply. By H. B. WOODWARD, F.R.S. Illustrated. Crown 8vo., 7s. 6d. net (inland postage 4d.).

A Text-Book of Geology. By P. LAKE, M.A., Royal Geographical Society Reader in Regional and Physical Geography at the University of Cambridge; and R. H. RASTALL, M.A., F.G.S. Illustrated. Demy 8vo.

The Dressing of Minerals. By HENRY LOUIS, M.A., Professor of Mining and Lecturer on Surveying, Armstrong College, Newcastle-on-Tyne. x + 544 pages. With 416 Illustrations. Royal 8vo., 30s. net.

Traverse Tables. With an Introductory Chapter on Co-ordinate Surveying. By HENRY LOUIS, M.A., and G. W. CAUNT, M.A. Demy 8vo., flexible cloth, rounded corners, 4s. 6d. net (inland postage 3d.).

Mines and Minerals of the British Empire. Being a Description of the Historical, Physical, and Industrial Features of the Principal Centres of Mineral Production in the British Dominions beyond the Seas. By RALPH S. G. STOKES, late Mining Editor, *Rand Daily Mail*, Johannesburg, S.A. xx + 403 pages, 70 Illustrations. Demy 8vo., 15s. net (inland postage 5d.).

Outlines of Physiography. An Introduction to the Study of the Earth. By A. J. HERBERTSON, PH.D., Lecturer in Regional Geography in the University of Oxford. viii + 312 pages, with 118 Illustrations and Maps. Crown 8vo., 4s. 6d. (inland postage 4d.).

Modern Methods of Water Purification. By John Don, A.M. Inst. Mech.E., and John Chisholm. Illustrated. Demy 8vo.

Practical Photo-micrography. By J. Edwin Barnard, F.R.M.S., Lecturer in Microscopy, King's College, London. Illustrated. Demy 8vo. [*In preparation.*

Wood. A Manual of the Natural History and Industrial Applications of the Timbers of Commerce. By G. S. Boulger, F.G.S., A.S.I., Professor of Botany and Lecturer on Forestry in the City of London College. Second Edition. xi + 348 pages, with 48 Plates and other Illustrations. Demy 8vo., 12s. 6d. net (inland postage 5d.).

A Class Book of Botany. By G. P. Mudge, A.R.C.Sc., and A. J. Maslen, F.L.S. With over 200 Illustrations. Crown 8vo., 7s. 6d.

Elementary Botany. By E. Drabble, D.Sc., Lecturer on Botany at the Northern Polytechnic Institute. 234 pages, with 76 Illustrations. Crown 8vo., cloth, 2s. 6d.

The Development of British Forestry. By A. C. Forbes, F.H.A.S., Chief Forestry Inspector to the Department of Agriculture for Ireland. Author of "English Estate Forestry," etc. Illustrated. Demy 8vo., cloth, 10s. 6d. net.

English Estate Forestry. By A. C. Forbes, F.H.A.S. x + 332 pages, Illustrated. Demy 8vo., 12s. 6d. net (inland postage 5d.).

House, Garden, and Field. A Collection of Short Nature Studies. By L. C. Miall, F.R.S., late Professor of Biology in the University of Leeds. viii + 316 pages. Crown 8vo., 6s. (inland postage 4d.).

Astronomical Discovery. By Herbert Hall Turner, D.Sc., F.R.S., Savilian Professor of Astronomy in the University of Oxford. xii + 225 pages, with 15 Plates. Demy 8vo., cloth, 10s. 6d. net (inland postage 5d.).

The Evolution Theory. By Dr. AUGUST WEISMANN, Professor of Zoology in the University of Freiburg in Breisgau. Translated, with the Author's co-operation, by J. ARTHUR THOMSON, Regius Professor of Natural History in the University of Aberdeen; and MARGARET THOMSON. Two vols, xvi+416 and viii+396 pages, with over 130 Illustrations. Royal 8vo., cloth, 32s. net.

The Chances of Death and Other Studies in Evolution. By KARL PEARSON, M.A., F.R.S., Professor of Applied Mathematics in University College, London. 2 vols., xii+388 and 460 pages, with Illustrations. Demy 8vo., 25s. net (inland postage 6d.).

Hereditary Characters. By CHARLES WALKER, M.D., Lecturer in the University of Liverpool. Demy 8vo., 8s. 6d. net.

The Life of the Salmon. With reference more especially to the Fish in Scotland. By W. L. CALDERWOOD, F.R.S.E., Inspector of Salmon Fisheries for Scotland. Illustrated. 7s. 6d. net.

A Text-Book of Zoology. By G. P. MUDGE, A.R.C.Sc. (Lond), Lecturer on Botany and Zoology at the London School of Medicine for Women, and Demonstrator on Biology at the London Hospital Medical College. Illustrated. Crown 8vo., 7s. 6d.

Animal Behaviour. By C. LLOYD MORGAN, LL.D., F.R.S., Professor of Psychology in the University of Bristol. viii+344 pages. Second Edition. 7s. 6d. net (inland postage 5d.).

BY THE SAME AUTHOR.

Psychology for Teachers. New Edition, entirely rewritten. xii+308 pages. Crown 8vo., cloth, 4s. 6d.

An Introduction to Child-Study. By W. B. DRUMMOND, M.B., C.M., F.R.C.P.E., Medical Officer and Lecturer on Hygiene to the Edinburgh Provincial Committee for the Training of Teachers. 348 pages. Crown 8vo., 6s. net (inland postage 4d.).

BY THE SAME AUTHOR.

Elementary Physiology for Teachers and Others. 206 pages. Crown 8vo., 2s. 6d.

The Child's Mind: its Growth and Training. By W. E. URWICK, University of Leeds. Crown 8vo., cloth, 4s. 6d. net.