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# CEMENT CHEMISTRY

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H.F.W. TAYLOR

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H. F. W. TAYLOR

*Emeritus Professor of Chemistry, University of Aberdeen*  
*Visiting Professor, Imperial College (University of London)*



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## Preface

This book deals with the chemistry of the principal silicate and aluminate cements used in building and civil engineering. It is a completely re-written successor to the two volumes on 'The Chemistry of Cements' that I edited in 1964,\* and, like them, is directed primarily to those whose background is in chemistry, materials science or related disciplines. Emphasis is placed throughout on the underlying science rather than on practical applications, which are well covered in other works.

The earlier volumes are outdated. Since 1964, several major areas previously unknown or neglected have been widely studied due to changes in the ways in which cement is made or used, or to increased awareness of the problems encountered in producing concrete of adequate durability. Alongside this, much information has accrued from the introduction of new and powerful experimental techniques, of which scanning electron microscopy and X-ray microanalysis have proved especially important. In 1964, some topics, though practically important, were so imperfectly understood from the standpoint of basic chemistry that I did not consider it useful to deal with them. Increased understanding now makes it possible, and indeed essential, to include them. On the other hand, descriptions of standard experimental techniques, included in the earlier book, have been omitted, except for some matters of specialist relevance to cement chemistry, as good textbooks on all of them are available.

All the cements considered in this book fall into the category of hydraulic cements; they set and harden as a result of chemical reactions with water, and if mixed with water in appropriate proportions continue to harden even if stored under water after they have set. Much the most important is Portland cement. Chapters 1 to 4 of the present work deal mainly with the chemistry of manufacture of Portland cement and with the nature of the resulting product. Chapters 5 to 8 deal mainly with the processes that occur when this product is mixed with water and with the nature of the hardened material. Chapters 9 to 11 deal with the chemistry of other types of cement, of admixtures for concrete and of special uses of cements. Chapter 12 deals with chemical and microstructural aspects of concrete, including ones relevant to processes that affect its durability or limit its service life.

The literature of cement chemistry is voluminous; the abstracting journal, *Cements Research Progress* has latterly listed about one thousand new contributions annually. Inevitably, coverage in the present work has been selective. I have tried to strike a balance between classical and recent contributions, in order to produce a book that will serve both as an

\* *The Chemistry of Cements* (ed. H. F. W. Taylor), Vol. 1, 460 pp., Vol. 2, 442 pp., Academic Press, London and New York (1964).

introduction that assumes no previous specialist knowledge of cements, and as a guide to research. It is hoped that the more important contributions up to early 1989 have been covered.

## Acknowledgments

I am most grateful to former colleagues at the University of Aberdeen and friends elsewhere with whom I have had productive discussions over a period of many years. More directly in relation to the present book, Mr C. P. Kerton, Dr G. R. Long, Dr G. K. Moir and Mr M. S. Sumner (Blue Circle Industries PLC) gave invaluable help, especially on the chemistry and technology of Portland cement production, composite cements, and clinker and cement properties. My thoughts on the hydration chemistry of calcium silicates owe much to discussions with Drs P. W. Brown, G. Frohnsdorff and H. M. Jennings, then all at the National Bureau of Standards (now National Institute of Standards and Technology), USA. Those on microstructural aspects of the hydration of calcium silicates and cement similarly owe much to discussions with Professor P. L. Pratt and Dr K. L. Scrivener, of Imperial College, London. Dr L. J. Parrott (British Cement Association) helped greatly with a discussion on the pore structures of cement pastes. Dr A. Capmas (Lafarge Fondu International, France) and Drs D. Ménétrier-Sorrentino and F. Sorrentino (Lafarge Coppée Recherche, France) gave quite exceptional help in providing a draft manuscript on calcium aluminate cements and with subsequent discussions, in which Dr C. M. George (Lafarge Calcium Aluminates, USA) also participated. Dr J. Bensted (The British Petroleum Company PLC) corrected some important errors on oil well cementing. For discussions and comments on various aspects of concrete durability, I am most grateful to Mr J. S. Lumley and Dr J. J. Kollek (Blue Circle Industries PLC). Many of those mentioned above gave help that included comments on parts of the manuscript, but any errors are mine.

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reproduce the figures noted below. Authors and sources, including copyright years, are given in the captions and reference list, and where it was requested, additional information is included below. *American Ceramic Society*, Fig. 5.4C and D (Ref. J10, Issue 10, Oct., on "Morphological development of hydrating tricalcium silicate as examined by electron microscopy techniques"); Fig. 5.6 (Ref. M38, Issue 12, Dec., on "Analytical electron microscopy of cement pastes: IV,  $\beta$ -dicalcium silicate pastes"); Figs. 5.8 and 5.9 (Ref. T24, Issue 6, June, on "Proposed structure for calcium silicate hydrate gel"); Fig. 5.12 (Ref. J15, Issue 8, Aug., on "Aqueous solubility relationships for two types of calcium silicate hydrate"); Fig. 9.3 (Ref. T44, Issue 12, Dec., on "Analytical study of pure and extended Portland cement pastes: II, fly ash- and slag-cement pastes"). *American Concrete Institute*, Fig. 11.6. *American Journal of Science*, Fig. 6.5. *British Cement Association*, Fig. 5.11. *Cemento*, Fig. 11.4. *Dunod and RILEM*, Figs. 5.10 and 5.13. *Editions Septima*, Fig. 10.7. *Elsevier Applied Science Publishers Ltd*, Figs. 10.1, 10.6 and 10.8. *International Cement Microscopy Association*, Figs. 4.3A, 4.3B and 7.2. *John Wiley and Sons Ltd*, Fig. 8.4. *Materials Research Society*, Figs. 8.7, 9.1, 9.2, 9.6 and 12.1. *Palladian Publications Ltd*, Fig. 7.1. *Pergamon Press PLC*, Figs. 1.2, 3.3, 5.3, 5.5, 5.14, 5.15, 8.8, 11.1, 11.5 and 12.5. *The Royal Society*, Fig. 7.7. *Sindicato Nacional da Indústria do Cimento (Brazil)*, Fig. 6.8. *Society of Chemical Industry*, Fig. 5.1. *Stroyizdat*, Fig. 3.4. *Thomas Telford Ltd*, Figs. 12.4 and 12.6. *Transportation Research Board, National Research Council, Washington DC*, Fig. 7.8 (Ref. L32, on "Changes in composition of the aqueous phase during hydration of cement pastes and suspensions").

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# Portland cement and its major constituent phases

## 1.1 Introduction

### 1.1.1 Portland cement: general

Portland cement is made by heating a mixture of limestone and clay, or other materials of similar bulk composition and sufficient reactivity, ultimately to a temperature of about 1450°C. Partial fusion occurs, and nodules of clinker are produced. The clinker is mixed with a few per cent of gypsum and finely ground to make the cement. The gypsum controls the rate of set and may be partly replaced by other forms of calcium sulphate. Some specifications allow the addition of other materials at the grinding stage. The clinker typically has a composition in the region of 67% CaO, 22% SiO<sub>2</sub>, 5% Al<sub>2</sub>O<sub>3</sub>, 3% Fe<sub>2</sub>O<sub>3</sub> and 3% of other components, and normally contains four major phases, called alite, belite, aluminate phase and ferrite phase. Several other phases, such as alkali sulphates and calcium oxide, are normally present in minor amounts.

Alite is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50–70%. It is tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>) modified in composition and crystal structure by incorporation of foreign ions, especially Mg<sup>2+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup>. It reacts relatively quickly with water, and in normal Portland cements is the most important of the constituent phases for strength development; at ages up to 28 days, it is by far the most important.

Belite constitutes 15–30% of normal Portland cement clinkers. It is dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>) modified by incorporation of foreign ions and normally present wholly or largely as the β polymorph. It reacts slowly with water, thus contributing little to the strength during the first 28 days, but substantially to the further increase in strength that occurs at later ages. By one year, the strengths obtainable from pure alite and pure belite are about the same under comparable conditions.

The aluminate phase constitutes 5–10% of most normal Portland cement clinkers. It is tricalcium aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>), substantially modified in