

A blue-tinted microscopic image showing the complex, crystalline structure of cement, with various grains and interlocking crystals visible.

CEMENT CHEMISTRY

H F W Taylor

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EDITION

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2nd edition

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This One



69RO-F24-LLPH

Published by Thomas Telford Publishing, Thomas Telford Services Ltd,
1 Heron Quay, London E14 4JD

First published 1990 by Academic Press
Thomas Telford edition published 1997

Reprinted 2003, 2004

Distributors for Thomas Telford books are
USA: American Society of Civil Engineers, Publications Sales Department,
345 East 47th Street, New York, NY 10017-2398
Japan: Maruzen Co. Ltd, Book Department, 3-10 Nihonbashi 2-chome, Chuo-ku, Tokyo 103
Australia: DA Books and Journals, 648 Whitehorse Road, Mitcham 3132, Victoria

A catalogue record for this book is available from the British Library

ISBN: 0 7277 2592 0

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Typeset by the Alden Group, Oxford
Printed in Great Britain by CPI Bath

1 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 calcium sulfate and finely ground, to make the cement. The calcium sulfate controls the rate of set and influences the rate of strength development. It is commonly described as gypsum, but this may be partly or wholly replaced by other forms of calcium sulfate. 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% SiO₂, 5% Al₂O₃, 3% Fe₂O₃ and 3% other components, and normally contains four major phases, called alite, belite, aluminate and ferrite. Several other phases, such as alkali sulfates and calcium oxide, are normally present in minor amounts. Hardening results from reactions between the major phases and water.

Alite is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50–70%. It is tricalcium silicate (Ca₃SiO₅) modified in composition and crystal structure by ionic substitutions. 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 (Ca₂SiO₄) modified by ionic substitutions 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.

Aluminate constitutes 5–10% of most normal Portland cement clinkers. It is tricalcium aluminate (Ca₃Al₂O₆), substantially modified in composition and sometimes also in structure by ionic substitutions.

It reacts rapidly with water, and can cause undesirably rapid setting unless a set-controlling agent, usually gypsum, is added.

Ferrite makes up 5–15% of normal Portland cement clinkers. It is tetra-calcium aluminoferrite ($\text{Ca}_2\text{AlFeO}_5$), substantially modified in composition by variation in Al/Fe ratio and ionic substitutions. The rate at which it reacts with water appears to be somewhat variable, perhaps due to differences in composition or other characteristics, but in general is high initially and low or very low at later ages.

1.1.2 *Types of Portland cement*

The great majority of Portland cements made throughout the world are designed for general constructional use. The standard specifications with which such cements must comply are similar, but not identical, in all countries and various names are used to define the material, such as Class 42.5 Portland cement in current European and British standards (42.5 is the minimum 28-day compressive strength in MPa), Types I and II Portland cement in the ASTM (American Society for Testing and Materials) specifications used in the USA, or Ordinary Portland Cement (OPC) in former British standards. Throughout this book, the term 'ordinary' Portland cements is used to distinguish such general-purpose cements from other types of Portland cement, which are made in smaller quantities for special purposes.

Standard specifications are, in general, based partly on chemical composition or physical properties such as specific surface area, and partly on performance tests, such as setting time or compressive strength developed under standard conditions. The content of MgO^* is usually limited to 4–5%, because quantities of this component in excess of about 2% can occur as periclase (magnesium oxide), which through slow reaction with water can cause destructive expansion of hardened concrete. Free lime (calcium oxide) can behave similarly. Excessive contents of SO_3 can also cause expansion, and upper limits, typically 3–5% for ordinary Portland cements, are usually imposed. Alkalis (K_2O and Na_2O) can undergo expansive reactions with certain aggregates, and some specifications limit the content, e.g. to 0.6% equivalent Na_2O ($\text{Na}_2\text{O} + 0.66 \text{K}_2\text{O}$). Other upper limits of composition widely used in specifications relate to matter insoluble in dilute acid, and loss on ignition. Many other minor components are limited in content by their effects on the manufacturing process, or the properties, or both, and in some cases the limits are defined in specifications.

Rapid-hardening Portland cements have been produced in various ways, such as varying the composition to increase the alite content, finer grinding of the clinker, and improvements in the manufacturing process,

* Confusion can arise because the names or formulae of compounds can be used to denote either phases or components; this applies especially to CaO and MgO . Here and elsewhere, chemical or mineral names of oxides (e.g. calcium oxide, magnesium oxide, lime, periclase) will generally be used for phases, and formulae (e.g. CaO , MgO) for components. Mineral names or prefixed formulae (e.g. $\alpha\text{-Al}_2\text{O}_3$) are never used for components.