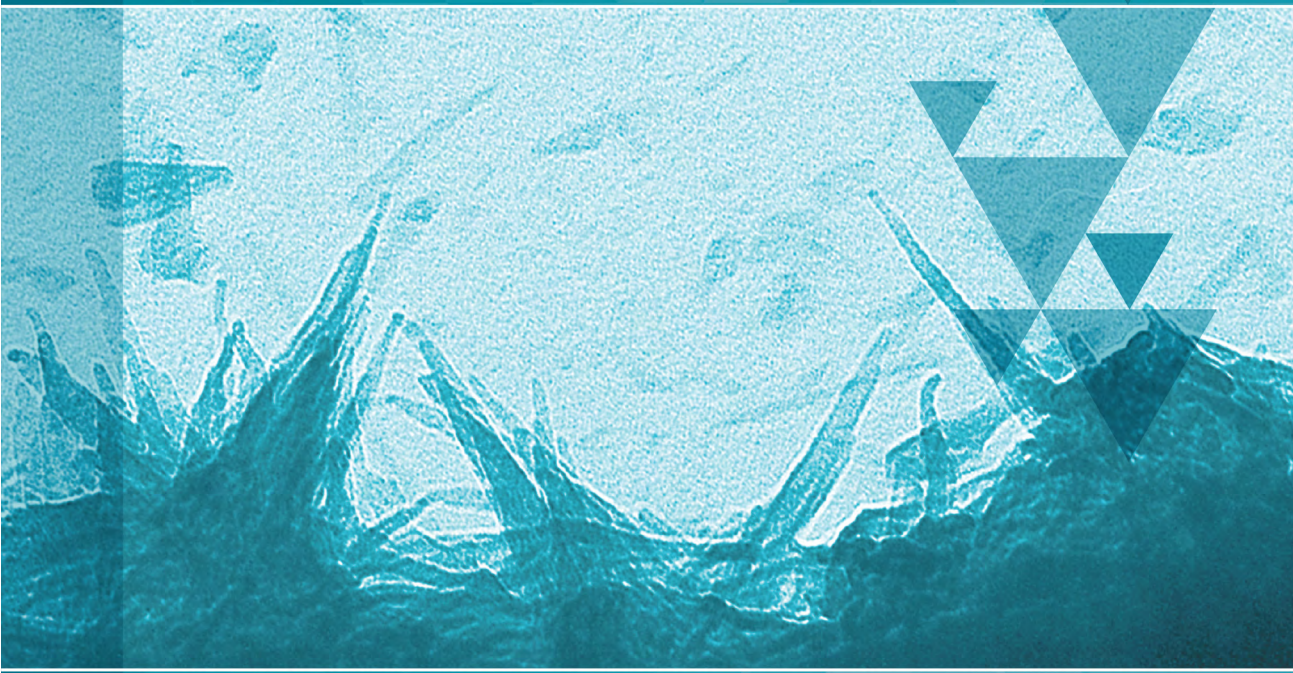
emerald PUBLISHING

ice Publishing

Cement Chemistry

Calcium silicates and anhydrous Portland cement

Third edition



Ian G Richardson and HFW Taylor

Cement Chemistry

This page intentionally left blank

emerald PUBLISHING
ice Publishing

Cement Chemistry

Calcium silicates and anhydrous Portland cement

Third edition

Ian G Richardson and HFW Taylor

Published by Emerald Publishing Limited, Floor 5, Northspring, 21-23 Wellington Street, Leeds LS1 4DL.

ICE Publishing is an imprint of Emerald Publishing Limited

Other ICE Publishing titles:
ICE Handbook of Concrete Durability, Second edition
Edited by Marios Soutsos. ISBN 978-0-72776-375-4
Structural Design of Buildings: Elemental Design
Edited by Feng Fu and David Richardson. ISBN 978-1-83549-573-5
Fibre-reinforced Concretes for High-performance Structures: Building a more sustainable future
Andreas Lampropoulos. ISBN 978-0-72776-556-7

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

ISBN 978-1-83549-777-7

Cover photo: courtesy of Ian G Richardson

Commissioning Editor: Michael Fenton
Content Development Editor: Cathy Sellars
Production Editor: Emma Sudderick and Benn Linfield

Typeset by KnowledgeWorks Global Limited
Index created by Ian Richardson and Lyn Nesbitt-Smith

Contents

Preface

Hal Taylor wanted his book *Cement Chemistry* to serve both as an introduction for those with no previous specialist knowledge of cements and as a guide to further research, and so he dealt with recent research but placed the development of the subject in a historical perspective. In retaining the broad scope and ambition of his book, it has been necessary to split the revised third edition into two volumes. This first volume updates second edition chapters on the chemistry and properties of anhydrous Portland cement and its constituent phases, and the hydration of calcium silicates. Highlights include:

- new evidence about the invention of Portland cement
- updated and enhanced treatment of crystal structure data, including the incorporation of space group numbers and extensive use of crystal-chemical information
- updated Bogue equations and illustrative calculation of enthalpy change on formation of Portland cement clinker
- expanded coverage of hydration of calcium silicates, including critical discussion of a wide range of data from the literature
- two new chapters about calcium (alumino) silicate hydrates: natural minerals and synthetic preparations

Hal was a Visiting Professor with me at the University of Leeds in the years 2000-2002, and during that time he reviewed research concerning natural and synthetic calcium silicate hydrates. The work that he produced was a good starting point for two new chapters in the revision of his book, and so we have both contributed to all seven chapters of this volume.

I have attempted to make the third edition of *Cement Chemistry* more accessible as an introduction for those entering the subject for the first time, for example, by setting out the calculations behind some results so that they are more easily understood. But the book has also been very extensively revised and updated to reflect advances in the field, and so there is a lot of material that will only be immediately accessible to those who are already experienced in the subject. In the preface to the second edition, written in 1997, Hal noted that the literature of cement chemistry is voluminous, and that there had been a significant increase in the seven years since publication of the first edition. There has of course been an enormous increase since that time, and so coverage in this edition has again of necessity been selective, but – as then – it is hoped that the most important contributions have been covered. Research on cements is generally very time limited, which constrains the number and length of experiments – for example, a typical PhD project might involve data collection over a period of only 30 months or so. As a consequence, throughout both volumes, I have combined data sets

from multiple studies – often conducted across many decades – in order to gain a better understanding of important topics. The result is a very large number of figures and tables, and I hope that the effort expended in creating and discussing them will be considered to have been worthwhile.

Acknowledgements

I have worked on material for this revision (both volumes) over an extended period of time between my work commitments, and I must thank a number of people for their extraordinary patience and support: the team at ICE Publishing / Emerald Publishing, especially Michael Fenton, my contact since 2016; some of the Heads of the School of Civil Engineering at the University of Leeds (in particular Prof Nigel Smith); and most importantly my children, Ella and Charlie, and my wife, Andrea. The publisher's requirement for the use of full references was problematic: anyone who has used the second edition will know that the references are presented in a truncated format and my decision to retain so many of them led to a rather time-consuming effort to obtain the missing information. I am most grateful to my daughter who very ably assisted in that endeavour, and also for transcribing many of the tables from the second edition, which were only available as images. I thank my former PhD students for generating some excellent data, some of which is used in a number of figures, the captions of which include the individual acknowledgement.
I have gained inspiration in cement chemistry from a number of people over the past 40 years: in addition to Hal Taylor, the most notable are Dr GW Groves, Prof CM Dobson, Prof HM Jennings, Prof RJ Kirkpatrick, Prof JF Young, Dr EM Gartner, Dr CR Wilding, Prof JG Cabrera, Dr DD Double, Dr SA Rodger, and Prof JH Sharp.

Ian G Richardson
Leeds
March 2025

About the authors

Harry FW Taylor received a PhD in 1947 for work on the physical chemistry of DNA (under JM Gulland and DO Jordan). This was followed by a Research Fellowship at Birkbeck College (1948–1953, under JD Bernal and JW Jeffery) on the hydrothermal chemistry of silicates that led to his lifelong research interest in the chemistry of cement. His early work laid the foundations for our understanding of the nanostructure of C–S–H, the principal product formed when cement is mixed with water, and the one mainly responsible for its hardening. Subsequent studies took him into many additional aspects of the chemistry and materials science of cement and concrete. He was Professor of Inorganic Chemistry at the University of Aberdeen from 1965 until his retirement in 1983 and was a Visiting Professor at Imperial College London (1989–1994) and at the University of Leeds (2000–2002). His work was recognised by Fellowships and by many other honours and awards.

Ian G Richardson received a DPhil from the University of Oxford in 1991 under GW Groves and was subsequently his assistant. He moved to the University of Leeds in 1995 where he is Professor of Civil Engineering Materials. He is a materials scientist whose main research interests concern the microstructure, chemistry and properties of cementitious materials, and the crystal chemistry of calcium silicate hydrates, and various oxides, hydroxides and carbonates. He is perhaps best known for his work on the composition, morphology and nanostructure of the C–(A–)S–H in cements that contain a wide range of supplementary cementitious materials. He has given numerous invited contributions at conferences or congresses and is a Fellow of the Institute of Materials, Minerals & Mining.

The authors in 1996

This page intentionally left blank

Ian G Richardson and HFW Taylor
ISBN 978-1-83549-777-7
https://doi.org/10.1108/978-1-83549-776-020253001

Chapter 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 it may be replaced partly or wholly 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 % SiO_2, 5 % Al_2O_3, 3 % Fe_2O_3 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 (Ca_3SiO_5) 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 (Ca_2SiO_4) 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 ($Ca_3Al_2O_6$), 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 (Ca_2AlFeO_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

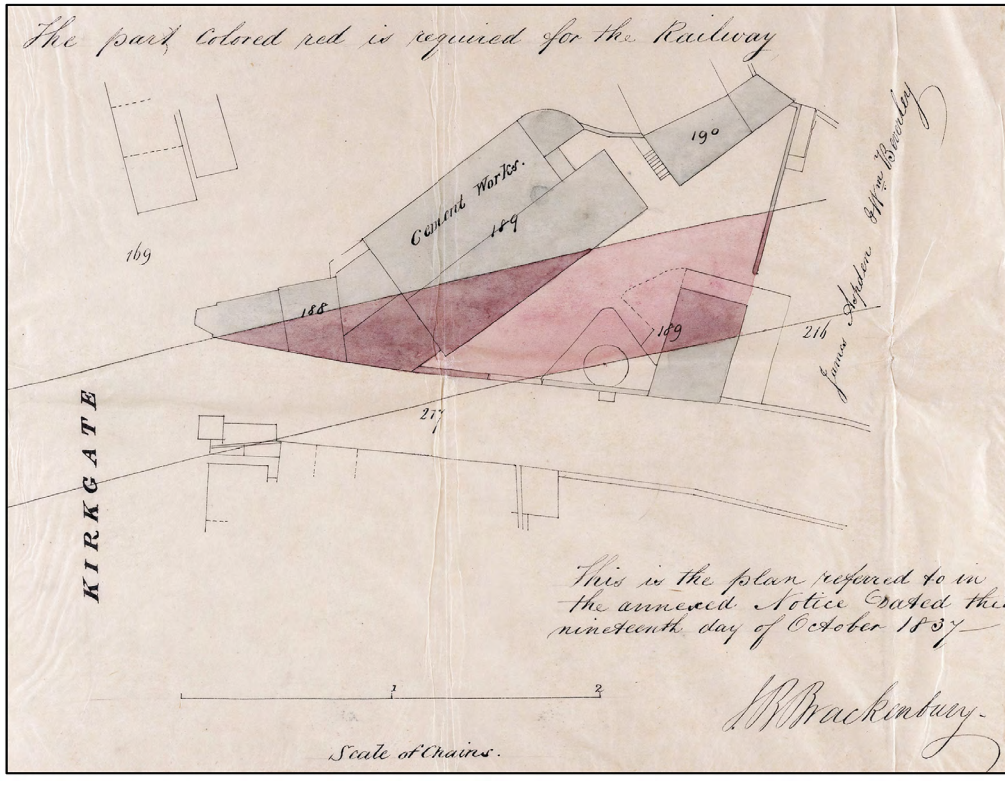
differences in composition or other characteristics, but in general is high initially and low or very low at later ages.

1.1.2 The invention of Portland cement

Portland cement has been central to the development of the modern world, with billions of tonnes now used annually (CEMBUREAU, 2018; US Geological Survey, 2019). It is perhaps surprising therefore that its early history is shrouded in mystery, and that there is no consensus about the identity of the inventor. While Joseph Aspdin, a bricklayer from Hunslet, Leeds, UK was granted a patent in 1824 for a material that he called Portland cement (Aspdin, 1824), conclusions differ considerably on how similar Aspdin's material would have been to the Portland cement that is in use today. For example, Blezard (1998) believed that Joseph had produced '*Nothing more than a hydraulic lime*', whereas Skempton (1962) stated that '*The truth would seem to be that the "breakthrough"* [of clinkering] *had been made by 1843 at the latest, and more probably a good deal earlier by the elder Aspdin* [i.e. by Joseph rather than his son William].' Microstructural characterisation of a sample of render from a former public house that is listed as '*…the only surviving example of a building covered with Joseph Aspdin's patent Portland cement*' (The Wakefield Arms: Historic England, 1992) combined with historical research has shown that the render, which was dated with high confidence to 1840 or early 1841, was certainly made using a Portland cement because it contained a lot of relicts of alite (Richardson and Zhu, 2022) and so Skempton was correct. The common belief that Joseph used a lime kiln is due to the vagueness of the description of his process in the patent (including the description of the kiln as being '*similar to a lime kiln*'), and also perhaps because of the regular publication of a painting that purports to depict his first cement works in Wakefield (e.g. in Anon, 1999; Beadle, 1977; Blezard, 1998; Stanley, 1979; Trout, 2017). Regarding the latter, it is most unlikely that the picture is genuinely of the Wakefield cement works. This is because it shows two lime kilns that are surrounded by trees and open ground, whereas extant plans of the works show a compound with buildings, a perimeter wall and one kiln, as shown in Figure 1.1(a) (WYAS JG001578, 1837).

The cement works shown in Figure 1.1(a) will be referred to as Aspdin Works 1. If the painting was really commissioned by the Aspdin family as claimed (e.g. by Stanley and Bond, 1999), then it is possible that it was part of a deliberate attempt to mislead competitors (Bogue, 1947; Davis, 1924; Steinour, 1960). Bogue (1947), for example, speculated '*…on the possibility that Aspdin may not have revealed in his patent certain features of his operation, and that he may have used much higher temperatures than are indicated.*' Halstead (1961) noted that a glass works existed in Hunslet when Joseph Aspdin lived there, and that '*a glass kiln would be more likely to reach the temperatures required for successful burning of Portland cement than would the lime-burning kilns used by his competitors*'. The glass works in Hunslet consisted of two parts: one for making crown glass and the other for flint glass. The works were owned by two brothers, John and Joshua Bower (and their partners). While referred to as a carpenter/joiner in early documents, John Bower had been a manufacturer of sulfuric and nitric acids at a site on Jack Lane in Hunslet since at least 1795 (WYAS Wakefield Deed 1795/DR/548/575; WYAS Calderdale WYC:1089/226), and he was as a consequence often described as an '*Oil of Vitriol and Aqua Fortis Maker*' (e.g. WYAS Wakefield Deeds 1795/DR/548/575 and 1814/GC/318/355) or chemist (e.g. in a newspaper announcement of his eldest daughter's marriage; *Leeds Mercury*, 1813). Abutting this site on the south were houses built by Joseph Aspdin's father, Thomas, who was a bricklayer, and who had been John Bower's neighbour since at least 1792 (WYAS Wakefield Deeds 1792/DH/716/925, 1792/DH/717/927, 1794/DO/51/67). These houses – which are referred to as '*Aspdin Row*' on the 1850 Town Plan of Leeds (Ordnance Survey, 1847) – were left by Thomas to his wife Mary (and on her death, to their

Figure 1.1(a) Plan of the world's first dedicated Portland cement works at Kirkgate Wakefield, West Yorkshire, England (reproduced by permission of WYAS, Wakefield: JG001578/1837 plan)



It was drawn to show the part of the cement works that was required for the new railway. The text states that the plan was referred to in a '*Notice Dated this nineteenth day of October 1837*'. It is based on the 1835 survey plan for the Manchester and Leeds Railway (WYAS QE20/1/1835/10). The book of reference that accompanies the survey plan indicates that plots 188, 189 and 190 were all owned by James and Rachel Strafford, which they inherited in 1832 from their father, George Strafford snr. (Exchequer Court of York Wills, 1832), who was a timber merchant (e.g. WYAS Wakefield Deed 1811/FP/84/82) and builder (e.g. WYAS Wakefield Deeds 1811/FP/52/56 and 1831/LD/364/256). Plots 189 and 190 were leased by Joseph Aspdin's eldest son, James, and their partner William Beverley, who also owned plot 216 (as indicated on the plan). Plot 216 consisted of '*Cement Pits and Garden*' and plot 189 consisted of a '*Cement Manufactory, Engine, Engine-house, and Burning-kiln*'. All of the buildings on the plan that are shaded grey are present on Walker's Wakefield town plan of 1823 (WYAS C509) and so were part of George Strafford's '*Sawing Mill*' with '*Engine House*' (WYAS Wakefield Deeds 1814/FX/447/518 and 1816/GK/325/340); the unshaded parts constitute the '*Burning-kiln*' that was built after 1823. The diameter of the circle (i.e. the chimney of the kiln) is about 14' $\approx$ 4·3 m.

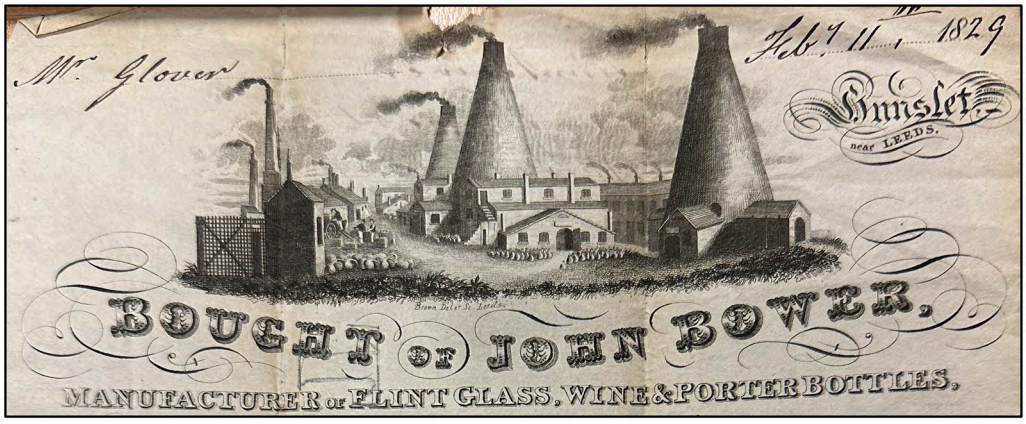
children), and John Bower was one of three witnesses to the will, which is dated 14 August 1800 (Exchequer Court of York Wills, 1802). Thomas Aspdin and his five sons were all bricklayers, and so it seems entirely plausible that they may have been involved in the construction of properties owned by their close neighbours John and Joshua Bower (including the furnaces of the glass

works), and that John may have supported Joseph with his experiments to develop a new cement. It is notable that the diameter of the '*Burning-kiln*' on Figure 1.1(a) is about the same as John Bower's first glass house (WYAS Leeds WYL160/14/113 and 114; probably his first), and it is also consistent with the maximum diameter of the bottle-shaped cement kilns in 19th century England (Butler, 1913; Eckel, 1905). It is relevant to note that John and Joshua Bower (and partners) were manufacturing glass in Hunslet some time earlier than November 1805 (WYAS Wakefield Deed 1805/EX/82/117) and that Joseph's younger son, William, claimed that his father had '*first introduced*' his cement in 1813 (Aspdin, 1848).

The compulsory purchase of Aspdin Works 1 by the Manchester and Leeds Railway Company in 1839 (WYAS Wakefield QE21/49) resulted in the construction of Aspdin Works 2 only a short distance from Works 1. Works 2 is present on a scale plan of Wakefield Kirkgate Railway Station that was prepared in March 1851 (National Archives, 1851). Richardson and Zhu (2022) and Richardson *et al*. (2024) showed that the diameter of the base of the kiln of Works 2 is $> 30'$ (or $> 9{\cdot}1$ m), which is much larger than the kiln of Works 1 (Figure 1.1(a)). Comparison of the contemporary images of Aspdin Works 2 that were drawn by Kilby (1843) and Tait (1845) with Figure 1.1(b) reveals that it is very similar in appearance to the cones and associated buidings of John Bower's glass houses in Hunslet in 1829. The cement in the render of the Wakefield Arms public house mentioned above would have been produced at Aspdin Works 2.

Little appears to be known about Joseph Aspdin's education, but it is perhaps significant that another of the witnesses to his father's will was John Ryley (1747–1815) who was a schoolmaster (WYAS Wakefield Deeds 1811/FO/58/77, 1814/FX/487/560, 1814/GA/373/455). He was highly

Figure 1.1(b) Billhead (engraved) showing John Bower's flint glass works in Hunslet, Leeds, dated 11 February 1829 (reproduced by permission of WYAS, Leeds: WYL33/A/33)



The diameter at the base of the glasshouse cone that is at the centre of the image is 49′ (14·9 m) (measured using the scale bar on the Ordnance Survey (1850) Town plan of Leeds sheet 22, surveyed in 1847). The appearance of the cone and adjacent buildings is strikingly similar to contemporary images of Aspdin Works 2 drawn by Kilby (1843) and Tait (1845).

regarded as a teacher of mathematics in Leeds (Nichols *et al*., 1818), author of *The Leeds Guide* (Ryley, 1806) and the first editor of *The Leeds Correspondent*. While a Master at the charity school in Leeds from 1789, he also provided '*private tuition at the residence of different gentlemen in the town, or by sets of pupils who attended twice or thrice in each week at his own house, either early in the morning, at the hour of noon, or in the evening*' (Nichols *et al.*, 1818). It is plausible that John Ryley taught the children of Thomas Aspdin, including his eldest son, Joseph, who would have been 11 years old in 1789. Despite the assignment by some (e.g. Barfoot, 1974) of low social status to the occupation of bricklayer, and the modest average annual wage of bricklayers in Leeds in the early 19th century (Statistical Committee of the Town Council, 1840), it is quite possible that Thomas could afford to engage John Ryley as a tutor for his children: he left his wife 12 houses when he died in 1800 and he had at least one very wealthy relative, his brother-in-law Obadiah Willans (1745–1833), cloth manufacturer, who bequeathed an annuity to his sister (i.e. Joseph Aspdin's mother) in his 1831 will (Exchequer Court of York Wills, 1834). The houses would have provided Thomas with additional income from rent payments. Interestingly, one of Mary Aspdin's tenants in 1823/4 was John Kilner (WYAS Leeds LO/HU/5(1823–27)), the progenitor of the company where the famous Kilner® jar was invented. It is highly likely that he learned to make glass whilst working for John Bower because of the location of his abode, and the fact that baptism records show that all four of his sons were born in Hunslet and that his occupation is given as labourer for the eldest (Caleb, born Jan. 1818) but glass maker for the other three (George, born 11 Dec. 1823; William, born 20 Jan. 1826; John, born 25 Jan. 1828).

1.1.3 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 CEM I 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 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– for example, to 0·6% equivalent Na_2O ($Na_2O + 0{\cdot}66\ K_2O$). Other upper limits of composition widely used in specifications relate to matter insoluble in dilute

* 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. α-Al_2O_3) are never used for components.

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 – for example, finer grinding or better mixing of the raw materials. The alite contents of Portland cements have increased steadily over the time that they have been produced, and many cements that would be considered ordinary today would have been described as rapid-hardening only a few decades ago. In the ASTM specifications, rapid-hardening Portland cements are called high early strength or Type III cements. For both ordinary and rapid-hardening cements, both lower and upper limits may be imposed on strengths at 28 days, upper limits being a safeguard against poor durability resulting from the use of inadequate cement contents in concrete.

Destructive expansion from reaction with sulfates can occur not only if the latter are present in excessive proportion in the cement, but also from attack on concrete by sulfate solutions. The reaction involves the Al_2O_3-containing phases in the hardened cement; in sulfate-resisting Portland cements its effects are reduced by decreasing the proportion of the aluminate phase, sometimes to zero. This is achieved by decreasing the ratio of Al_2O_3 to Fe_2O_3 in the raw materials.

White Portland cements are made by increasing the ratio of Al_2O_3 to Fe_2O_3, and thus represent the opposite extreme in composition to sulfate-resisting Portland cements. The normal, dark colour of Portland cement is due to the ferrite, formation of which in a white cement must thus be avoided. It is impracticable to employ raw materials that are completely free from Fe_2O_3 and other components, such as Mn_2O_3, that contribute to the colour. The effects of these components are therefore usually minimised by producing the clinker under slightly reducing conditions and by rapid quenching. In addition to alite, belite and aluminate, some glass may be formed.

The reaction of Portland cement with water is exothermic, and while this can be an advantage under some conditions because it accelerates hardening, it is a disadvantage under others, such as in the construction of large dams or in the lining of oil wells, when a cement slurry has to be pumped over a large distance under pressure and sometimes at a high temperature. Slower heat evolution can be achieved by coarser grinding, and decreased total heat evolution by lowering the contents of alite and aluminate. The ASTM specifications include definitions of a Type II or 'moderate heat of hydration' cement, and a more extreme Type IV or 'low heat' cement. The Type II cement is also suitable for conditions exposed to moderate sulfate attack and is widely used in general construction work. Heat evolution can also be decreased by partially replacing the cement by fly ash (pulverised fuel ash; PFA) or other materials, and this is a widely used solution.

1.1.4 Cement chemical nomenclature and other abbreviations

Chemical formulae in cement chemistry are often expressed as sums of oxides; thus tricalcium silicate, Ca_3SiO_5, can be written as $3CaO{\cdot}SiO_2$. This does not imply that the constituent oxides have any separate existence within the structure. It is usual to abbreviate the formulae of the commoner oxides to single letters, such as C for CaO or S for SiO_2, Ca_3SiO_5 thus becoming C_3S. This system is often combined with orthodox chemical notation within a chemical equation, for example

$$3CaO + SiO_2 \rightarrow C_3S \tag{1.1}$$

or even within a single formula, as in $C_{11}A_7{\cdot}CaF_2$ for $Ca_{12}Al_{14}O_{32}F_2$. The abbreviations most widely used are as follows.

$C = CaO$	$S = SiO_2$	$A = Al_2O_3$	$F = Fe_2O_3$
$M = MgO$	$K = K_2O$	$\overline{S} = SO_3$	$N = Na_2O$
$T = TiO_2$	$P = P_2O_5$	$H = H_2O$	$\overline{C} = CO_2$

The formulae of the simple oxide phases (e.g. CaO) are usually written in full. Other abbreviations and units used in this book are as follows.

1.1.4.1 Techniques

BEI = backscattered electron imaging; BSE = backscattered electron; DTA = differential thermal analysis; EPMA = electron probe microanalysis; ESCA = electron spectroscopy for chemical analysis; GLC = gas–liquid chromatography; GPC = gel permeation chromatography; IR = infrared. MIP = mercury intrusion porosimetry; NMR = nuclear magnetic resonance; QXDA = quantitative X-ray diffraction analysis; SEM = scanning electron microscop(e,y); STEM = scanning transmission electron microscop(e,y); TEM = transmission electron microscop(e,y); TG = thermogravimetry; TMS = trimethylsilyl(ation); XPS = X-ray photoelectron spectroscopy; XRD = X-ray diffraction; XRF = X-ray fluorescence.

1.1.4.2 Materials

C–S–H = poorly crystalline or amorphous calcium silicate hydrate of unspecified composition; GGBS = ground granulated blast-furnace slag; HCP = hardened cement paste; MK = metakaolin; PFA = pulverised fuel ash (flyash).

1.1.4.3 Properties or reactions

AR = alumina ratio (alumina modulus); C_x = analytical (total) concentration of x, irrespective of species; LSF = lime saturation factor; Na_2O_e = equivalent Na_2O (mass % $Na_2O + 0{\cdot}66\,K_2O$); RH = relative humidity; SR = silica ratio (silica modulus); $[x]$ = concentration of species x; $\{x\}$ = activity of species x; (+)2V, (–)2V, optic sign and optic axial angle.

1.1.4.4 Pressure units

$1\,MPa = 1\,N\,mm^{-2} = 10\,bar = 9{\cdot}87\,atm = 7500\,torr = 145{\cdot}0\,lb\,in^{-2} = 10{\cdot}198\,kg\,cm^{-2}$.

1.2. Alite

1.2.1 Polymorphism and crystal structure

On being heated, pure C_3S undergoes a series of reversible phase transitions, which have been detected by a combination of DTA, high-temperature XRD and high-temperature light microscopy (Bigaré *et al*., 1967; Maki, 1979, 1986, 1994; Maki and Chromý, 1978a, 1978b; Maki and Kato, 1982; Guinier and Regourd, 1969; Regourd, 1967; Regourd and Guinier, 1976; Yamaguchi and Takagi, 1969).

$$T_1 \overset{620\,^\circ C}{\rightleftarrows} T_2 \overset{920\,^\circ C}{\rightleftarrows} T_3 \overset{980\,^\circ C}{\rightleftarrows} M_1 \overset{990\,^\circ C}{\rightleftarrows} M_2 \overset{1060\,^\circ C}{\rightleftarrows} M_3 \overset{1070\,^\circ C}{\rightleftarrows} R$$

where T = triclinic; M = monoclinic; R = rhombohedral.

The pure compound, when cooled to room temperature, is thus T_1. In production clinkers, due to the incorporation of substituent ions, the form present at room temperature normally approximates to M_1 or M_3 or a mixture of these; rarely, T_2 is found (Maki, 1979, 1986, 1994; Maki and Chromý, 1978a, 1978b; Maki and Kato, 1982; Timashev, 1980). There has been some uncertainty as to the number and nomenclature of these polymorphs; reported M_{1b} and M_{2b} forms appear to be identical with M_3, leaving reported M_{1a} and M_{2a} forms to be called simply M_1 and M_2, respectively (Maki, 1986; Maki and Kato, 1982).

Jeffery (1952) made the first determination of the crystal structure. He showed that the forms now known as R, T_1 and M_3 had closely similar structures, and determined the approximate or pseudostructure common to all three; it was built from Ca^{2+}, SiO_4^{4-} and O^{2-} ions, the last being bonded only to six Ca^{2+} ions, as in CaO. Later, more exact determinations were reported for T_1 (Golovastikov *et al*., 1975), M_3 stabilised by Mg^{2+} (Nishi *et al.*, 1985), M_3 with increased disorder isolated from a works clinker (Mumme, 1995), R at 1200 °C (Nishi and Takéuchi, 1984) and R stabilised with Sr^{2+} (Il'inets *et al.*, 1985). Figure 1.2 shows the structure of the R form. The known structures are all closely similar as regards the positions of the Ca^{2+} and O^{2-} ions and of the Si atoms, but differ markedly in the orientations of the SiO_4^{4-} tetrahedra, which show varying degrees of disorder. Table 1.1 gives crystal data for the C_3S polymorphs that have been obtained using both single-crystal and powder methods. The unit cells of the T_1, M_3 and R forms are superficially somewhat different, but all are geometrically related; transformation matrices have been given (Hudson and Groves, 1982; Ilyinets *et al.*, 1986), and structural studies reviewed in detail by Dunstetter *et al.* (2006) who proposed a unified analysis of T_1, M_1, M_3 and R polymorphs.

The structural differences between the polymorphs affect the coordination of the Ca^{2+} ions and the O atoms of the SiO_4^{4-} tetrahedra, with the coordination of a given Ca site sometimes varying because of the orientational disorder of the SiO_4^{4-} tetrahedra. The number of crystallographically distinct Ca sites varies between polymorphs, with 3, 6 and 29 in the asymmetric units for the R (Il'inets *et al*., 1985; Sr stabilised), M_3 (Mumme, 1995), and T_1 (Golovastikov *et al.*, 1975) polymorphs, respectively. In the unit cell of the M_3 polymorph, all 18 of the Ca sites are in six-fold coordination (Mumme, 1995), and so the mean coordination number (CN^{Ca}) is of course 6·00. In the T_1 polymorph (Golovastikov *et al.*, 1975), 42 of the 54 Ca sites are coordinated to six O, with the remaining 12 Ca coordinated to seven, and so $CN^{Ca} = 6{\cdot}22$. In the R polymorph (Il'inets *et al.*, 1985; Sr stabilised), 18 of the 27 Ca sites are coordinated to six O, with the remaining nine Ca coordinated to seven, and so $CN^{Ca} = 6{\cdot}33$. In relation to reactivity towards water, the coordination of the oxygen atoms is possibly more important than that of Ca. In all three of these structures, the proportion of O that are O^{2-} ions bonded only to six Ca^{2+} ions is 20 % (see Table 4.4 in Chapter 4), but the mean oxygen coordination number (CN^{O}) increases with that of calcium (CN^{Ca}), with $CN^{O} = 4{\cdot}4$, 4·53 and 4·6 for the M_3, T_1 and R polymorphs, respectively, and thus $\overline{CN^{O}} = 0{\cdot}6039\left(\overline{CN^{Ca}}\right) + 0{\cdot}7759$.

The silicate tetrahedra do not share O atoms, and so are monomers, or Q^0 using the Q^n notation (see §5.3.1.7). There is some variation in the average Si–O distances of the silicate tetrahedra, with those for the R (Il'inets *et al*., 1985) and M_3 (Mumme, 1995) polymorphs being rather short when compared with the expected values: i.e. d(Si–O) = 1·607 Å (R) and 1·595 Å (M_3) compared with 1·639 Å from Equation 5.32 in Chapter 5, or with the values calculated using the equations given in Baur (1978) and Brown and Gibbs (1969). The value for the T_1 polymorph (1·633 Å; Golovastikov *et al.*, 1975) is close to the expected value. While Jeffery (1950, 1952) used arguments about the