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The History of Calcareous Cements

Edwin A.R. Trout

'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 these very differences have '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'. As these contain 'compounds of lime as their principal constituents … the term 'cements' in this restricted sense then becomes equivalent to 'calcareous cements''.

That, in excerpt, is how Cecil H. Desch described the scope of the first edition of this book, written jointly with Sir Frederick Lea in 1935, but with the opening pages drawn verbatim from his earlier book of 1911.[1] After the passage of more than a century, this expresses the topic succinctly enough, and excludes from present consideration—which concentrates on calcareous cements, a term first published by Higgins[2] in 1780—a multitude of organic, bitumen- or oil-based materials with which the development of building materials has long been entwined.

1.1 PREHISTORY

Lime occurs in many natural forms and for several millennia different chalks and limestones have been burnt to make a range of building materials that harness their cementing qualities. In modern usage, however, we should distinguish between pure and hydraulic 'limes' and gypsum-based plasters and the stronger, harder 'cements' that contain a greater proportion of siliceous materials. But until the time of the Industrial Revolution, such a distinction would not have been made.

Numerous authors have mined prehistory for precedents in the use of cementitious binders. Their inclusion depends upon an accommodating definition of 'cement', but the following are ancient examples of the practical exploitation of cementitious reactions: the religious structure at Gobekli Tepe in Anatolia, erected 12,000–10,000 BCE, in which pillars are set in a terrazzo floor of burnt limestone and clay; and the city of Catal Hayuk, 9000 BCE, where gypsum plaster was used as the base for decorative frescos. Then at Yiftah'el in Galilee, a double-layered concrete floor of 30–60 mm was discovered in 1985 that dated from 7000 BCE. The binder was quicklime, made from burning limestone in wood-fired kilns at temperatures of 850°C–900°C, and mixed with stone and water: evidence of an advanced production process from quarrying and crushing to kiln construction and temperature management. Chemical analysis indicated a composition of calcium carbonate and a small quantity of silica, and physical test results from cube samples returned strengths of 34 MPa in the lower layer and 45 MPa for the upper.[3]

A 250 mm thick floor at Lepenski Vir, in Serbia, was cited for many years as the earliest known concrete.[4] There the sand and gravel was bound with a red limestone calcined to make quicklime. Quicklime was also used as stucco for the protection of walls in Minoan Crete, around 2000 BCE.[5]

Production of cementitious materials in ancient Egypt commenced perhaps as early as the fourth millennium BCE, when mortar was used as bedding for masonry. Limestone was abundant in the Nile valley, but the fuel to achieve temperatures of 850°C–1000°C required to burn it, was not. So largely for that reason the ancient Egyptians used impure gypsum ($CaSO_4$), which formed a hemi-hydrate when burned at the lower temperatures that could be achieved easily with small fires at about 170°C. The earliest Egyptian cements then were essentially gypsum plasters. Plasters and cements based upon gypsum would have had adequate strength, but, because they would have been soluble in water, limited durability. In the arid climate of Egypt, however, this was not a disadvantage in practice and cements of this kind were used successfully until the Roman period.[6]

According to the controversial contention advanced by Dr. Joseph Davidovits in the 1980s, one possible application of the Egyptian mastery of low-heat cements was the casting in situ of a 'geopolymeric limestone concrete'[7] for the construction of the Great Pyramids at Giza, rather than the placing of quarried natural stone. Such technology would depend upon a catalyst triggering the inherent chemistry to form an artificial stone, much like the Egyptian development of synthetic sandstone known as faience. Whatever the final conclusion of that debate, and whatever binders they used, it seems certain that the Egyptians prepared and made use of concrete by at least 1950 BCE, when the production process was illustrated on a panel in Thebes, as reproduced in Fig. 1.1.[8]

Lea's Chemistry of Cement and Concrete. https://doi.org/10.1016/B978-0-08-100773-0.00001-0

FIG. 1.1 Panel from Thebes.

To the east of Egypt, beyond Sinai, lay the desert kingdom of Nabataea—in the arid region to the south of Judea, around the city of Petra in modern Jordan. Here the Nabataeans developed a system of subterranean cisterns to capture and store water, which they proofed with a cementitious lining. Ancient fire pits have been discovered in modern times that contain evidence of limestone calcination, suggesting a conscious effort to produce a calcareous mortar.[9]

1.2 THE CLASSICAL WORLD

It is to the Greeks of their golden age, however, that we owe a technological leap forward. The first use of a natural pozzolan appears to date from about 500 BCE. Lime mortars used in the southern Aegean were enhanced by the inclusion of volcanic tuff from the island of Thera (now known as Santorini), to produce a material with greatly improved water resistances and durability. An ancient cistern in Kamiros on the island of Rhodes illustrates the successful use of this material, combining lime with 'Santorin earth' and fine sand in a ratio by volume of 6:2:1. Indeed Santorin earth has continued to be used in the modern world, in combination with Portland cement or lime. Of its use in major structures that in the Suez Canal is perhaps the best known example.[10]

As with much of their culture, the Romans borrowed heavily from the Greeks, and it is the use of volcanic ash that is perhaps most distinctive of Roman binders. Indeed the very word 'pozzolana' derives from the Roman place name, Puteoli—or Pozzuoli in Italian—in the district of Vesuvius, whence the ash was obtained.

> *There is a species of sand which naturally, possesses extraordinary qualities. It is found under Baiae 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.*[11]

The earliest major building thought to use pozzolana was the theatre at Pompeii, at the heart of this district, dating from 75 BCE.[12] Pozzolana was a red or purple volcanic tuff found in locations around the Bay of Naples and the name has since been extended to an entire class of materials that shares its mineralogical characteristics. One such is the Rhenish tuff known as 'trass' that was found originally on Rome's imperial border, yet continues to be used to the present day.

The use of pozzolana was advocated by a Roman writer, Marcus Vitruvius Pollio (known to us now simply as Vitruvius), whose *De Architectura* was written in 25 BCE. He expanded on the theme of cement and its use in construction, proposing alternative raw materials too and describing their use. If pozzolana were not available, Roman builders might add brick or tile dust to the lime to achieve similar effects: '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'.[13] There is evidence that such use occurred also in the Minoan civilisation in Crete and so may represent another borrowing from Greek practice.

Recent studies have replicated the Roman recipe, heating limestone to form quicklime, and adding water and volcanic ash in a ratio of three parts ash to one part lime. The mortar was then mixed with four-inch volcanic fragments to make concrete. Investigation by X-ray revealed clusters of Stratlingite crystals that act like micro fibres in counteracting crack formation by reinforcing the interfacial zones and enhancing durability.[14]

But it was not just in the combination of materials that the Romans excelled. Their methods and standards of workmanship also were rigorously applied. Pliny the Elder in his *Natural history* (CE c.78), when describing a concrete composed of

FIG. 1.2 The Pantheon, Rome.

quicklime, sand and silex, or flint, recommended that 'the floor and walls built of this material should all alike be beaten with iron bars'.[15] Indeed in the 18th century the Frenchman Rondelet examined Roman mortars and came to the conclusion that their excellence depended on the thoroughness of mixing and extensive ramming during placement. Certainly remaining Roman works often exhibit a remarkable degree of density in their material composition that such care in preparation would explain. Sophisticated structures such as the famous Pantheon (CE 128—Fig. 1.2) with its 43 m-diameter dome and the multi-level aqueduct at Pont du Gare (CE 150) bear testimony to the Roman achievement.

Roman practice evolved over the succeeding centuries of Republic and Empire, and its essence has been recorded by more than archaeological remains. Of all the varied output of Latin literature the *De Architectura* of Vitruvius, though its treatment of cement is not extensive, was to carry the flame of construction technology through the Dark Ages that followed the fall of Rome. A copy was retained in Charlemagne's scriptorum and was the source of many of the later mediaeval copies that have survived today.

1.3 THE MIDDLE AGES

The Roman legacy was variously maintained or swept aside in the realms that arose in western Europe during and after the Migration Period. In Britannia the 400-year-old Romano–British civilisation was succeeded by a Germanic Anglo-Saxon culture in which construction practices were overwhelmingly based on timber. Evidence of lime burning does exist—implied, for instance, by an 8th century mortar mill found in Northamptonshire[16]—but the quality of mortar is thought to have declined because of low kiln temperatures (and consequentially incomplete burning), the absence of pozzolanic additions, and poor mixing. As church builders turned to masonry in the century or so before the Conquest, and stone built castles were introduced by the Normans, the demand for mortar increased and by the 12th century quality had improved. What had almost become a lost art in the early mediaeval period experienced a revival in the high Middle Ages, manifested in better standards of burning, grinding and sieving. In a reflection of this improvement lime is mentioned by Bartholomew Anglicus in his encyclopaedic compendium of 1240, entitled *De Proprietatibus Rerun*. In it an entry reads: 'Lyme … is a stone brent; by medlynge thereof with sonde and water sement is made', though this middle English translation of the original Latin did not appear until 1397.[17] The commonly held confusion of the terms 'cement' and 'mortar' is anticipated here; 'sement' is used for mortar, as was generally the case in early usage, though 'mortar' had already appeared in English by 1290.[18]

Mediaeval mortar was made from non-hydraulic lime that weathered easily on exposure, but in major buildings such as castles and cathedrals, the elements were designed to act in compression and so the low bond strength of masonry mortar was of minor consequence. Beside jointing, lime mortar was also used for hearting—the mortar-bound rubble core of walls, filling the void between skins of dressed stone—as at Reading abbey, and for foundations, as at the 13th century Salisbury cathedral.

After the 14th century excellent mortar is found, the sand generally washed to remove fine particles dirt or clay, and by the 17th century pozzolanic trass (cited in documents of the day as 'tarras' or 'tarrice') was often added. In addition to experience gained in practice, the example of Rome must be acknowledged for much of the improvements gained in the early modern period. The Renaissance saw a revival in the understanding and appreciation of classical civilisation, across the spectrum of culture and scholarship, and where the architecture of the ancients was applauded, so the associated technology was sought.

A copy of *De Architectura* was rediscovered in 1414, by Poggio Barccioline at St Gallen abbey, and the first printed edition was published in 1486 by Fra Giovanni Sulpitius. A scholarly edition, complete with woodcut illustrations, was prepared in 1511 by the Franciscan monk, antiquary and member of the Freres du Pont, Fra Giovanni Giocondo,[19] and the text was translated successively into Italian (1520s), German (1528), French (1547), Spanish (1582) and eventually into English (1692).

Architects such as Alberti (1404–72), de l'Orme (1515–70) and above all, Palladio (1508–1580)—whose *I Quattro libri dell'Architettura* of 1570 had such influence on architecture in both Italy and England—all cited Vitruvius in their writing.

Likewise, in a book of more practical utility, Joseph Moxon of Wakefield (1627–91) quoted Vitruvius in the plain English of his *Mechanick Exercises, or the Doctrine of Handy Works*, 1685.[20] Trass, supplied from the Rhineland through the Netherlands to England, became an increasingly accepted addition to lime during the 17th century.

1.4 THE AUGUSTAN AGE

Trass was used in the 1660s for what was then the largest English engineering project to have been attempted: the mole at Tangier, constructed between 1663 and 1683, following the city's acquisition on Catherine of Braganza's marriage to Charles II. The project was directed by Sir Henry Shere. Shere was advised by, among others, Genoese engineers who recommended and supplied pozzolana from Italian sources. Anticipating future investigations, he experimented with a series of mortar formulations to determine the optimum mix for setting and hardening under water.

In England the restoration ushered in a new era of scientific experimentation and discovery, with parallels found in the Enlightenment of 18th century France and all across Europe, and though far from the forefront of endeavour, the improvement of binders and the search for hydraulic cements was not ignored. An early authority was Bernard Forest de Belidor whose *Science des ingenieurs* of 1729 touched on mortar, and was followed by the four-volume *Architecture hydraulique* in 1737–53. Although he promoted the use of trass, he also perpetuated the widely held error that the purer the limestone the better the lime, with marble the apogee and chalk the nadir. In his later work he proposed a method of placing foundations under water, as tried at the harbour of Toulon, using a mixture of 12 parts pozzolana or trass, 9 of quicklime and 6 of sand. After slaking the quicklime, the constituents were mixed with seawater, and a combination of pebbles and slag or cinders added. Having partially hardened the concrete was reworked and lowered into the sea in crates. This use of pozzolana at Toulon was the subject of a later study published in 1778 by Barthelemy-Fauja de Saint Fond.

Similar aims were attempted by George Semple in 1752, when reconstructing the foundations of Essex Bridge across the Liffey. Here he filled a cofferdam with 'small stones, grave, sharp clean sand and finely powdered lime, thrown in promiscuously so as to mix equally together'.[21] (In the usage of the day, 'promiscuously' simply meant, 'intimately mixed'.) But like Bellidor, he accepted that the best limestone yielded the best lime.

The late 17th century, and then the reign of Queen Anne, saw a considerable increase in the use of brickwork for domestic building, and an adaptation of earlier buildings to suit the classically inspired precepts of fashionable taste, with new wings, porticos and facades. Not only was lime mortar being used for hydraulic engineering, but for increasingly for bricklaying and as stucco, or render marked to look like dressed stone. Demand for the latter led to the development of a class of materials known as oil cements, which may be thought of now as an 'evolutionary dead end': In his Sir Frederick Lea Memorial Lecture, John Newman set out a list of patents, as reproduced in Table 1.1, that traces the ultimately doomed pursuit of such cements (Tables 1.2–1.3).

TABLE 1.1 Patents for Cements Granted in the 18th Century[a]

Date	Name	Medium	Possible Fillers
1737	Alexander Emerton	Pail and oil	Stone dust, powdered glass, sand
1765	Rev Dr. Daniel Wark	Oil	Stone dust, marble drift sand, clay, brick dust, brown sugar, lime, various calcareous earths
1772	Charles Rawlinson	Linseed oil	Whiting, sea-coal, brick dust, white and red lead
1773	John Liardet	Drying oil	Any absorbent matter, lead, sand, gravel
1776	John Liardet	Oil	Calcined and pulverised calcereous matter, white or red lead, sand, marble, mineral powder
1777	John Johnson	Oil	As above but with addition of serum of blood

[a]Listed by Newman.[17]

TABLE 1.2 Analyses and Computed Compound Composition of Cement[a]

		Analysis by % of Weight				Compound Composition		
Source	Date	CaO	SiO_2	Al_2O_3	Fe_2O_2	C_3S	C_2S	Total
English	1849–55	58.50	20.40	5.90	3.80	38	30	68
German	1865	59.00	24.10	7.30	2.80	4	66	70
English	1880	59.40	22.40	7.80	4.20	13	54	67
German	1880	60.80	22.10	5.90	3.00	36	35	71
English	1890	59.10	22.80	8.00	3.40	9	59	71
French	1890	60.70	23.20	7.20	2.80	18	53	71
German	1890	61.50	22.50	7.50	3.20	24	46	70
English	1905	60.20	22.30	7.10	4.10	22	47	69
American	1905	61.10	21.80	7.40	3.30	29	41	70
English	1925	62.30	21.50	7.00	2.80	39	32	71
English	1950	63.10	21.40	5.80	2.70	51	23	74
English	1960–3	64.77	21.60	5.65	2.57	51.6	23	74.6

[a]Selected figures abstracted from Halstead 1961/2.[6]

Nonetheless, though the medium was oil, the purpose to which these cements were put acted as a stimulant to the later Roman and Portland cements, as we shall see. The great leap forward in this period was the investigation into hydraulic lime conducted by John Smeaton in the 1750s.

1.5 JOHN SMEATON, 1756

Smeaton was the first in England to undertake a scientific investigation into why certain limes would set under water and what it was that moderated its rate of hardening. Commissioned to replace Rudyard's wooden lighthouse on the Eddystone Rocks, the second such structure there to have been destroyed by the elements, he commenced a series of experiments in 1756 to find a suitable masonry mortar that would withstand the frequent drenching of this storm swept location off the south west coast near Plymouth. It has been said of him that in doing so, 'the results he arrived at were very remarkable not only for their practical utility, but also as an illustration of the ease with which a very acute observer may stop short of the attainment of a great truth'.[22]

Contradicting the contemporary belief that the hardest stones yield the best limes—'Its acquisition of hardness under water did not depend upon the hardness of the stone; in as much as chalk lime appeared to be as good as that burnt from Plymouth marble'[23]—he discovered that the best raw material for a 'water lime' was, in fact, impure limestone. Those limes that did set underwater all contained a naturally occurring proportion of clay, varying between 6% and 20%: 'The fitness of lime for water-building depended on the amount and composition of clay impurity.' Smeaton tested 300 limestones and the best of these appeared to be Aberthaw Blue Lias, occurring on either side of the Bristol Channel and typically containing 86.2% calcium carbonate and 11.2% clay. Added to this he found that the Roman practice of combining pozzolana—in his case an unwanted consignment from Civita Veccia purchased from a merchant in Plymouth—gave the best results for his purposes, though he also considered trass and 'some ferruginous substance of a similar nature' as alternatives. He even tried burnt ironstone and forge scales. His preferred proportion of pozzolana to calcined lime was 50:50.[24]

FIG. 1.3 Smeaton's Eddystone lighthouse.

This hydraulic combination was used to seal the 1493 interlocking granite blocks with which the Eddystone Lighthouse—Fig. 1.3—was eventually completed in 1759, resisting the constant spray over the foundations. The construction was so successful that the lighthouse stood in situ until its replacement by a larger structure in 1882—and relocation to Plymouth Hoe, where it remains to this day—and Smeaton's hydraulic lime mixture was specified for government contracts until as late as 1867 when Portland cement was finally substituted during the extension of the Chatham Dockyard.[25]

Having searched for a lime that would set under water Smeaton didn't quite discover cement, but he did help point the way for others to follow, and his findings—which he finally published in 1791—directly influenced the subsequent development of both natural and artificial cements.

Until Smeaton's *Narrative* was published in 1791, however, other investigators remained unaware of his conclusions. Notable among these was 'Bry' (Bryan, sometimes rendered Brindley)[26] Higgins, whose *Experiments and observations made with the view of improving the art of composing and applying calcareous cements and of preparing quick-lime* was published in 1780, just months after obtaining a patent for hydraulic cement-based stucco. His experiments, and they were extensive, were to investigate the principles governing the 'induration' (or hardening) and strength of cements in order to produce a mortar that was better than the Roman equivalent. He prepared mixtures from various sources of lime and sand, recording their characteristics, and subjected the resulting specimens to a range of exposure conditions. The data thus obtained enabled Higgins to comment on the choice of constituents and the optimum proportions when mixed. He also examined the effects of organic admixtures such as ox blood and linseed oil, and additions including various types of ash. The specification he finally patented was for a mixture of quartzitic sand with a binder that combined equal quantities of bone ash with a finely ground lime that 'heats the most in slaking and which slakes the most when watered'.[27] Although Higgins appears to have been unaware of Smeaton, he did cite other researchers of the day—including a Monsieur Loriot whose *New discovery in the art of building* was published in 1774—and quoted from the classical source, Vitruvius.

Despite his experiments Higgins's patented stucco proved unstable in practice, and the output of other investigators, such as Perronet and Fourcroy de Ramecourt in France, remained ephemeral. Commercially successful cement finally came in 1796 with the patenting of 'Roman cement' by the Rev. James Parker.

1.6 JAMES PARKER'S DISCOVERY OF ROMAN CEMENT, 1796

In 1791, the year of Smeaton's eventual publication, Parker was the leaseholder of a plot of land on the riverside at Northfleet, and from 17 May, the patentee of a process of calcining chalk and limestone. In 1796, having been in business and Northfleet and Lambeth during the intervening years, he took out another patent for 'a certain cement or terras to be used in aquatic and other buildings and stucco work',[28] a material we would now describe as a natural cement. An account of Parker's discovery was published retrospectively, describing it as 'purely accidental'.

> *When on a visit to the Isle of Sheppey, he was strolling along under its high cliffs on the northern side and was struck with the singular uniformity of character of the stones upon the beach and which were also observable sticking in the cliffs here and there. On the beach, however, the accumulation of ages, they lay very thick. He took home with him two or three in his pocket and without any precise object in view, threw one onto the parlour fire from which in the course of the day it rolled out thoroughly calcined. In the evening he was pleased to recognise his old friend upon the hearth, and the result of some unpremeditated experiments with it has been the introduction to this country of a strong, durable and valuable cement.*[29]

Parker's patent specifies the reduction to powder of 'certain stones or argillaceous products called noddles of clay'.[30] These, known today as septaria, he described in turn as 'concretions of clay containing veins of calcareous matter …', traces of iron oxide giving the resulting cement a characteristically brown colour. Once ground the cement was mixed in proportions of two measures of water to five of powder, the mixture setting within 10–20 minutes, either in or out of water.

In March and April 1796, just prior to the grant of patent on 28 June, the eminent engineer Thomas Telford tested the new material and wrote to his client that he considered himself 'fully justified in recommending to the Directors to use Mr. Parker's Composition, in place of Dutch Tarras, in constructing of the Pier at Lochbay in Skye'.[31] Besides marine applications, Telford also proposed its use for cisterns, arches, flat roofs and, when mixed with lime, as stucco.

Bringing his new material to market, Parker named it 'Roman cement' in a promotional pamphlet headed *Roman cement, artificial terras and stucco*, presumably for the hydraulic qualities which enabled it to take the place of the pozzolanas currently available. Certainly the precedence of classical Rome was widely appreciated at the time, and previous investigations into cement production had cited the Romans' example, such as Loriot's *Cement and artificial stone: justly supposed to be that of the Greeks and Romans* in 1774, and de la Faye's *Recherche sur la preparation que les Romains donnoient a la chaux* in 1787. However, despite Telford's endorsement and the protection afforded by his patent, Parker found business slow and he soon sold his rights to Samuel Wyatt, who traded henceforth as Parker and Wyatt.

Septaria—the cement stones used as the raw material for Roman cement—were to be found around the British Isles, particularly in the Thames estuary at Sheppey and Harwich, and off the Yorkshire coast. When Parker's patent expired in 1810, a considerable industry built up in these and other locations, and Roman cement became the leading cement of the first half of the 19th century. The first new entrant was James Frost at Harwich in 1807—government contracts protecting him from prosecution for breach of patent—followed in 1810 by Messrs. Francis and White at Blackfriars, in 1811 by James Grellier at Sheerness and William Atkinson at Sandsend, Yorkshire, and by Samuel Shepherd at Faversham in 1813. Sundry other companies were established in Kent, Essex and along the Thames during the 1820s, as well as on the Humber, and in Derbyshire and Glasgow in the 1830s. Manufacture of Roman cement commenced in Somerset and Staffordshire in the 1840s.[32]

Mr. J. Mitchell of Sheerness Dockyard conducted a series of experiments on the various sources of Harwich and Sheppey septaria, the results of which were recorded by Pasley,[33] but perhaps the best known demonstration of the qualities of Roman cement was a test to destruction of an 'Experimental Brick Beam' erected for the Southampton Railway near its London terminus in Vauxhall. This beam, built of brickwork, had an unsupported span of 21 ft 4 in. between piers. Burdened with a suspended cradle loaded with pig iron, it bore nearly 11 t without deflection or cracks for almost 2 years. The *Civil Engineer and Architect's Journal* described it as 'a surprising proof of the strength of adhesion of Roman cement'.[34] Eventually, in February 1838, it was loaded as an experiment witnessed by the Council of the Institution of Civil Engineers and many Fellows of the Royal Society. It broke only when the suspended weight—illustrated in Fig. 1.4—reached about 30¼ t.

Parker was not the only pioneer at the turn of the century, however, and nor was the British industry alone in manufacturing cement. Developments in Britain had parallels in America and France too. In 1796 a French military engineer named Lesage discovered the hydraulic properties of pebbles on the beach at Boulogne-sur-Mer and commenced production, and across the Atlantic, in 1817, Canvas White found a natural cement rock in the state of New York. By 1818 natural cements derived from argillaceous magnesian limestone were being produced at Rosendale in the United States and were used initially for building the Erie Canal. An American industry developed and from an output of 300,000 barrels in its first decade, production rose to an annual peak of 9,868,179 barrels in 1899.[35] Likewise in Europe the manufacture of Roman cement was gradually taken up during the century, especially in the German states, Switzerland and the diverse provinces of the Austro-Hungarian Empire, as indicated in Fig. 1.5.

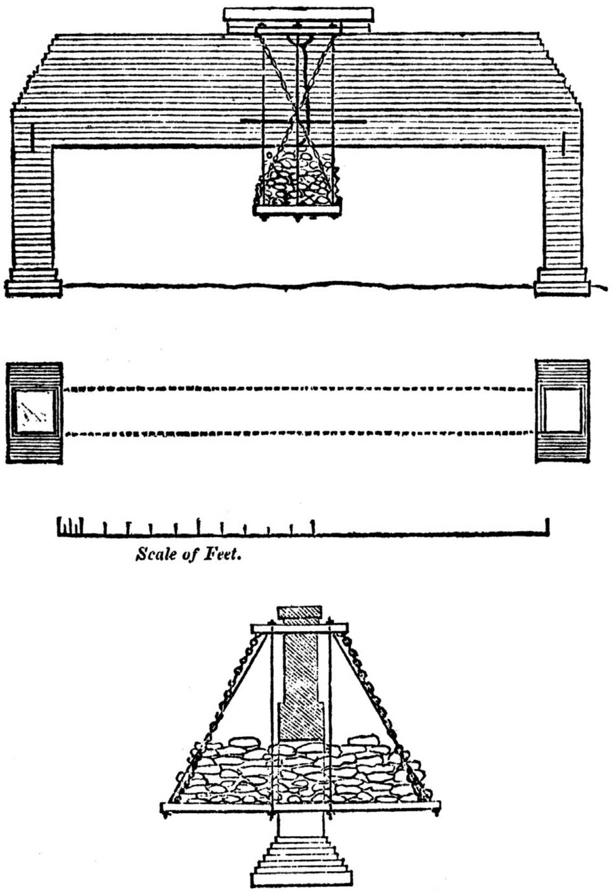

FIG. 1.4 Experimental brick beam erected in front of Messrs. Francis and Sons Roman cement manufactory, Nine Elms, near Vauxhall Bridge. *(From the* Civil Engineer and Architect's Journal*; Mar. 1838;1:135.)*

1.7 FRENCH INVESTIGATION, 1805–13

As Enlightenment gave way to Revolution in France, the Napoleonic Empire developed a legacy of scholarship and practical experiment, given greater prominence by the exigencies of war and the requirements of naval and military engineering. Among the most prominent investigators were the following[36]:

1787. *Jean Antoine Chaptal*, *chemist*: experimented in making artificial pozzolana by calcining clays and schists found in Languedoc, and tested at the harbour of Cette.

1805. *M. Gratien le Pere, Engineer-in-chief at Cherbourg*: experimented with calcined shale, especially of Haineville, to replace the wartime shortage of pozzolana needed for works at the port of Cherbourg.

1807. *J.B. Vitalis, Professor of Chemistry at Rouen*: analysed hydraulic limestone near Rouen, discounting manganese and proposing clay as the source of hydraulicity. Also experimented on local earths to convert to artificial pozzolana and tested in the Seine.

1808. *M. Daudin, engineer of roads and bridges, engaged on the Canal du Midi*: investigated the properties of natural and artificial pozzolanas, and proposed the use of calcined siliceous iron ore as a substitute for pozzolana (silica 50%, iron oxide 31%, alumina 16% and manganese oxide 3%).

1807. *M. Fleuret, Professor of Architecture at the Royal Military College at Paris*: used tile dust or iron slag to supplement the lime that he mixed with sand or ground stone when manufacturing artificial stone at his own factory.

1812. *Jean Rondelet, architect*: drawing heavily on Vitruvius, he described good practice in making and using mortar, and offered the results of experiments into crushing strength and adhesion.

1813. *Collet Descotils, Professor of Chemistry at the School of Mines*: analysed Senoches limestone and found it contained silica that, after calcinations, proved to be soluble in acids. He attributed its hydraulic properties to this combination of soluble silica with lime.

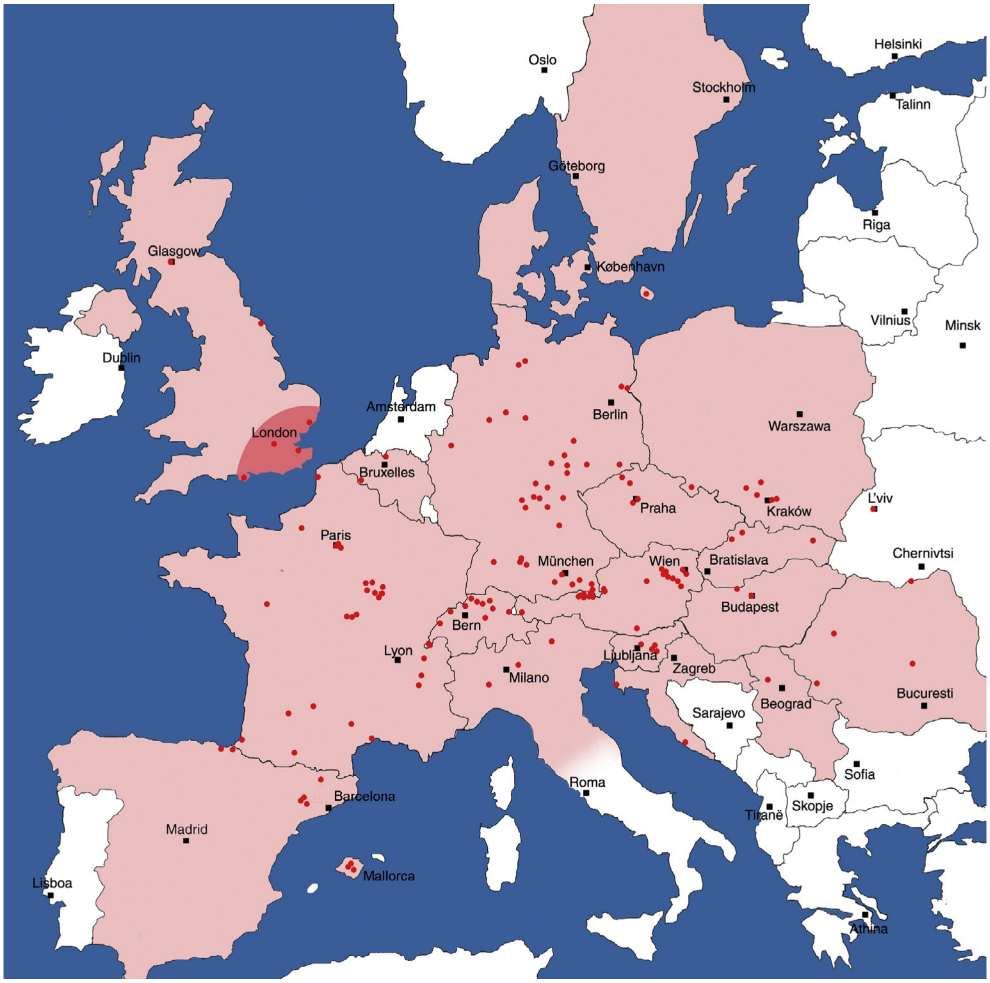

FIG. 1.5 Location of the principal Roman cement plants in 19th century Europe (Weber[128]).

This period of experimentation culminated in the work of Louis Joseph Vicat, the only one of his contemporaries whose name is readily recalled today, continuing as it does in that of test apparatus and a modern manufacturing company.

1.8 LOUIS JOSEPH VICAT, 1812–18

Vicat trained as a civil engineer and in 1812, just a few years after graduating from the Ecole des Ponts et Chaussees, was commissioned to build a bridge over the Dordogne at Souillac. The challenges of this site, however, acted as a catalyst for his career defining experimentation with suitable materials with which to fulfil the project, and which he wrote up and published in 1818 as *Recherches experimentales sur les chaux de construction, les beton et les mortiers ordinaries*, illustrated in Fig. 1.6.

This work tabulated the findings of his tests on 15 sources of lime, and later he set out the first systematic classification of limes and hydraulic limes. Drawing on the data—and referring to the classical authors Vitruvius and Pliny, and the British investigators Smeaton and Parker—he proposed a theory of the setting and hardening of lime mortars in water, even coining the term 'hydraulic' (or 'hydraulique' in French).[37] He applied his conclusions to the invention of an artificial hydraulic lime, a calcined mix of powdered limestone and slaked lime with clay. He experimented with the grinding process and firing temperatures, and established the optimum proportions of constituent materials. His specification was for limestone (43 m^3), slaked lime (34.55 m^3) and clay (5.76 m^3), ground in a wet mill and burnt for six days with 150 m^3 of wood. Having reported his preliminary findings in 1817, he demonstrated his hydraulic lime a year later to the French Academy of Sciences, which approved its use unhindered by patents. His suggestion that hydraulic limes or cements could be produced artificially by firing blends of chalk (or limestone) and clay was taken up by others—including Maurice St Leger at Meudon near Paris, and

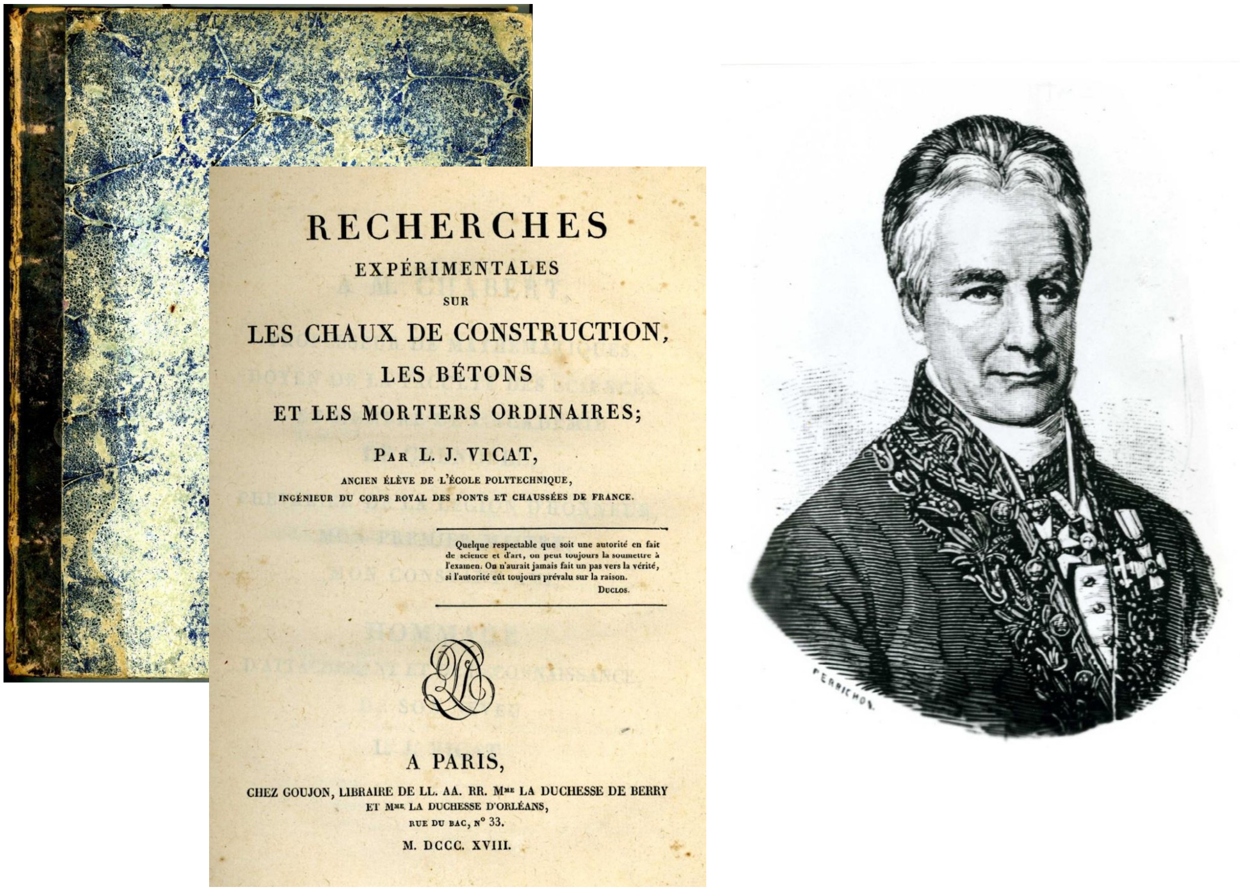

FIG. 1.6 Vicat and the first edition of his *Recherches Experimentales*, 1818.

James Frost and Colonel Pasley in England—and independently confirmed by the experiments of Johann Friedrich John (1782–1847) of Berlin, a Professor of Chemistry, in his *Uber Kalk und Mortel* (1819).[38]

On the other hand, practical experiments undertaken during the repair of the French fortress at Strasbourg convinced Vicat's contemporary, General Treussart, that the ancient use of pozzolana in lime mortar was a preferable substitute for naturally hydraulic limes than its artificial alternative. The pamphlet Treussart published in 1829 challenged opinions expressed by Vicat.

1.9 EARLY SPECIFICATIONS FOR ARTIFICIAL CEMENTS, 1811–30

Although the production of Roman cement expanded considerably after the expiry of Parker's patent in 1810, there were several early attempts to artificially replicate the naturally cementitious qualities of septaria. Edgar Dobbs of Southwark was among the first in England, filing a patent in 1810 for a mixture of three parts of chalk, one part of clay and one of ash 'such as is sold by the dealers in breeze',[39] but his business was short-lived. James Frost, having commenced in Roman cement, also turned to the manufactured product. Travelling to France he sought the advice of Vicat before bringing his experiments to a conclusion with a patent dated 1822 for a material he named 'British Cement'.

> *I select such limestones or marls or magnesian limestones or marls as are entirely or nearly free from any admixture of alumina or argillaceous earth, and contain from 9% to 40%. of siliceous earth, or silica, or combinations of silica and oxide of iron, the silica being in excess and in a finely divided state, and break such selected materials into small pieces, which are then calcined in a kiln … until all carbonic acid be expelled, and … the calcined material is to be ground to a fine powder ….*[40]

Frost ground his materials according to local practice, rather than Vicat's preferred method, though he adopted the Frenchman's use of the wash mill. He set up a works in 1825 at Swanscombe, on the Thames in Kent, from which he introduced his product to the market. It was first used at Hungerford Market, for foundations and stucco. British Cement was lightly calcined and sold at a cheaper price than Roman cement, having a 'cohesive strength' of about two thirds when tested in 1837.[41] Its quality relative to other cements may be gauged by the following tensile strengths at 11 days: Frost's British cement (17.6 lbs./in.^{2}); Francis's Roman cement (30.6 lbs./in.^{2})—and Pasley's (*see below*) (34.9 lbs./in.^{2}).[42]

Experimenting with artificial cements shortly after Frost commenced production was Lt. Col. Charles (later Gen. Sir Charles) William Pasley, the officer commanding the Royal Engineers' establishment at Chatham from its foundation in 1812 and who is portrayed in Fig. 1.7. In 1826 he introduced a course in Practical Architecture and turned his attention to the challenge of making an artificial Roman cement. He instigated an extensive series of experiments, and visited Frost at Swanscombe in 1828 to compare materials and methods. Eventually he proposed a mixture of five parts of chalk to two parts clay, specifying the blue clays of the Medway mudflats, and published his conclusions in 1830: *Observations, deduced from experiment, upon the natural water cements of England and on the artificial cements that may be used as substitutes for them*. He went on to write in much greater detail 8 years later and, by the time of its second edition in 1847, his *Observations on Limes, calcareous cements,* etc. was the standard text on the subject in English.

Another contemporary of Frost was William Lockwood. With Roman cement being used largely for stucco and architectural modelling, Lockwood—the proprietor of a building firm in Woodbridge, Suffolk, which in 1804 had become agents for Parker and Wyatt's Roman cement—was drawn to the idea of producing a stone-coloured cement by careful selection of the sources of lime used. In 1817 he toured the country for appropriate limestone: to the East Midlands, to Dorset, and to Bristol and South Wales. At some point between 1819 and 1822 Lockwood extended his operations to premises in Spitalfields and, with James Pulham placed in charge, began the small-scale production of an experimental stone-coloured cement for his firm's own use. Swansea lime was considered to combine adequate quality with ease of availability by sea. Joined by his son William Jr. in 1822, Lockwood set up in full-scale manufacture in Woodbridge, using lime from Swansea and Barrow, and a windmill for grinding. Significantly, in view of Joseph Aspdin's patent of 1824, Lockwood was already trading as a 'Portland and Roman cement manufacturer' in 1823, as attested by the trade directories of that year.[43]

FIG. 1.7 General Sir Charles Pasley.

1.10 ASPDIN'S PATENT FOR PORTLAND CEMENT, 1824

Joseph Aspdin's patent for Portland cement is the most famous of its kind by far, and the direct progenitor of the present Portland cement manufacturing industry. It is reproduced here as Fig. 1.8. However its wording is obfuscatory, either by oversight or design, as no useful information is supplied regarding the relative proportions of limestone and clay, the kiln temperature, the duration of firing or the fineness of grinding.

> *I take a specific quantity of limestone such as that generally used for making and repairing roads, after it is reduced to a puddle or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself and I cause the puddle or powder, or the limestone as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay and mix them in water to a state approaching impalpability, either by manual labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan, until the water is entirely evaporated. Then I break the said mixture into suitable lumps and calcine them in a furnace similar to a limekiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat or rolled to a fine powder and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it to the consistency of mortar and thus applied to the purposes wanted.*[44]

Although the name 'Portland cement' is introduced—from its association with the qualities and prestige of the then fashionable Portland stone which cement stuccos were designed to emulate; a comparison also made by Higgins in 1780 and Smeaton in 1791—it is certain that the material specified was somewhat removed from the cements of today.

'Nothing more than a hydraulic lime', Blezard argued in the previous edition of this chapter: 'its mineralogy was completely different, as was its hydraulic activity.[45] It offered 'little evidence of $CaO–SiO_2$ interaction', he states elsewhere,[46] as the firing temperature was 'too low for compound synthesis'. Nonetheless, Aspdin's patent marks an essential step in the development that led to the Portland cements of today. Aspdin's gravestone of 1855 is clearly inscribed 'Inventor of the Patent Portland Cement'.[47]

Despite doubts as to the quality of Aspdin's early binders, often expressed by historians of the industry, double burning the limestone and the fine subdivision achieved by slaking during the intermediate stage would have represented an advance on the light burning of wet-mixed chalk and clay such as Frost and others relied on.[48] Aspdin is known to have used a kiln of glass furnace design rather than the traditional limekiln.[49] The importance of a thorough amalgamation of materials is recognised in the specification of 'a state approaching impalpability'.[50] It is also without doubt that Aspdin and his sons produced cement with commercial success for many years into the Portland era.

1.11 THE 'PROTO-PORTLAND' ERA, 1824–44

For the early years of production, in which it seems likely that kiln temperatures failed to reach the point of incipient fusion or vitrification (i.e. around 1450°C, at which clinker forms), Blezard proposed the term 'Proto-Portland'.[51] This was a period in

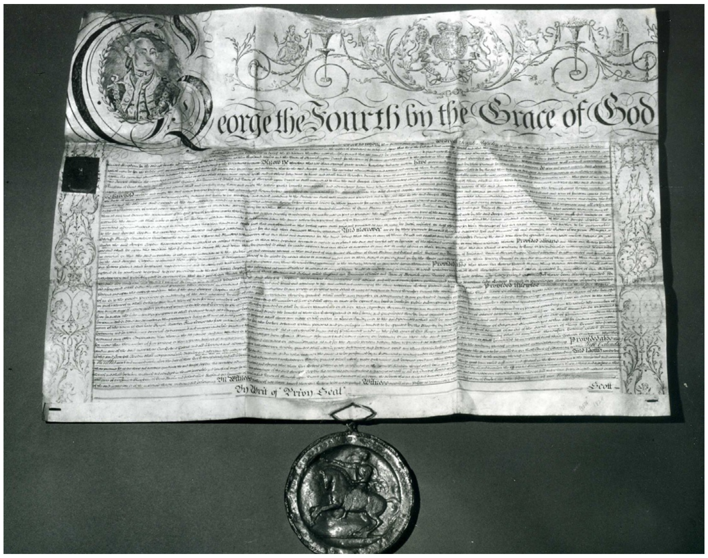

FIG. 1.8 British patent No. 5022 (21 October 1824) granted to Joseph Aspdin.

FIG. 1.9 Joseph Aspdin's first cement works at Kirkgate, Wakefield.

which the technology, while constantly improving, had not achieved the characteristics we would recognise today as a true Portland cement, regardless of the name under which it was marketed.

Aspdin was a bricklayer and builder from Leeds, whose experiments with cement from 1811 onward indicate a familiarity with the work of fellow Yorkshireman John Smeaton, and his own contemporaries, Parker, Frost and others. Indeed a copy of the 1813 edition of Smeaton remains with his descendants. Having registered his patent on 21 October 1824, and a supplementary one the following year, Aspdin established a factory in Kirkgate, Wakefield—depicted as Fig. 1.9—where he continued to manufacture until 1838. He resumed production at a nearby site in 1839 and relocated to Ings Road in 1848. When the cement industry consultant and publicist Henry Reid visited in 1870s, he considered the cement had been much improved during these 20 years. However, there is little evidence to adduce for this: Reid was writing years after the event, having visited replacement works, while the claim by Joseph's son William Aspdin that Brunel had employed Portland cement in repairing the Thames Tunnel in 1828 does not bear scrutiny.[52]

Blezard went on to characterise two further periods—those of Meso-Portland and Normal Portland cements—which we will also consider below.

1.12 WILLIAM ASPDIN AND 'MESO-PORTLAND' CEMENTS

In July 1841 William left the family firm in Wakefield and made his way to the capital where by the summer of 1843 he had become involved with cement manufacture in Rotherhithe at a works owned by J.M. Maude, Son & Co. An announcement by this firm made it clear that Portland cement was being introduced to the London market, its manufacture locally overcoming the high cost of carriage from Yorkshire. But this same announcement indicated it was a new cement: 'as a consequence of improvements introduced in the manufacture … it is stronger in its cementive qualities, harder, more durable, and will take more sand than any other cement now used'.[53] Clinkering or over-burning had been found to improve strength, even if one can only presume the discovery was accidental.

It was not long before this new Portland cement was investigated. In 1843 the contractors rebuilding the Houses of Parliament, Messrs. Grissell and Peto, undertook comparative tests. They summarised the results, illustrated in Fig. 1.10, in a letter of 13 November, acknowledging 'very satisfactory evidence of the superiority of your cement'.[54] Mixed with three parts sand, Portland cement was more than double the strength of Roman. Positive publicity and some influential advocacy followed shortly afterwards, while the threat of shortages and taxation, and a building site disaster at Euston in 1848, undermined the previous dominance of Roman cement.

Responding to the evident potential of this improved 'meso-Portland', and 'attracted by the flourish of trumpets, that was then being made about the new cement',[55] the long-established Roman cement firm J.B. White and Sons turned to its manufacture in 1844. The company's works at Swanscombe were under the direction of Isaac Johnson who, having studied chemistry in his spare time, attempted to emulate the rival firm's product. First seeking a chemical analysis of Maude and Aspdin's cement, he experimented with additions of bone ash, then with the mineral constituents of septaria respectively from Sheppey

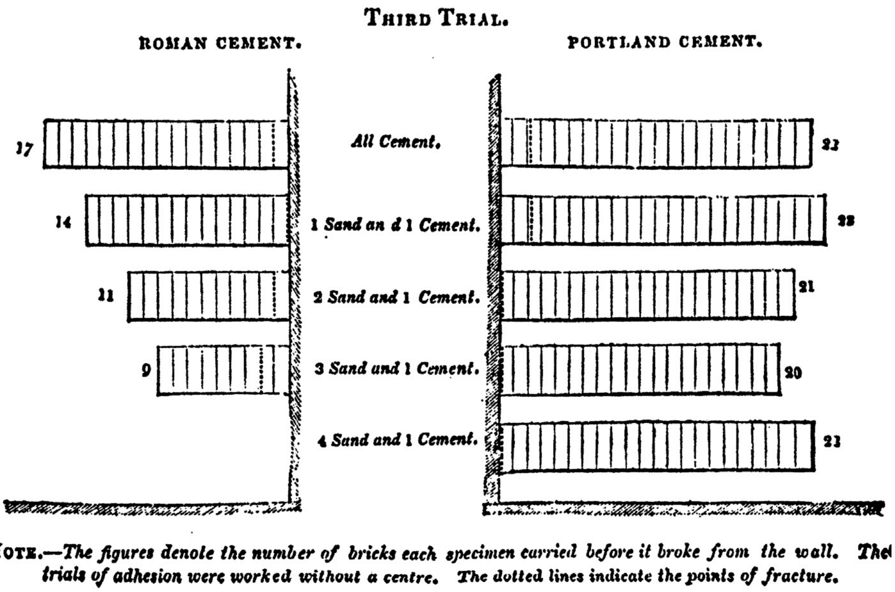

FIG. 1.10 Results of the first official tests of William Aspdin's Portland cement, undertaken by Messrs. Grissell and Peto at the Houses of Parliament, October 1843.

and Harwich, before combining chalk and alluvial mud in the manner of Frost. Finding material that had accidentally vitrified, probably during the winter of 1844/45, he 'pulverised some of the clinker and gauged it'.

> *It did not seem as though it would harden at all and no warmth was produced. I then made mixtures of the powdered clinker and powdered light burnt stuff and this did set and soon became hard. On examining some days later the clinker only, I found it much harder than the mixture, moreover the colour was of a nice grey.*[56]

Independently Johnson had discovered the secret of Portland cement, one that the Aspdins had been at pains to protect, and for the rest of his long life—he died in 1911 aged 100—Johnson claimed to be its true inventor.[57] Advertisements in *The Builder* from April 1845 indicate that J.B. White & Sons were manufacturing Portland cement, alongside their existing Roman and Keene's cements, the latter an alum-based gypsum plaster patented in 1838.

In early 1846 William Aspdin responded to an opportunity to rent the former Parker and Wyatt works at Northfleet and later entered a partnership with William Robins and his son-in-law, to engage in business there as Robins, Aspdin & Co. An early kiln from these works has been preserved and is illustrated in Fig. 1.11. Commercial rivalry between the two enterprises, now neighbours on Kent's Thameside, led to further testing, claims and counter claims, which spurred the development of the product and leaves us a record of its progress.

In December 1847 White's Portland cement was submitted for trials at Messrs. Grissell's works, and the results were published in *The Builder*. As in the 1843 tests of Maude and Aspdin's cement, White's demonstrated a clear superiority over Roman cement. Aspdin appears to have been irked by the publicity and, in the following September, issued a circular quoting favourable test results and calling for public trials of his cement. These trials were conducted on 18 September and at Messrs. Bramah's works on the 26th. These indicated that Portland cement was 2.4 times as strong as Roman (and double the price). It was also 20% stronger than White's equivalent.

Retrospective microscopical examination of preserved Portland cement made in Aspdin's plant at Northfleet indicates that he had attained sufficient temperature to achieve vitrification and produce alite crystals—see Fig. 1.12. Several investigators independently have examined evidence from the *Ship-on-Shore* public house, constructed from solidified barrels of hydrated cement in 1848, and from mouldings at Portland Hall, erected in Gravesend in around 1850.[58] They agree in identifying similar material of meso-Portland characteristics, rather coarsely ground. D.L. Rayment, for instance, using electron microprobe analysis, has proved that hydrates were identical to the compositions of inner and outer hydrates of modern Portland cements.

Further demonstrations of this enhanced cement were made at the Great Exhibition of 1851. Among the many exhibits from the building industry was a brick-and-cement beam, intended as a replica of the one erected by Francis and White in 1836 to provide a comparison between Roman and Portland cements. Tested to destruction during the exhibition it clearly

FIG. 1.11 Preserved beehive kiln at William Aspdin's works in Northfleet, Kent along with the photograph of a model of an adjacent kiln now demolished.

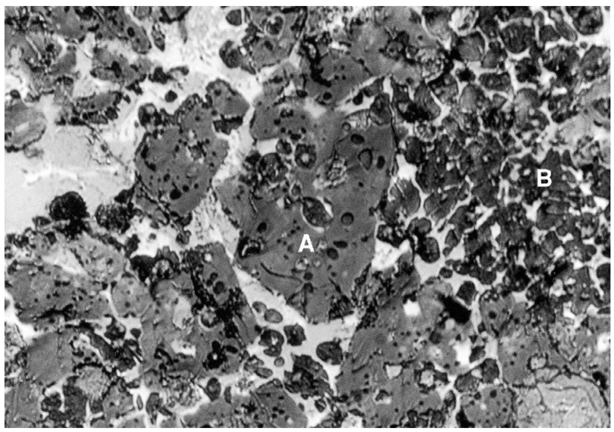

FIG. 1.12 Photomicrograph of a polished section of meso-Portland cement clinker from Aspdin's preserved kiln (magnification ×300). Note: The alite and belite crystals cooled slowly in a well-differentiated flux. *A* indicates a large alite crystal; *B* indicates small belite crystals. The view portrays a very slow cooling regime.

showed the superior strength of Portland cement, though the last minute insertion of an iron hoop undermined the value of the result. Several cement makers were represented, including William Aspdin:

> *Messrs. Robins, Aspdin & Co are exhibitors of a gigantic slab of Portland cement measuring 20 feet by 10 feet and 10 ins thick weighing 15 tons; numerous blocks of cement and concrete proved to various pressures up to 154 tons and showing the strength to be greater than that of Portland stone; of bricks cemented together and placed so as to give a pressure of 3 tons on the first brick; and several other similar illustrations. The Jury have award a Prize medal to these Exhibitors.*[59]

Shortly afterwards Aspdin fell out with his partners and in 1852 relocated to a new works in Gateshead. Johnson likewise moved on to exploit his discovery, and after a period in partnership with George Burge on the Medway, took over the very works in Gateshead that Aspdin abandoned in 1856. Aspdin moved to Germany where he was influential in the early cement industry there, before dying at the age of 48, while Johnson—Fig. 1.13—returned to Kent and lived into the next century as the 'grand old man' of British cement manufacture. Meanwhile this period of rapid improvement in Portland cement manufacture was the subject of a paper read to the Institute of Civil Engineers by George Frederick White in 1852.[60]

Based on an analysis of the test results published during the decade 1843–52, Skempton has argued that the 'break through' of clinkering the raw meal would seem to have been the Aspdins', and the discovery brought to the Thames-based industry by William by 1843. The superior nature of the cement promoted by Aspdin and Maude prompted the more scientific investigation of Johnson in 1844, though despite his claim to be 'the inventor',[61] the adoption of the existing name 'Portland' suggests a consciousness that White's new cement was not a different material. Johnson's role was one of 'introducing more

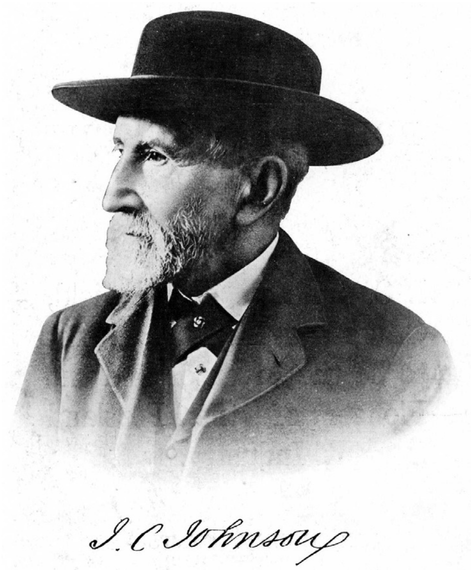

FIG. 1.13 Isaac Charles Johnson.

consistent and rational procedures'[62] than reliance on the more empirical methods of Aspdin, and putting manufacture on a firmer business footing.

The manufacture of Portland cement was soon taken up on the Continent. In France, for long the seat of scientific study into cements, production of Portland cement is thought to have started around 1850.[63] Emile Dupont obtained a patent (No. 796) for his *Provisional specification for the manufacture of cements* in 1854 and commenced production in Boulogne. Also in the early 1850s cement manufacture took root in the German states; an early factory was established in Buxtehude by Brunckhorst and Westphal, and was producing Portland cement in 1850.[64] The first plant of significance was at Zullchow near Stettin, which was founded by Hermann Bleibtreu in 1853 and came into full production in 1855. Quistorp followed nearby and Gundmann's works at Oppeln in 1857, and by 1864 there were at least 15 works. In 1878 the rapidly growing industry was producing 440,000 t a year and had achieved an output of 1 million tons by 1887. Portland cement manufacture spread across Europe and America and was introduced to the following countries in turn: Russia (1857), Austria (1860), Denmark (1868), Switzerland (1871), United States (1871), Belgium (1872), Sweden (1873), Netherlands (1875) and Norway (1888).[65]

1.13 ADOPTION OF PORTLAND CEMENT IN MAJOR PROJECTS

While cement in these early years found applications in bricklaying mortar and stucco, its use in civil engineering was limited to the formation of concrete blocks in breakwaters at harbours along the Channel coasts of both England and France. But in 1859 its property of gaining strength in the presence of moisture suggested its use in the newly approved London main drainage scheme.

> *Previous to 1859, Roman cement was, with few exceptions, the only cement used for the inverts of the London sewers; the arches being set in blue lias lime; Portland cement was scarcely ever used. Up to this time Portland cement had been confined to ordinary building operations such as external plastering and a few harbour works on the south coast where it was most used in the form of concrete blocks.*[66]

Portland cement was largely untried, 50% more expensive than Roman, and sensitive to errors or variation in production 'in an industry where production control and quality control process were still rudimentary'.[67] However, its hydraulic nature and strength increase over time made it an obvious choice for consideration. In 1859 project engineer John Grant make an initial investigation, advised by the early manufacturer and consultant Henry Reid. He conducted 302 experiments between January and July on cement supplied by 12 manufacturers. Cubes of neat cement and mortar were immersed for 10–14 days and crushed; other samples were made into briquettes and subjected to tension. The

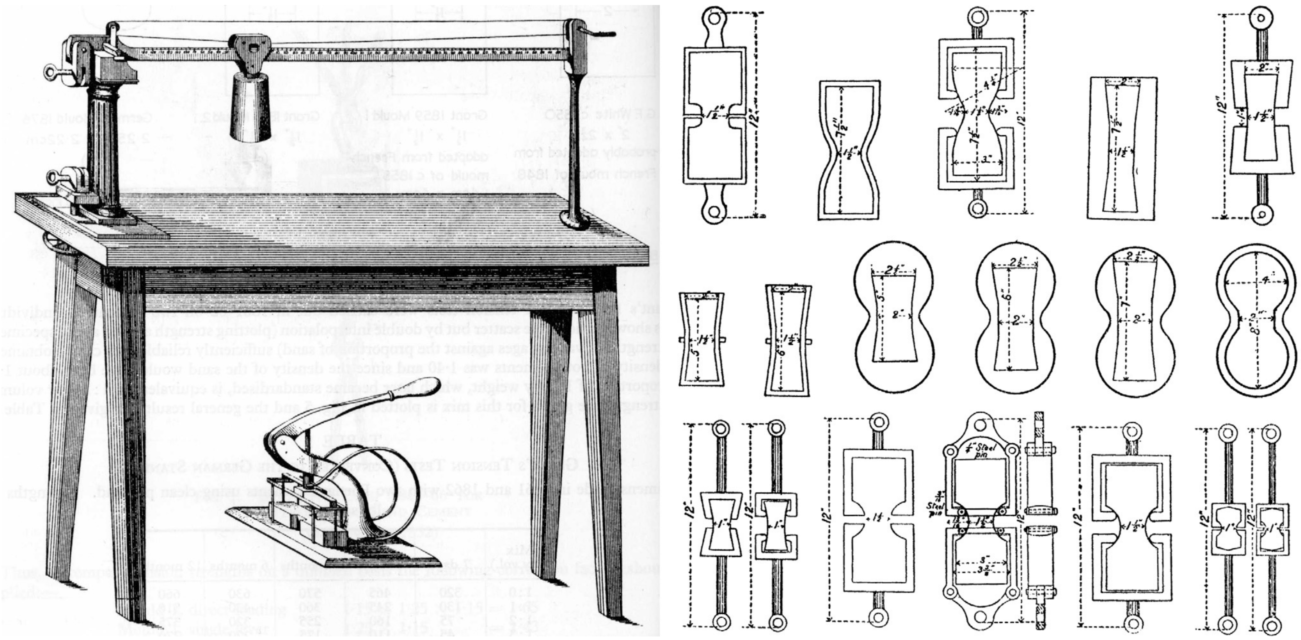

FIG. 1.14 Adie's apparatus for testing tensile strength of cement samples for the London Main Drainage, 1859 and a range of moulds for producing test briquettes.

results of this testing again reflect the progress of the material properties of cement at the time and the superiority of Portland over Roman cement.

Consequently Grant recommended its use and Joseph Bazalgette, the Metropolitan Board of Works' chief engineer, authorised its adoption for laying the brickwork for the sewers—the first use of the material in a large-scale public work. (It was specified for Government contracts in the United Kingdom after 1867, when at Chatham Dockyard it was 'found beyond all question, that concrete made of 1 part of Portland cement to 12 parts of ballast was in all respects better and more uniformly trustworthy than the lias concrete of the original specification'.)[68]

Crucially, Bazalgette's specification implied ongoing quality control to ensure that minimum standards were being met, and Grant instituted a systematic testing regime to determine the acceptance of materials. Originally few manufacturers could supply at the required minimum strength,[69] but the project spurred improvements in production and new entrants to the industry, and by 1865 a total of 70,000 t, from 14 manufacturers, had been subjected to 11,587 tests for the 'southern drainage' contracts alone. Test methods and apparatus—Fig. 1.14—were improved and Grant's conclusions were thrice published by the ICE. Consequently the use of cement was extended to concrete pipe manufacture, and to in situ concrete hearting and backfill. The London Main Drainage was Portland cement's first comprehensive large-scale trial, and success had a huge impact on its production and use. Roman cement 'gradually succumbed to the merits of the new product, and the impetus given to its use by the London Drainage works in 1859 settled the question of its superiority'.[70]

Testing became routine and independent test houses were established in the United Kingdom by specialists such as David Kirkaldy, Henry Faija and his successor David Butler, and Bertram Blount with partner Harry Stanger.

1.14 TESTING AND IMPROVEMENTS IN QUALITY CONTROL

Testing was vigorously and systematically adopted in Prussia and the German states. Among the pioneers in this field was Dr Wilhelm Michaelis (1840–1911), who wrote extensively on his lifelong investigations into the material, starting with his classic *Die hydraulishen mortel* (1869), and from 1872 operated an independent cement testing laboratory in Berlin. It was his and his partner Fruhling's design of tensile and compressive strength testing apparatus, illustrated in Fig. 1.15, that became the standard in the German and Austro-Hungarian empires for decades to come. Also in the early 1870s Rudolf Dyckerhoff, who had studied chemistry at Heidelberg, introduced systematic quality control processes to his family's cement works; proportioning of the raw meal was henceforth guided by chemical analysis rather than rules of thumb.

Chemical analysis further improved during the later 1870s and into the 1880s. Professor Bauschinger (1833–93), who had run the university engineering laboratory at Munich from 1871, undertook what Skempton has described as a 'superb'[71] series

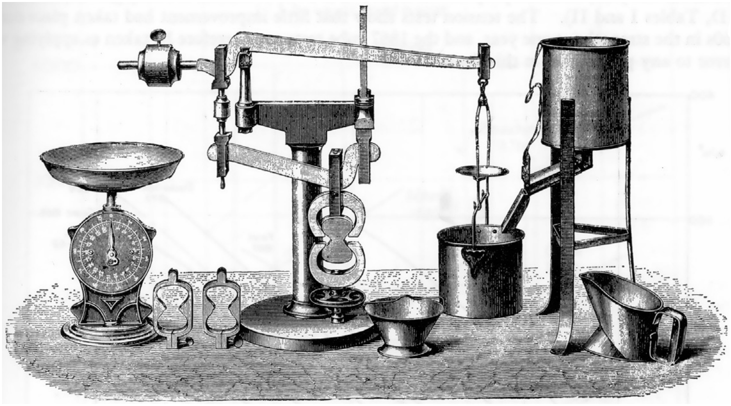

FIG. 1.15 Michaelis and Fruhling's improved apparatus for testing the tensile strength of cement, 1869, widely used in the German-speaking lands.

of tests on 10 Portland cements between 1876 and 1879. He determined their chemical composition, setting time, particle size, volume change and strengths in tension, compression, bending and shear at different ages. Published in 1879 Bauschinger's results demonstrated the quality and consistency of German cements. Similar consistency was revealed in 1883 when Dr. Bohme of the Royal Technical Testing Station published the results of testing a group of 11 cements in 1881. The CaO content of German cement was generally around 62%; a level that would not be improved until the advent of the rotary kiln in the 20th century permitted levels of 64%.

Control of the chemical composition of cements had led to great improvements in quality and strength. German cements of 1885 had strengths about double that of English cements made 20 years previously and three times higher than those made before 1860. Evidence from the early years is fragmentary, but Skempton has analysed the surviving data and proposed the following averages:

TABLE 1.3 Strength (lb/in.[2]) of Portland Cements, 1847–87[a]

			Tension				Compression	
			1:0		1:3		1:3	
Date	Authority	Cement	7 Days	28 Days	7 Days	28 Days	7 Days	28 Days
1847	GF White	White	—	—	—	—	—	800
1848	W Aspdin	Aspdin	—	—	—	—	—	1000
1852	GF White	White	250	—	45	—	—	—
1859	MBW specification		255	—	—	—	—	—
1859	Grant	6 cements	260	390	—	—	—	—
1860–2	Grant		320	465	50	115	—	900
1860	Leblanc	Boulogne	—	—	55	100	—	—
1864	GF White	White	350	480	75	130	—	—
1865	Grant		—	—	—	—	—	1200
1868	Grant		420	570	—	160	—	—
1869	Gillmore	Boulogne	310	240	85	155	800	—
1873–5	Bauschinger	Perlmoos	—	—	—	—	—	1570
1875	Bauschinger	Dyckerhoff	—	—	—	—	—	1680
1875	Bauschinger	Schiffendecker	—	—	—	—	—	1700
1876	Bauschinger	5 cements	375	500	115	170	1070	1620
1877	Dyckerhoff	2 cements	360	550	110	190	—	—
1878	Barreau	4 cements	—	—	105	180	—	—
1879	Guarantee	Stern	570	710	213	284	—	—
1878	German standard		—	—	—	142	—	—
1878	Aus standard		—	—	114	170	—	—
1880	Grant's specification		400	550	—	170	—	—
1883	Swiss standard		—	—	—	213	—	2130

TABLE 1.3 Strength (lb/in.) of Portland Cements, 1847–87—cont'd

			Tension				Compression	
			1:0		1:3		1:3	
Date	Authority	Cement	7 Days	28 Days	7 Days	28 Days	7 Days	28 Days
1880–4	Bohme	8 cements	620	740	220	290	1600	2100
1881	Bohme	11 cements	625	770	205	295	—	—
1884–6	Bohme	47 cements	—	—	230	300	1900	2600
1885	French specification		284	498	114	213	—	—
1887	Ferret	6 cements	560	680	150	220	1250	1550
1887	German standard		—	—	—	228	—	2280
1887	Swiss standard		—	—	—	228	—	2280

[a]Abstracted from Skempton's[37] Table 10, p. 139.

Progress was also down to improvements in the design of production plant. The Hoffmann ring kiln was one such innovation and the later shaft kiln likewise originated in Germany. Variant designs by Stein and Dietzche (patented in 1884), and later by Schneider, became popular in the British, as well as German, industry. Improved methods of milling to achieve a finer finish were explored, and roller mills developed. In 1880 Dr. Tomei of Quistorp Works undertook comparative experiments to establish the strength of the cement obtained by the new and traditional methods, and the roller mill was widely adopted in Germany in the 1880s. The use of fine sieves to ensure consistency of grinding likewise helped improve quality.

British industry was not unaware of German developments, and many innovations were adopted. Indeed Reid repeatedly drew his readers' attention to their example, even publishing a translation of Lipowitz's treatise in his own book of 1868. By 1877 he was yet more forthright in his admiration and Grant, in his paper of 1880, also alluded to the German and Austrian rules for testing. However, some years later, Redgrave was to lament the passing of British leadership in cement technology:

Our own country, the original seat of the manufacture, has been distanced in certain directions in consequence of the superior scientific skill and the energy of foreign rivals. The supremacy we have so long enjoyed has undoubtedly been to some extent wrested from us by the products of Continental industry and enterprise.[72]

However progress was to be found not only in Germany. From the introduction of the Blake stone crusher onward, American mineral processing equipment became more widely available, as did Danish production machinery. Slag cements—which we'll address below—were produced in Germany and later in France. In Britain the dry grinding of limestone was introduced in the 1860s and improved wash mills for the wet process developed by Goreham and de Michele in the 1870s. Johnson's invention of the chamber kiln in 1872, that incorporated the drying of slurry before its addition to the kiln by recycling waste gases, was a great improvement on the traditional 'bottle' kiln. Reid (1877), Burnell (1878), and Scott and Redgrave (1880) describe the production methods of this period.

1.15 THE ADVENT OF 'MODERN PORTLAND' CEMENT, 1887–1904

Several authorities (Skempton and Blezard among them), have identified 1887 as a pivotal year in the material development and understanding of Portland cement—a watershed after which the 'meso-Portland' cement became recognisably the 'modern' binder we know today.[73] Various criteria are advanced for this distinction: publication of Le Chatelier's thesis in Paris; trials of the first practical design of rotary kiln at West Thurrock, and the start of Ferret's comprehensive series of tests on French cement at Boulogne.

Le Chatelier, whose work shaped the science of cement for decades to come, was hugely regarded by his peers and successors, and was described by the American chemist Bogue as 'the father of cement chemistry':

His works on the chemistry of Portland cement are of fundamental importance. Through microscopical and chemical studies he has demonstrated that clinker contains a number of different minerals of which tricalcium silicate is the bearer of hydraulic properties. He has also demonstrated that gypsum, calcium aluminates and Portland cement attain their set through a crystallization process from supersaturated solutions. He was one of those men who believe that we cannot intelligently control industrial processes until we know the nature of things with which we are dealing.[74]

Perhaps the most immediately indicative significance of 1887 was the publication the German standard for Portland cement (as opposed to the Prussian standard of 1878 for which the Verein Deutscher Zement Fabrikanten was originally formed). According to Skempton,[75]

> *The French specification of 1885 marked a further advance in cement testing, but the second German Standard of 28 July 1887 was even more important. ... Simultaneously the Swiss regulations were modified and the strength requirements were identical with those given above. The residue on the 900 sieve and the final set were also similar. If we add to the German and Swiss Standards of 1887 the initial set and the 7-day (1:3) tensile strength of the French Specifications, and Grant's 7-day tensile strength for neat cement, we have a set of rules which covers all subsequent Standards until 1901. In other words, by 1887 the pattern of modern cement specifications was already established.*[76]

Arguably the other turning point, certainly in Britain, came at the end of a series of production improvements in the 1890s. These included the discovery of calcium sulfate as a set regulator by Edouard Candlot in 1890 (building on work by Henry Scott, who patented the selenitic process in 1871); the development of ball- and tube-mills in Germany and Denmark—by the firms Polysius and FL Smidth in 1891 and 1893 respectively—and the introduction of electrical power for mill drives and other process machinery. These improvements culminated with the introduction of the rotary kiln at the turn of the century.

This (literally) revolutionary conception was initially patented by Thomas Crampton in 1877 and prototype kilns by Ransome, such as the one at Arlesey illustrated in Fig. 1.16, were brought to practical trials at Mitcheldean and Barnstone between 1885 and 1887. Ransome's patent of 1887, and improvements by Stokes led to further experiments at West Thurrock, Arlesey and Penarth. However practical difficulties in achieving sufficient temperature were not overcome until the Keystone (later Atlas) Portland Cement Co in the United States pioneered to the use of pulverised coal as kiln fuel in the early 1890s. Successful designs by the company's engineers, Hurry and Seaman, and their rivals Lathbury and Spackman at the Alpha Portland Cement Co, were patented in 1895. Versions of the American designs were adopted in Germany in 1896, and in Britain three years later[77]:

- Shoreham (ordered 1899 and commissioned 1900)—FL Smidth orders no. 3 and 4, based on Lathbury & Spackman design
- Martin, Earle & Co (erected 1900 and tested until 1902)
- Swanscombe (ordered by JB White & Sons—before the formation of APCM—and erected 1900/1) and Wouldham shortly afterwards—16 kilns in total, manufactured by Fellner & Ziegler to the Hurry & Seaman design

The scale and speed of the change from the bottle or chamber kiln to the new rotary kiln,[78] and to a lesser extent the Schneider shaft kiln, is illustrated by figures drawn from reports of the Alkali Inspectorate in East and South East England. In 1900 there were 270 bottle and 1639 chamber kilns distributed throughout 58 cement works, yet only 10 Schneider kilns and no rotary kilns at all. Conversely in 1911, with only 35 works in operation, there were 53 Schneider and 62 rotary kilns. The number of chamber kilns had halved to 807 and there were only 2 bottle kilns remaining in service.[79]

The capital investment required was such that it added momentum to the proposal to consolidate the British industry with the formation of Associated Portland Cement Manufacturers in July 1900, which in turn facilitated agreement on the publication in 1904 of the first British Standard Specification for cement: BS 12. These changes set the course for the British cement industry until the end of the 20th century. Similar comments apply to the American industry which, experiencing an explosion of output at the turn of the century[80]—rising from 250,000 barrels in 1889 to 5,156,064 in 1899—agreed its own national standard: *Standard specification for cement* (ASTM C9), 1904.

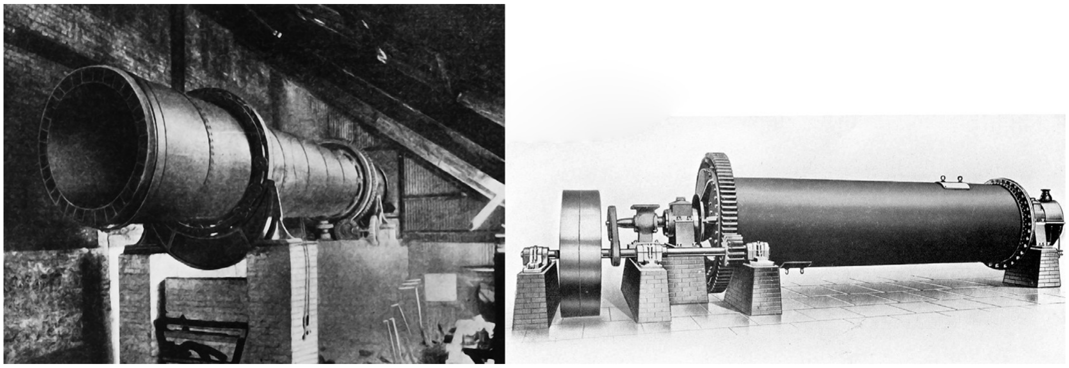

FIG. 1.16 Ransome's experimental rotary kiln as tested at Arlesey and (right) one of the first tube mills.

1.16 EVOLUTION OF 'MODERN PORTLAND' CEMENTS IN THE 20TH CENTURY

The properties of the product altered with the transformation of the production process at the beginning of the century. Jackson has identified three principal properties by which the changes in cement can be assessed: soundness, setting times and strength, of which the latter is the most conspicuous.[81]

1.16.1 Strength

The increase of strength has been one of the underlying trends in the development of Portland cement from its earliest manufacture. However, the adoption of rotary kilns and switch to ball mills for finer grinding (augmented later by the use of grinding aids) enabled the achievement of greater cement strengths in the 20th century than previously was possible. Records of laboratory testing at the United States' Portland Cement Association and the UK's Building Research Station (now BRE) indicate long-term trends of increasing strength, notably at early age.

Laboratory tests at PCA and its predecessor (the Association of American Portland Cement Manufacturers), ranging from 1904 to 1950, were published in 1952 and indicate changes in composition, fineness and strength producing characterises over this period.[82] PCA investigators concluded there had been a marked increase in the average C_3S content and a greater degree of fineness, with a particular improvement in the period 1926–40. Strength gain at early age was accelerated by changes in production technology in the interwar years, and though some improvements were also noted at ages of 28 days–10 years, these were minimal compared with the improvements in early age strength.

In the United Kingdom consistent testing of compressive strength of water-cured concrete at 28 days, using sand and gravel extracted from the same Ham River workings, was conducted by BRE from 1934 to the 1980s, allowing a direct comparison of cements produced over a 50-year period. As in American experience, the figures indicate an improvement in strength gain, too; 'at all ages, but particularly at early ages'.[83] There was a noticeable increase in strength of British cements tested between 1950 and 1970.

Skempton included similar findings in his analysis of cement strengths, from the early tests of Grissel and Grant and the German investigators of the 1870s and 1880s to the 1960s. His widely reproduced graph was updated by Blezard as Fig. 1.17, and subsequently by Livesey.[84]

The early part of the time (Period 1 on the graph) was dominated by British technology, but the later part of the 19th century (Period 2) showed a domination by German technology before being supplanted by the international use of the rotary kiln.

1.16.2 Soundness

A tendency to produce unsound cement had been a characteristic of the early static kilns, but with the adoption of rotary kilns lack of soundness diminished as a problem. High lime saturation factors could still arise when feedstock was monitored for its carbonate values alone, and therefore became susceptible to insufficiently low levels of silica, resulting in uncombined

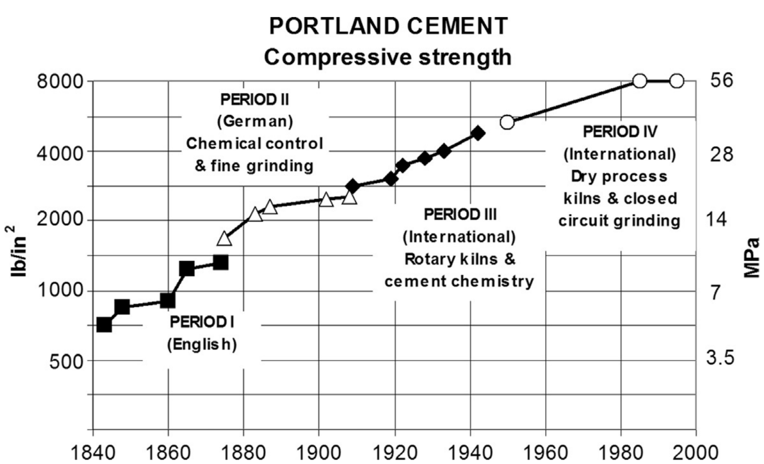

FIG. 1.17 Stages of technological improvement, reflected by compressive strength of Portland cement mortar (1:3 by weight at 28 days stored in water). Note: The compressive strength scale units are not linear.

quicklime and unsound cement. Variable coal quality, such as afflicted the industry in the years following the Second World War, could also cause unsoundness, but by the 1960s improved feed stocks and advances in chemical analysis had overcome the remaining problems.[85]

1.16.3 Setting Times

Early in the 20th century manufacturers struggled to control setting times, despite the widespread adoption of calcium sulfate as a regulator from the 1890s onward—usually by intergrinding gypsum with the clinker. Water added at the grinding stage was another approach, and the variation of methods encouraged significant discrepancies in setting times between manufacturers and, indeed, products. By the mid 1920s, however, the problem appears to have subsided.

1.17 EXPANSION OF MANUFACTURING OUTPUT

The improvement of cement strengths and associated properties has largely been a consequence of enhanced production efficiency,[86] as well as scientific enquiry and quality control, while economic return has been a major motive in both developing the product and marketing new outlets for it. And there is no doubt that during the 20th century cement became a vital construction material. From the international output of 1900, dominated by Britain, Germany and America, with new entrants emerging, global production has ballooned and, as indicated by Fig. 1.18, continues to grow.

New applications have demanded new cements, and newly available sources of raw material have opened up possibilities for production. The huge upswing in German output in the 1870s and 1880s was made possible by developments in the mechanisation of production processes and in the implementation and increasing sophistication of quality testing, but it was driven by a broadening perception of its possibilities as a construction material. Reinforced concrete, for instance, required cements of sufficient strength for the resulting concrete to complement the performance of embedded steel. This attained in the 1880s, use of reinforced concrete was rapidly taken up throughout Germany and Austria, and created further demand for cement in its turn.

1.18 SPECIAL PORTLAND-BASED CEMENTS

As new demands emerged, so producers responded and a range of variations on the basic material developed. Jackson identifies the following[87]:

Water-repellent cements: The origins of these cements date to before the First World War with the incorporation of the metallic salts of fatty acids, and have been made in the United Kingdom since the 1930s.

Rapid and ultrarapid hardening cements: Introduced before the First and during the Second World Wars respectively, achieved by finer grinding and the addition of calcium chloride.

White and coloured cements: Introduced from America in the 1920s and 1930s respectively, with cement paint developed for camouflage purposes in 1941.

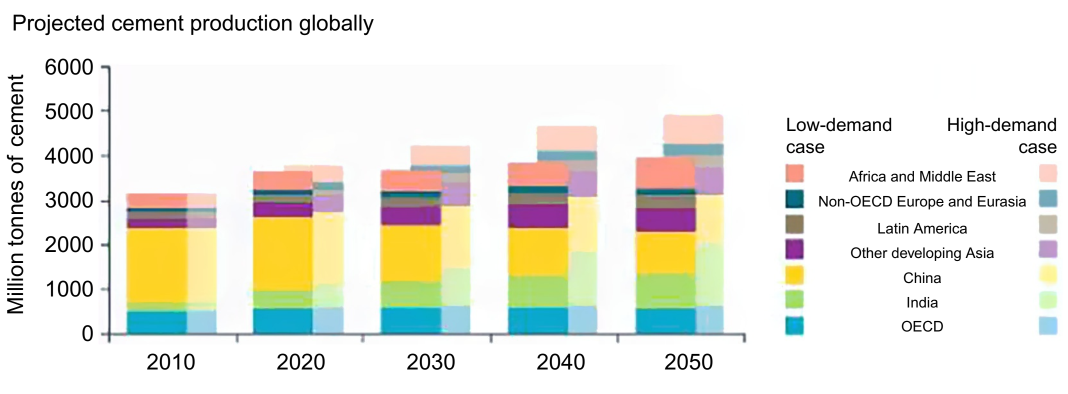

FIG. 1.18 Global cement trends to 2050. *(Source: Fold-out of the CSI/IEA roadmap for India: low carbon technologies for the cement sector in India; 2013.)*

Masonry cements: An American innovation from the 1930s, combined 80% Portland cement with 20% chalk and air-entraining agent.
Low-heat cements: Developed in the United States from experience of dam building in the 1930s and standardised for use in the United Kingdom in 1947.
Sulfate-resisting cements: Blends of Portland cement with the addition of limited quantities (under 5%) of tricalcium aluminate were developed in America during the late 1930s and extended to Britain after the War.[88]
Oil well cements: Dominated by American practice from the 1950s onwards.
Air entraining cements: Developed in the United States and introduced much later to the United Kingdom in the 1990s.
Limestone cements: Blends of up to 20% limestone have been successfully used in France and Spain for many years and have latterly been standardised across Europe.

Expanding and non-shrinking cements are among other variants, originating in France and developed subsequently in both the United States and USSR.

1.19 SUPPLEMENTARY CEMENTITIOUS MATERIALS

Other developments were pushed by availability, rather than pulled by demand. The recycling of waste materials has been a recurrent theme in the history of cement, from the Roman use of crushed tiles as a replacement pozzolana, to Joseph Aspdin's use of road scrapings as a source of argillaceous limestone. Indeed William Aspdin went on to experiment with alkaline refuse in the 1850s,[89] and in the 1870s, Reid remarked that he had been consulted by 'one of the largest manufacturing firms in St. Helens district in regard to the possibility of turning their waste to account in Portland cement-making', but found that 'the large amount of sulfur in it, forming sulfate of lime, prevented its applicability for a hydraulic cement'.[90]

By the 1890s, however, a modification of the treatment of alkali waste arising from the production of soda, by which sulfate and polysulfides of calcium were extracted, suggested the resulting by product of lime as a possible raw material for Portland cement manufacture. After the failure of several earlier proposals, it was revealed in 1895 that, 'Mr. C. Spackman, F.C.S., appears to have been successful in producing Portland cement from this material'. According to Redgrave, 'Mr. Spackman states that if it is so far free from sulfur compounds as to give in the cement a quantity not exceeding 5% of calcium sulfate, alkali waste may, after treatment by the Chance process for the recovery of its sulfur, be successfully utilised for the manufacture of Portland cement'.[91] This treated waste was adopted as a raw material at Ditton, Gateshead, Jarrow and Crosfield's Works, while carbonate sludge from the soda recovery process in the paper industry was used at South Hylton.[92]

Likewise Lt. Col. Henry Scott (the patentee of selenitic cement) developed a method of cement production in the 1870s based on recovering the lime used for treating sewage sludge, a method that, while successful for a while, fell in to disuse with changes to the treatment process.[93] Similarly, British experiments with iron slag in the 1870s had limited uptake. Use of 'slag sand', or granulate, was patented by Charles Wood of Middlesborough, and initiatives were undertaken by Frederick Ransome and John Watson, but slag remained a minority interest in the United Kingdom until the after the First World War.

However, on the Continent slag was explored with greater purpose and in 1865 the first Portland blastfurnace slag cement was produced in Germany; it was used for construction in Paris by 1869. A significant step forward came with the patenting by Bosse and Wolters in the 1880s of a method that added thoroughly burnt slaked lime in the form of a fine powder to ground granulate at a proportion of one part to three—replacing the earlier, less efficient process of re-calcining the mixture of slag and calcium carbonate. In 1908, Hermann Passow published his thesis on blastfurnace slag and partly as a result of his research, and that of his colleague Arthur Guttmann, *eisenportlandzement* ('iron Portland cement') and *hochofenzement* ('blastfurnace cements') were standardised in 1909 and 1917 respectively, and this erstwhile waste material gained acceptance for use in structural concrete under the German regulations of 1916.[94] In the United Kingdom factory blended combinations became available from early 1900s, and a standard for Portland Blastfurnace cement was issued in 1923. The first use of ground granulated blastfurnace slag (ggbs) as an addition at the concrete batching plant was for the construction of the Avon Dam in 1957.[95]

In 1908 Hans Kuhl was granted a patent in Germany for the use of slag as the basis of super sulfated cement—a low-heat and chemical resistant cement made by intergrinding ggbs, calcium sulfate and a little Portland cement—and this was first made commercially in Belgium and France in the 1930s.

Shortly afterwards, in 1910, the Dane A Poulsen was granted a patent for another specialist cement, a seawater-resistant blend of Portland cement inter ground with up to 30% of a Tertiary clay known as 'moler'. This material contained a high proportion of diatomaceous silica. Supplies were eventually obtained from waste arising from the manufacture of moler bricks.[96]

Of similarly wide acceptance today as slag, but of more recent vintage, is fly ash from pulverised coal used in power generation (known until recently in British useage as pulverised fuel ash or PFA). The first comprehensive research into the behaviour of fly ash was by RE Davis at University of California and its first major use in repairs to the spillway of the Hoover Dam by the US Bureau of Reclamation in 1942. This was followed by the use of 120,000 t in constructing the Hungry Horse Dam in 1948, also in America, while and the first British use was in 1954 for building the Lednock Dam.[97]

Since then secondary cementitious materials (SCMs) for replacing or enhancing the use of Portland cement have been developed, including silica fume, metakaolin and, in emerging markets, rice husk ash. 'Extending cement with SCMs has proven to be one of the big success stories of the past 40 years'.[98] Indeed, the testing of newly identified cementitious materials and the effects of blending dominates present day research into cements.

A greater acceptance of additions has forced a change in the very definition of Portland cement and permitted a range of approved composites. After many years of trying, from the 1970s onward, the standards governing cement in Europe were finally harmonised in 1999 with the publication of BS EN 197.1. Cements may now comprise up to 5% of another material—slag, fly ash or limestone—and still be designated Portland cement, or CEM 1. By combining these materials in larger proportions as many as 27 common cements can now be specified as standard.

1.20 NON-PORTLAND CEMENTS

Besides factory-produced composite cements, and combinations of material mixed on site, several cements with alternative chemistries have been introduced over the years, with varying degrees of commercial success. The most obvious, perhaps, are high alumina, or calcium aluminate cements (CAC) that were developed in France as a sulfate-resisting cement, and first marketed in 1918. Although no longer used in structural concrete, CAC occupies niches such as for rapid setting underwater, biogenic and refractory, high temperature applications.

Environmental concerns since the late 1990s have encouraged the development of an ever increasing range of novel, or low-clinker cements, to reduce the industry's reliance on technologies that inherently generate high levels of carbon dioxide. Sulfoaluminate cements are one such, a material that has been produced in China for many years, as are magnesium-based cements. During the 20th century the proportion of alite in the composition of cement clinker has increased in line with the increasing early age strengths of Portland cement. It is currently in a ratio to belite of >2. As this greater proportion of alite is associated with higher calcium content and consequently carbon dioxide emissions, environmental pressures in the 21st century have encouraged the reversion to higher measures of belite, and consequently belite-rich cements have been introduced commercially by companies such as Lafarge.[99]

Magnesium carbonate cements were proposed by J. Macleod of the East India Company in 1826[100] and Sorel cements based on magnesium oxychloride, developed by Stanislas Sorel in France, have been produced since 1867. But the range of magnesium cements has recently been extended by use of new technologies that produce magnesium oxide based materials such as that patented by Novacem.[101] Also being developed and increasingly adopted is a new generation of alkali activated materials, or geopolymers.

1.21 THE SCIENTIFIC STUDY OF CEMENTS

Market- and production-led improvements in the development of calcareous cements have been underpinned by scientific study. Lea identified three broad areas of study for the cement chemist[102]: (1) the changes that occur in the kiln, the compounds formed and their contribution to the cementing action, (2) reactions during hydration, the nature and properties of new compounds formed and the factors influencing the setting and hardening process; and (3) the physical structure of the set cement and the underlying causes of its physical and chemical properties, and the nature of the bonding action.

Early explanations of these phenomena were highly speculative. Vitruvius, for instance, conjectured 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 adhere thereto, and thence, in drying, binds the stones together, by which sound work is obtained.*[103]

We have already indicated the range of empirical investigation conducted by the likes of Smeaton, Higgins, Vicat and Pasley, and the reliance on physical testing for tensile and, later, compressive strength.

The scientific study of Portland cement gained momentum towards the end of the 19th century with the advent of specialist investigators such as Michaelis (proposer of the colloidal-gelatinous theory), and developed through a number of phases that have been categorised by Professor Hans Kuhl.[104] The first was the era of 'chemical-analytical methods' (pre 1880) in which Portland cement was thought to be a single chemical compound whose constitution could be deduced from analysis. A clear understanding of the composition of cements was achieved, and the quantitative relationships between their constituents, though some structural formulae were advanced that have since been discarded. Meyer's formula, for instance, described the 'Portland cement molecule' as a hexacalcium disilicate containing 18 atoms.

As chemistry absorbed influences from the related sciences of mineralogy and petrography a new approach arose that owed its success to the pioneering use of the microscope by Le Chatelier and Tornebohm, a phase Kuhl calls the period of 'petrographic-synthetic methods', which had its heyday in the 1880s and 1890s. In France between 1882 and 1887, Le Chatelier—portrayed in Fig. 1.19—discovered that clinker contains four principal compounds: C_3S, C_2S, C_3A and C_4AF, and the descriptions 'alite', 'belite', 'celite' and 'felite' were coined by Tornebohm in 1897 after an independent investigation in Sweden. Though it was recognised to be the major constituent, many years passed before agreement on the nature of alite was achieved. Fundamental re-investigation followed 20 years later in the work of the Russian, von Glasenapp, while Assarson and Sundius re-examined Tornebohm's specimens and demonstrated that alite was $3CaO{\cdot}SiO_2$, belite and felite were B-$2CaO{\cdot}SiO_2$ and celite a solid solution. Scientific debate on this issue continued into the 1950s.[105]

Physical chemistry emerged as a distinct branch of science at the turn of the 20th century, and was soon applied to complexities of cement clinker. Initially interest was in the application of the phase rule to the study of heterogeneous systems, the so-called 'Static' period. The pinnacle of achievement in this direction of research was that of the Geophysical Laboratory of the Carnegie Institute of Washington in which the ternary lime-alumina-silica system, fundamental to all cement chemistry, was worked out and described in the classic paper by Rankin and Wright (1915), with the now standard abbreviations introduced by John Johnston. RH Bogue, also of the United States, later published a method of calculating their proportions from an oxide analysis of the cement.[106]

Soon after researchers turned to 'the study of the course of reactions as a result of which Portland cement clinker is formed'—the 'Dynamic' period.[107] Another American, Cobb, typified this approach, studying the reactions that take place when mixtures of lime, silica and alumina are heated. 'He laid a foundation for the later researches of Endell, Nacken and Dyckerhoff on the incomplete equilibria of the ternary system and the cement raw meal of practice …'.[108]

FIG. 1.19 Henri Le Chatelier.

Kuhl concluded his review with an acknowledgement that scientific knowledge can only be advanced by incorporating the use of technical methods such as strength tests, and so termed the period in which he wrote—the early 1930s—the 'synthetical-technical' period.

Scientific study did not proceed in isolation as new organisations emerged to champion research. Numerous laboratories were established in the German-speaking lands during the final quarter of the 19th century, with work sponsored by the German cement and related associations, and undertaken by the new technical universities and government testing stations. Organisations in France and Sweden made significant contributions to knowledge before the turn of the century and, in the USA, the Association of American Portland Cement Manufacturers was established in 1902.

The First World War accelerated research; setting, for instance, was studied by the US Bureau of Standards. In 1916 the newly re-named Portland Cement Association established its research laboratory at the Lewis Institute, Chicago, where Duff Abrams made his fundamental discovery of the water:cement ratio's vital contribution to strength in 1918.[109] Simultaneously, the British Portland Cement Research Association was set up by cement industry interests in the United Kingdom, though the task of researching the material properties of cement had passed to the Building Research Station by the late 1920s, and to the Cement and Concrete Association's research station at Wexham Springs after 1947.

1.21.1 Symposia on the Chemistry of Cement

Much of this newly gained knowledge was shared and advanced at international congresses and the personal links established through them, not to mention the voluminous proceedings published in their wake. The first such congress to be organised by the International Association for Testing Materials was held in Stockholm in 1897. Others followed in Budapest (1901) and Brussells (1906), while the Faraday Society—at the bidding of Bertram Blount, Britain's foremost cement chemist at the time—held an international meeting to discuss *The setting of cements and plasters*. When developments prompted, in 1938, a further meeting was held in Stockholm—at which Sir Frederick Lea was the British representative—and was described as the Second Symposium on the Chemistry of Cements, acknowledging the 1918 meeting as the First. At the time of writing there have been a further 13 Symposia.

1.21.2 Literature

The proceedings from these symposia, while important, are but a fraction of the total literature of cement. Conference papers and other occasional literature abound, as do trade and research journals. Early periodical publishing tended to be through the framework of existing institutions, the ICE's *Minutes of Proceedings*. For instance, then by the newly formed industry associations, such as the VDZ's *Portland-cement and its uses in the building industry* by Busing and Schumann, published on its behalf by Ernst Toesche of Berlin in 1892. Commercial publishing followed and the opening years of the new century saw an explosion in the number of technical periodicals published in the United States, matching the rapid growth of the American cement industry, with titles including: *Cement*, 1900; *Cement Era*, 1903; *Cement Age*, 1904; and *Cement World*, 1907.[110]

While bibliographies such as Spackman's *Some Writers on Cement* (1929) are capable of describing the published monographs on the subject up to the early years of the 20th, and Wecke's *Handbuch der Zement Literature* abstracts of papers to 1925, the academic infrastructure of libraries, abstracting services and databases are required for comprehensive coverage today.

Building Science Abstracts, prepared by BRE between 1928 and 1976, was an exhaustive review of the periodical literature in English, and the *Documentation Bibliographique* (now *Bulletin de Documentation* from ATILH) a similar and more recent service in French. Libraries are maintained by many of the industry's research and representative bodies: VDZ in Germany, PCA in America, and equivalents in, among others, Argentina, Australia, Brazil, Chile, Colombia, France, Japan, New Zealand, South Africa and Sweden. In the United Kingdom the library established by the former Cement and Concrete Association in 1937, and now maintained by The Concrete Society, is one of the world's largest specialising in the subject, and since 1976 has developed a continually expanding database of bibliographical records to reflect the growing literature.

This first chapter has reviewed the history of calcareous cement as yesterday's technology. The development of Portland and other cements, with their application in concrete over the past couple of centuries, has resulted in the technology described in the following chapters. But, as Blezard noted in the 1998 edition, 'today's technology will become tomorrow's technical history'[111] as the development of cements continues to advance, an evolution indicated by the need for successive revisions of this book.

1.22 SOURCES

The approach of this chapter, as rewritten by the present author, is based on the evolution of its predecessors over successive editions: the original Desch and Lea published in 1935—drawing on Desch's earlier book of 1911—Lea's second and third editions of 1956 and 1970 respectively, and Blezard in the fourth (1998). This heritage has helped shape the present work from its title through to its conclusion with an account of the scientific study of cement and resulting literature. Desch and Blezard's identification of 1887 as a key milestone has been retained, as has Blezard's typology of 'proto-', 'meso-' and 'normal Portland'. These earlier versions have been supplemented with other work by Lea (his Aspdin lecture of 1974) and Blezard (1981 and 1998), and updated by reference to John Newman's paper presented as the Sir Frederick Lea Memorial Lecture in 2012.

All of these relied upon a shared corpus of authorities: Pasley (1838), Reid (1877), Redgrave (1895), Davis (1924), Spackman (1929), Thurston (1938), Halstead and Gooding (1952), Skempton (1963) and Francis (1977). Of course the complete literature is much more extensive and for my own research into specific aspects of cement history I have been fortunate to have the resources of the Concrete Society's library at my disposal, of which the following have been consulted.

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