

SCI LECTURE PAPERS SERIES  
**REFLECTIONS ON THE  
HISTORY OF THE  
CHEMISTRY OF CEMENT**

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**(Retired, ex Blue Circle Cement)**

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*This paper was presented by R G Blezard at a meeting of the Construction Materials Group of the Society of Chemical Industry (SCI) at Belgrave Square, London (UK) on 21 May 1998.*

*The paper is dedicated to the memory of Timothy P Lees (1933–1998). Timothy Lees was a long serving member of the SCI's Construction Materials Group and Chairman 1984–1986.*

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*(click image)*

**Frontispiece: Joseph Aspdin's original beehive kilns.**  
*In 1824 he took out the first patent for 'Portland Cement'.*

## **The pattern of reflections**

The history of the use of calcareous cement as a binding medium goes back several millennia. The understanding of the chemistry of cement, however, is very much younger.

The key words in the title of the paper are 'History, Chemistry and Cement', and it is the aim for the reflections considered that all three words are embodied in the ensuing discussions.

For the devotees of Lewis Carroll, I will not be following the advice<sup>1</sup> given by the King of Hearts to the White Rabbit in that one should "*begin at the beginning and go on till you come to the end: then stop*". I will, chronologically speaking, start at the biggest 'milestone' in the understanding of the chemistry of cement. Then, I will review the events that preceded this 'milestone' in technology and then the direction of thought and technology to the present day.

### **1887: The Ransome trials**

I choose to start my reflections at the year 1887. This was a year of failures and success. 1887 was the year of the first trials of the rotary kiln based on the 1885 patent<sup>2</sup> by Frederick Ransome. Among the first of the trials was that at Arlesey near Hitchin (Bedfordshire); the kiln was 26 feet long and 5 feet in diameter. The trial was a failure as were subsequent trials at Barnstone (Nottinghamshire), Grays (Essex) and Penarth in South Wales. The cause of the failures is described by Davis,<sup>3</sup> and a later design by Messrs Hurry and Seaman<sup>4</sup> overcame these defects. The rotary kiln subsequently revolutionised the manufacture of cement clinker both in the quality and the quantity aspect but it did not become a practical manufacturing unit until the early twentieth century. The then recently formed Company, The Associated Portland Cement Manufacturers, purchased certain rights from the American patentees Messrs Hurry and Seaman and proceeded to build a number of rotary kilns at Grays, by the Thames, to produce cement for the Dover Harbour contract.

### **1887: Henry Le Chatelier**

The success of 1887 was the presentation of Henry Le Chatelier's classic doctoral thesis<sup>5</sup>. Henry Le Chatelier (1850–1936) brought to the cement industry a hand of unusual experimental skill, a brain of marvellous perception and a spirit of achievement that placed him at the front of all his contemporaries.

Two years after the death of Le Chatelier, his achievements were publicly honoured in a homage address by Dr R H Bogue at the Second Symposium on the Chemistry of Cements<sup>6</sup> held at Stockholm in 1938. To be precise, the date was Wednesday 6 July 1938 at the end of the afternoon session when Dr Bogue presented his address and I reproduce his speech:

*“Mr Chairman, Gentlemen,  
Cement chemists cannot gather and discuss the problems of cement chemistry without thinking of the man whom we have come lovingly to recognize as the father of cement chemistry, Henry Le Chatelier, formerly of the Sorbonne. Physical chemists generally think of him as one of the great savants of physical chemistry and know him best for his contributions to thermodynamics, particularly, perhaps, for the law that has come to be known as the principle of Le Chatelier. But cement chemists think of him for other reasons. 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 the things with which we are dealing.*

*For these reasons, Mr Chairman, I suggest that we send a resolution to the Rector of the University of Paris indicating the honour and respect with which we hold the name of Le Chatelier. After that resolution has been read by the Secretary I move that we have an unanimous rising vote of approval.”*



**Figure 1. Henri Le Chatelier (1850–1936)**  
(Photo Courtesy of Portland Cement Association, Chicago)

The address to the memory of the late Henry Le Chatelier delivered to the Rector of the University of Paris read:

*“A l’occasion du ‘Symposium on the Chemistry of Cements’ tenu à Stockholm le 6–8 Juillet 1938 sur invitation de l’Académie Royale des Sciences Polytechniques et de la Société Suédoise du Ciment les participants au Congrès, venus d’Allemagne, D’Angleterre, de Belgique, du Canada, du Danemark, des Etats Unis, de Finlande, de Norvège, de Pologne, de Suède et de Suisse, sont heureux d’accomplir un devoir de profonde reconnaissance en rendant hommage à la mémoire du grand savant français...”*

### **Henry Le Chatelier**

*...qui par son génie a tant contribué à la prospérité de la Science chimique et de la Technique en frayant spécialement la voie à la Chimie des Ciments par ses travaux proéminents et fondamentaux.*

*Signed by Axel F Enström (President)  
and W de Shärengrad (Vice President)*

*on behalf of the 2<sup>nd</sup> Symposium of the Chemistry of Cements”.*

Le Chatelier’s publications began in 1882. His work of greatest merit was his doctoral thesis of 1887, which was translated into English some eighteen years later by J L Mack<sup>5</sup> (1905).

His earliest paper postulated the orthosilicate  $2\text{CaO}\cdot\text{SiO}_2$  as the main and only hydraulic constituent of Portland Cement. He noted the presence of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ , uncombined lime and minor crystals. In 1887,  $3\text{CaO}\cdot\text{SiO}_2$  was postulated as the main constituent from the analysis of grappiers but at that time he failed to synthesize it. With limited means of precision measurement available in 1887 he succeeded in discovering and postulating so many points which are today acknowledged to be facts. There cannot be said to be any precise knowledge of the constitution of cement clinker prior to the microscopic examinations of Le Chatelier (1882–1887) and of Törnebohm (1897). Le Chatelier’s examinations (1887) were substantially in agreement with respect to the classification of phases denoted by Törnebohm, alite, belite, celite, felite and an

isotropic residue, but the actual chemical nature of the phases remained a matter of controversy up to the late 1930s with regard to alite and the mid 1940s for the ferrite phase when Swayze's work resolved its constitution.

Alite was considered to be  $3\text{CaO}\cdot\text{SiO}_2$  by Le Chatelier in 1887; this view was confirmed in 1911 by Shepherd and Rankin,<sup>7</sup> and in 1915 by Rankin and Wright.<sup>8</sup> This will be discussed later under the heading of the Alite Problem. Le Chatelier was the first to appreciate that chemical analysis revealed little concerning the nature of compounds formed at high temperatures during fusion and subsequent crystallisation.

Before I leave this reflection I note that Ramachandran's book on thermal analysis (1969)<sup>9</sup> was dedicated to Le Chatelier with the statement... "*as much a pioneer in thermal analysis as cement chemistry*".

Le Chatelier's work laid the foundation for current thinking on cement technology and in Bogue's words he was the father of cement chemistry.

## A chronological review

Having justified drawing a line at 1887 across the chronological table we will reflect on aspects of the chemistry of cement:

- 1 Before 1887
- 2 Post 1887

### 1: Before 1887

There is no point in considering the Lepinski Vir concrete of some 7,600 years ago. It was too friable and its study is essentially in the realm of the archaeologist not the chemist.

Looking at the key words of the paper I reflect that it is interesting to note a historic mural found on a wall at Thebes 2,500 years ago.

In figure 2 we see an early example of lime based cement mixing, and also that the ancient name of Egypt was the land of Khami or Chemi – this being the origin of the word chemistry.

Cement up to the late 18<sup>th</sup> Century was essentially lime-based and incapable of producing an hydraulic binding medium. Lime, by itself, when hydrated is an imperfect cement and in the following section we will review the history of hydraulic cement.

Many industrial processes involving mineral resources received an impetus during the so-called Industrial Revolution, which occurred in Britain during the period 1730–1830. The cement industry was one such industry. Like other developing industries, ideas and discoveries were empirical giving rise to numerous patents. The real technological growth and theoretical understanding came later.



(click image)

**Figure 2. Concrete work in ancient Egypt ca 1950 BC**

*This is probably the first illustration of the use of concrete and is taken from a mural in Thebes. The top of the picture shows workmen filling earthenware jars with water that is then mixed with lime and used as a mortar for stone masonry. Below, a concrete wall faced on both sides with stonework is under construction. Notice the 'site agent', whip on shoulder, keeping a watchful eye on the workers.*

Table 1 gives a chronological list of early workers with calcareous cements showing their involvement up to 1887. Professor A W Skempton produced a classic paper<sup>10</sup> in 1962 entitled 'Portland Cements, 1843–1887' and this is an excellent reference for physical testing of concrete and mortar in Victorian times. In Skempton's paper the significance of 1887 was the second German standard specification of 28 July 1887 and the Swiss specification (which together set the pattern of modern cement specifications) not Le Chatelier's thesis.

Different historians will review the technical growth of the knowledge of cement with different priorities. I suppose if Dr C H Desch had written his reflections on the history of the chemistry of cement it would probably be based on Tables 2 and 3 which I have taken from his 'Chemistry and Testing of Cement' (1911, Arnold)<sup>13</sup> and divided into two parts:

- Pre-1887 (Table 2)
- 1887 and Post 1887 (Table 3)

Dr C H Desch did not mention the events of 1887 viz Le Chatelier's doctorate and the abortive trials of Ransome's patent rotary kiln but the author has included these events in Table 3.

**Table 1. Early workers on calcareous cements**

John Smeaton	1756	published 1791
Brindley Higgins	1780	experiments and observations with the view of improving the art and applying calcareous cements
Bergman	1780	
Joseph Parker	1796	Roman cement 1791 patent No 1806 1796 patent No 2120
Descotels	1813	
L J Vicat	1818	
St Leger	1818	
J F John	1819	
James Frost	1822	British Cement 1822 patent No 4679 1823 patent No 4772
Joseph Aspdin	1824	Patent Portland Cement patent No 5022 (A proto Portland cement) Book on cement (1 <sup>st</sup> Edition 1838; 2 <sup>nd</sup> Edition 1847)
Sir C W Pasley	1838	(A meso Portland cement)
William Aspdin	1845	Later developed chamber kiln
I C Johnson	1851	Doctorate. 'Father' of cement chemistry
H Le Chatelier	1887	
Törnebohm	1897	
G A Rankin and F E Wright	1915	

**Table 2. Developments pre 1887 (after Desch, 1911)\***

1756	Smeaton's researches on hydraulic limes and pozzolanas.
1765	Lavoisier's researches on plaster.
1780	Higgin's book on cements.
1796	Parker's invention of Roman cement.
1796	Lesage's invention of Boulogne cement.
1818	Start of Vicat's researches on hydraulic limes and artificial cements.
1824	Aspdin's invention of Portland cement.
1829	Discovery of cement rock in America.
1829	Fuch's memoir on constitution of cement.
1830	Reinforcement of concrete proposed by J C Loudon.
1838	Sir C W Pasley's book on cements.
1850	First German Portland cement works at Stettin.
1855	First employment of reinforced concrete.
1856	Winkler's theory of hydrolysis of silicates.
1862	Hydraulic properties of granulated slag discovered by E Langen.
1863	Zalkowsky's first paper.
1867	Michaelis's first paper.
1882	Beginning of controversy regarding addition of slag to Portland cement.
1882	Le Chatelier's first paper.
1885	Ransome's invention of rotary kiln.

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**John Smeaton**

My first thoughts are to reflect on the discovery of a hydraulic lime in 1756 by a Yorkshire instrument maker, John Smeaton. Smeaton, as a result of his pioneering structural work was acknowledged as the father of Civil Engineering in England. He was a meticulous worker; he appeared to take nothing for granted and looked at all aspects of a problem.

He was commissioned to build a replacement lighthouse for the ill-fated Rudyard lighthouse (1709–1755) on the Eddystone Reefs which was destroyed by fire. The original Winstanley lighthouse (1689–1703) was washed away in a storm on 26 November 1703.

There was no quick hardening cement in those days and the Eddystone Reefs, some 14 miles off Plymouth, were almost submerged at high water and on calm days the water continuously eddies wickedly around the rocks. The frontispiece of Smeaton's book "Narrative of the Building of the Eddystone Lighthouse" (1791) illustrates the waves breaking over the lighthouse. This picture was based from a sketch by John Smeaton and is also shown in the first chapter of Bogue's second edition of 'The Chemistry of Portland Cement'. Note that Smeaton's book was published 33 years after the completion of the lighthouse and this was done because in the intervening time several people claimed that they had discovered the first hydraulic cement.

Smeaton's experiments in devising an hydraulic cement showed that the best hydraulic raw material was fired impure limestone. He examined limestone from all over the country and in the end he discovered that calcined Aberthaw blue lias stone (from Watchet) produced the best hydraulic lime. The details of the rather empirical test experiments are given in A C Davis's Aspdin centenary book (1924).<sup>3</sup> It is possible that an initial lime-silica reaction was achieved during calcination but the potential durability of the hydrated lime may be questioned.

Smeaton capitalised on this discovery by mixing his calcined Aberthaw lime with a pozzolana, a procedure the Romans had used, but he did not do an in-depth survey of pozzolanas. He did compare a pozzolana with a trass. He was not a chemist and did not appreciate the reactions involved. The primary reaction of any pozzolanic material is an attack on the  $\text{SiO}_2$  framework or  $\text{SiO}_2\text{-Al}_2\text{O}_3$  framework by  $\text{OH}^-$  ions. The  $\text{OH}^-$  ions attach themselves to Si or other network atoms with consequent breaking of bonds between the latter and oxygen atoms. After this has occurred several times the silicate or other oxy anions are detached from the framework to remain in-situ or pass into solution finally producing the ultimate C-S-H structure. Smeaton could not afford a failure and he recognised the need for a clay or silicate content in the calcined limestone to ensure an hydraulic cement. The use of equal proportions of pozzolana with the calcined Aberthaw lime was effective and made sure of a durable bonding agent.

By luck Smeaton found a merchant in Plymouth, who had imported a considerable quantity of Civita Vecchia pozzolana as a speculation hoping to sell it to the constructors of what is now the old Westminster Bridge in London, but the contractors, engineers and commissioners refused to consider it. Smeaton had proved that pozzolana was superior to trass and he now had access to all his required materials.

Smeaton's new hydraulic cement sealed the 1,493 interlocked granite blocks which had been secured by 700 marble plugs. There was a constant spray of seawater over the foundations and

footings, and the surface would never dry out properly. Smeaton's aim was to make a cement that would equal the best merchantable Portland stone in solidity and durability. A hundred years after the building of the lighthouse people began to realise his achievement. Numerous medals and awards were presented to cement and concrete exhibits at the 1851 Exhibition. Smeaton's achievement was celebrated belatedly not on a postage stamp but in a more unique manner. The lime-silica reaction precursor was perpetuated on the humble pre-decimal penny – the Eddystone lighthouse appearing on the left side of Britannia from 1860 until 1970. Smeaton did not patent his cement but his lime-pozzolana mixture for a hydraulic cement was specified for Government contracts and for mortar up 1867, over 43 years after the invention of Portland cement.

### **Joseph and William Aspdin**

The Aspdin story is now well known. Joseph Aspdin (1779–1855) was born in Leeds. He served his apprenticeship as a bricklayer and plasterer, which was a combined trade in those days, and he was aware of Smeaton's work with hydraulic cement. Aspdin experimented with calcareous cement formulations and in 1824 he took out a patent, No 5022, giving a specification for the manufacture of an artificial stone. At this time he was thinking of surface rendering and stucco work, not massive concrete structures. His patent cement was lightly calcined lime with little if any lime-silica reaction. Aspdin called his patented material 'Portland cement' but it bore no relation to the normal Portland cement we use today. One may wonder if he had called his patent material 'Aspdin cement' would it have had the same impact with builders?

Roman cement was greatly used up to 1865, then the modified Portland cement (a harder burnt, meso-Portland cement) gradually superceded it. It was Joseph Aspdin's son William who made the first in depth CaO-SiO<sub>2</sub> reaction by accident. At his Northfleet plant the so-called overburnt clinker (yellow) which had been previously rejected was incorporated into his product. William Aspdin had no chemical training and F Quietmeyer<sup>11</sup> (in 1860) reported that Dr Heinkel had stated that Aspdin had scant chemical knowledge.

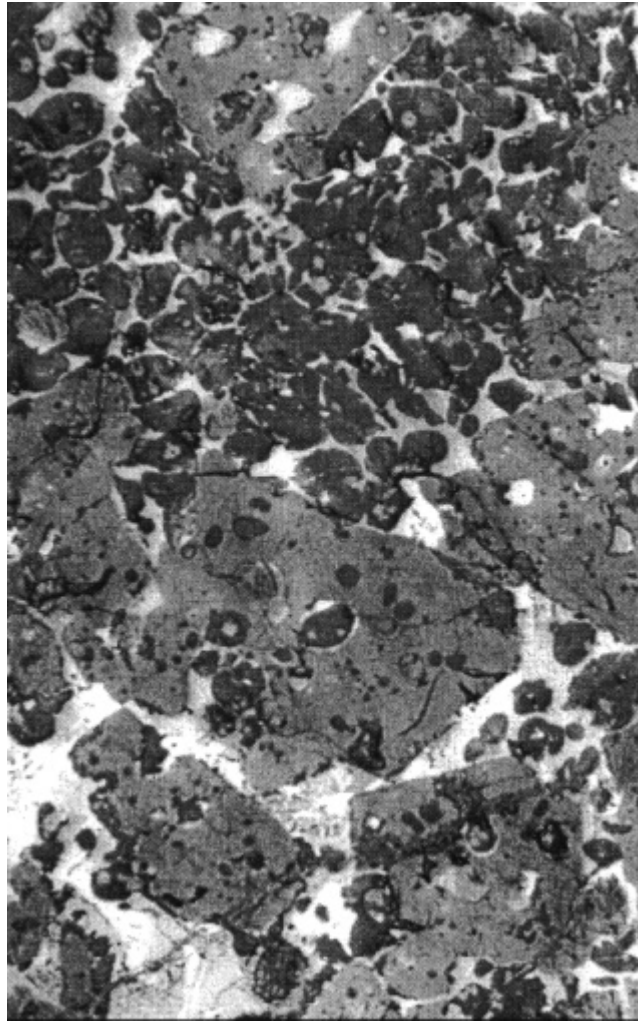
A microscopic examination of clinker coating from Aspdin's kiln at Northfleet (burnt circa 1845) showed that the material had an extremely heterogeneous structure. The microstructure was examined using Ono's micro-mensuration<sup>44</sup> technique, and a typical area examined is illustrated in Figure 3. The huge size of the alite shows that the clinker was burnt very slowly. The minute size of belite shows that the time at a high temperature was short. Probably this clinker was burnt lower than 1400°C.

The wide extent of dark interstitial material shows slow cooling. This is typical of the burning condition of an old vertical kiln. The birefringence of the alite is very weak, less than 0.002, and the alite has minute polysynthetic twinning which looks like microcline and has no zone structure.

The birefringence of belite is very high (0.028); it has a single set of polysynthetic twinning and deep parting and was colourless.

The clinker was burnt at a low temperature with slow heating and slow cooling.





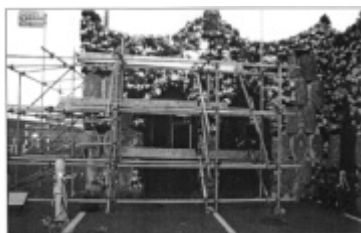
**Figure 3. Photomicrograph of material from William Aspdin's kiln at Northfleet**  
(magnification x 400)

### ***'Ship-on-Shore' Sheerness***

I have discussed the story of 'Ship-on-Shore' before.<sup>12</sup> Briefly, a consignment of Aspdin cement was being transported in barrels aboard the ship 'Lucky Escape' in 1848, and whilst moving down to Thames it ran aground at Sheerness on the Isle of Sheppey. The recovered barrels were used to build an extension to the local public house which was renamed the 'Ship-on-Shore'. A microscopical examination of unhydrated sections of a barrel from the 'Ship-on-Shore' wall showed that it was very similar to the material examined from the kiln coating at Northfleet.

Last September (1997) I visited the 'Ship-on-Shore' again to get further information for this paper and I was surprised to see scaffolding around the wall built with the barrels of Aspdin cement. A vehicle had collided with the wall, so I presume that the hydrated meso-Portland cement may be 'contaminated' with modern normal Portland cement by the subsequent repair

work. A discussion with the landlord produced an old letter from the Science Museum who, in 1976, took as a museum exhibit half of one of the hydrated barrels. The museum informed me that the Museum Inventory number is 1976-444 and it is kept in the museum's reserve collection at the Wroughton site near Swindon, Wiltshire. No chemical or microscopic examination had been made on the Aspdin exhibit at the museum. The dimensions are recorded as being approximately 40 inches in circumference, 15 inches high and weight about 180 lb.



**Figure 4. 'Ship-on-Shore' Sheerness with scaffolding erected for repair**

Professor Skempton's findings on strength evaluation of Victorian cements<sup>10</sup> point to the fact that William Aspdin was the first to discover the necessity for attaining a clinkering temperature and microscopic evidence has confirmed this. Isaac Johnson, unlike William Aspdin, did have some chemical training and his innovations had great influence on the quality of later Victorian cement. Johnson died in 1911 within a fortnight of his 101<sup>th</sup> birthday. Johnson enjoyed a distinguished lifetime in the cement industry. What of the two characters, William Aspdin and Isaac Johnson? They were deadly rivals. Aspdin was a maverick, a roving masterless person whilst Johnson was an honest conventional character. Johnson was religious and an abstainer from drink. Aspdin was the opposite. As men they were as different as chalk is from cheese but isn't that the statement used by Johnson to compare his meso-Portland cement with Joseph Aspdin's proto-Portland cement. For a time William Aspdin always kept one step ahead of Johnson, that was until his luck ran out. William Aspdin died in 1864, aged 48, as a result of a street incident at Itzehoe in Germany.

## **2: Post 1887**

Having reflected on aspects of early cement technology prior to 1887 we move to post 1887 when Le Chatelier 'fathered' the embryonic mineralogical conception of cement, the rotary kiln was conceived and the second German Portland cement standard was initiated. These items were not fully considered by C H Desch (1911)<sup>13</sup> but in the spirit of this paper a chronological list of the developments is given in Table 3.

Gigantic strides in the development of cement technology are reflected in the sequence of International Symposia on the Chemistry of Cement. The reflections of the post 1887 period consider:

1. The origin of cement chemists' abbreviations
2. The alite controversy
3. Journey to Tjuvholmen
4. Aspects of the history of quality control for cement

**Table 3 Developments in 1887 and later** (after Desch 1911<sup>\*</sup>)

1887	Le Chatelier's doctoral thesis
1887	Abortive trials of Ransome's patent rotary kiln
1892	Introduction of tube mills into cement works by F L Smidth.
1895	Hurry and Seaman's invention of modern form of rotary kiln.
1897	Törnebohm's researches on microscopic structure
1897	Newberry's investigations.
1901	Passow's first patent for the treatment of slag.
1903	Richardson's investigations.
1904	First British Standard Specification for cement BS12.
1905	Colloseus first patent for treatment of slag.
1906	Bamber's process for hydration in mill.
1906	Day, Shepherd and Wright's memoir.
1908	Stern's work on microscopic structure.

<sup>\*</sup> reproduced by kind permission of Edward Arnold (publishers)

### **International congresses**

Reviewing the numbered international congresses that are commonly listed at the front of comprehensive reference books on the chemistry of cement one gets the impression that they started in 1918. This is not so! As far as records show, the first international congress was organised by the International Association for Testing Materials and held in 1897 in Stockholm. This was 41 years before the Second Symposium on the Chemistry of Cements held, also, at Stockholm (1938). Since 1897 a number of similar congresses have been organised by the International Association in various capitals.

In 1901, a congress was held in Budapest, with papers presented by Prof H Le Chatelier (Paris), Bertram Blount (London) and other workers. In 1906, the next congress was held in Brussels, with papers presented by Le Chatelier, Blount, Peret and others.

In 1918, difficulties were experienced in inaugurating research into the setting of cement and on 14 January 1918 a meeting of the Faraday Society was held to discuss "The Setting of Cements and Plasters".

In 1938 important developments on the setting of cements had occurred and there was found to be a need for discussions. The ensuing meeting was termed "The Second Symposium on the Chemistry of Cements" and was held in Stockholm. Thus the 1918 meeting of the Faraday Society was acknowledged to be the First Symposium. It is only the Second Symposium at Stockholm, of all the ten congresses that have been held, that has the word cement in the plural form in the English version of the title. All the other nine have the name cement in the singular form.

It was originally arranged that the Third Symposium should be held in Washington in 1948 but in the post war world economic conditions were not favourable for Europeans to travel to America. A decision was later taken to hold the Third Symposium in England in 1952. The Building Research Station and the Cement and Concrete Association acted as sponsors.

The introductory address of the Third Symposium (in London), prepared by Dr A A Bates (and read in his absence by Dr R H Bogue), paid tribute to "*national aspects of genius which shine forth in the history of the developments of Portland cement*" as exemplified in the great names of

Smeaton, Aspdin, Vicat, Le Chatelier, Michaelis and Törnebohm. At the beginning of these reflections I mentioned the speech of homage given at the Second Symposium to Professor H Le Chatelier (6 July 1938). A similar occasion happened at the close of the third session of the Third Symposium when Dr R H Bogue proposed a vote of appreciation to Professor T Thorvaldson for his lifelong service to the chemistry of cement.

There have been, up to date, ten international cement congresses, listed in table 4, and each successive congress updates and adds to the technology of the chemistry of cement.

**Table 4. International cement congresses**

1918	(14 January 1918), Faraday Society – general discussion “The setting of cements and plasters”. Published in Transactions of the Faraday Society ( <u>London</u> , 1918) <u>14</u> , 1–69. [Twenty years later, 1938, it was recognised as the First International Symposium on the Chemistry of Cement].
1938	Second International Symposium on the Chemistry of Cements (6–8 July) <u>Stockholm</u> .
1952	Third International Symposium on the Chemistry of Cement (15–19 September) <u>London</u> .
1960	Fourth International Symposium on the Chemistry of Cement (2–7 October) <u>Washington</u> . Published in 2 volumes.
1968	Fifth International Symposium on the Chemistry of Cement (7–11 October) <u>Tokyo</u> . Published in 4 volumes.
1974	Sixth International Congress on the Chemistry of Cement. <u>Moscow</u> . Published in 3 volumes.
1980	Seventh International Congress on the Chemistry of Cement. <u>Paris</u> .
1986	Eighth International Congress on the Chemistry of Cement. (22–27 September). <u>Rio de Janeiro</u> – Brazil.
1992	Ninth International Congress on the Chemistry of Cement. <u>New Delhi</u> , India.
1997	Tenth International Congress on the Chemistry of Cement. (2–6 June). <u>Gothenburg</u> , Sweden

### ***The system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and abbreviations***

The lime-alumina-silica system (Fig 5) is fundamental to all cement chemistry. The three oxides comprising this basic ternary system form some 90% of Portland cement and over 80% of high alumina cement.



(click image)

**Figure 5. The system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>**

This system was the first ternary oxide system to be worked out and the methods developed in its investigation have since been successfully applied to many other oxide systems. These investigations were made at the Geophysical Laboratory of the Carnegie Institute of Washington and the on-going work produced the classic paper of Rankin and Wright (1915).<sup>8</sup> Many papers have been produced on the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ternary system but this paper, which comprises some 79 pages, is interesting and important in that it introduced the cement chemists' abbreviated formulae. The abbreviated nomenclature first appeared on page 43 and not at the beginning of the paper as one would have anticipated. A later enquiry to the authors found that they did not initiate the abbreviations but that the new notation was requested by an editorial committee. One member of the committee, John Johnston, became so exasperated with the cumbersome mineralogical formulae that he suggested a style of abbreviation that we still use today. After Rankin and Wright's paper the abbreviations were commonly used. In 1915 John Johnston was a member of the Chemistry Department at Yale University, later becoming Chairman of the Chemistry Department and later still the Director of Research of the US Steel Corporation. Johnston used C, A and S as an abbreviation for CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

In 1921, P H Bates (National Bureau of Standards, Washington DC) introduced a different style of abbreviation in his paper entitled "Cementing Qualities of Calcium Aluminates (Technological Paper 197 of the Bureau of Standards 1921). Bates' style was to use 3CA, 2CS, 3CS and 12C7A in place of 'Johnston's style' C<sub>3</sub>A, C<sub>2</sub>S, C<sub>3</sub>S and C<sub>12</sub>A<sub>7</sub> etc, and he continued to use his style until his retirement in 1945. However, Johnston's style appealed to most cement technologists and is now commonly employed in the cement industry today.

Johnston's abbreviation style was extended by later workers.

F for Fe<sub>2</sub>O<sub>3</sub> Portland Cement Association Fellowship (PCAF) Paper No 21. "Calculation of Compounds in Portland Cement" by R H Bogue, October 1929.

N for Na<sub>2</sub>O PCAF Paper No 25 "The System CaO-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>" by L T Brownmiller and R H Bogue, 1932.

K for K<sub>2</sub>O PCAF Paper No 30 "A Study of the System Lime-Potash-Alumina" by L T Brownmiller, March 1935.

M for MgO;

L for Li<sub>2</sub>O;

T for TiO<sub>2</sub>;

H for H<sub>2</sub>O

in "The Chemistry of Portland Cement" First Edition by R H Bogue in 1947.

A limited use of Johnston's abbreviation style has been used by refractory technologists, but Z for ZrO has not been noted in the literature.

### ***The alite problem***

When a new edition of a book is published it is a normal reaction to compare it with the previous edition to assess the changes. In Bogue's first edition<sup>14</sup> of 'The Chemistry of Portland Cement' (1947) Chapter 7 entitled 'The Principal Constituents of Clinker', subsection Tricalcium Silicate, there is (page 111) a topic heading 'The Final Solution of the Alite Problem'. In the second edition<sup>15</sup> (1955) the corresponding topic heading is just entitled 'The Alite Problem'. Something

happened between 1947 and 1955 that caused Bogue to change the topic heading; it was a paper by J W Jeffery<sup>16</sup> presented at the Third Symposium of the Chemistry of Cement (1952) held in London.

To appreciate the alite problem it is best to follow the story from the very beginning. In 1887,<sup>5</sup> Le Chatelier determined the major constituent of Portland Cement clinker to be  $3\text{CaO}, \text{SiO}_2$ . In 1897 Törnebohm<sup>17</sup> gave the name alite to the major constituent of clinker. There then occurred, up to 1931, perhaps the most interesting and prolific controversy on constitution that the cement industry has experienced. The controversy was centred around the question what is alite?

In 1911, Shepherd and Rankin<sup>7</sup> reported results of their phased equilibria studies indicating the existence of  $3\text{CaO}.\text{SiO}_2$  and they inferred that this was identical with Törnebohm's alite.

In 1913, P H Bates reviewed the phase work of Shepherd and Rankin and in 1917 Bates, in conjunction with A A Klein<sup>18</sup> prepared pure  $3\text{CaO}.\text{SiO}_2$ .

In 1912<sup>19</sup> and again in 1915, E Janecke<sup>20</sup> believed that  $3\text{CaO}.\text{SiO}_2$  did not exist and alite was a ternary compound,  $8\text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$ . This may seem odd to us today but Janecke could not produce a binary compound and a reaction was only possible in the presence of  $\text{Al}_2\text{O}_3$ .

In 1924, W Dyckerhoff<sup>21</sup> confirmed the existence of both  $3\text{CaO}.\text{SiO}_2$  and  $8\text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$  but believed that neither of them could be the alite of cement clinker. Janecke, in his earlier work claimed that the ternary compound (Janeckite) had a congruent melting point at  $1382^\circ$  (as did alite in clinker) but Dyckerhoff proved that the congruent melting point did not exist.

In 1926, Dyckerhoff went to America and worked with Bogue's team and their results were published in 1927<sup>22</sup>. A stoichiometric mixture ( $8\text{CaO} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$ ), fused in an oxy-hydrogen flame, produced only a mixture of  $3\text{CaO}.\text{SiO}_2$ ,  $\beta 2\text{CaO}.\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

In 1929, E Janecke<sup>23</sup> considered that  $3\text{CaO}.\text{SiO}_2$ , as synthesized by Hansen, was a mixture of  $\beta 2\text{CaO}.\text{SiO}_2$  and  $\text{CaO}$ .

In 1929 Guttman and Gille<sup>24</sup> separated alite from commercial clinker by centrifuging finely pulverised clinker in liquids of high specific gravity and made a positive identification of the alite fraction as  $3\text{CaO}.\text{SiO}_2$ .

In 1930, Brownmiller and Bogue<sup>25</sup> proved that  $3\text{CaO}.\text{SiO}_2$  was a crystalline phase distinct from  $2\text{CaO}.\text{SiO}_2$  and not a solid solution of  $\text{CaO}$  in  $\beta 2\text{CaO}.\text{SiO}_2$ .

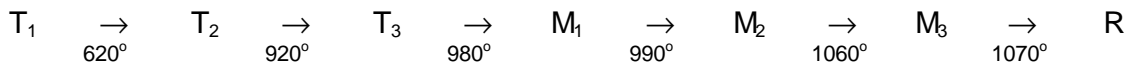
In 1931 Guttman and Gille<sup>26</sup> stated that alite was  $3\text{CaO}.\text{SiO}_2$ .

In 1932 Janecke<sup>27</sup> finally accepted that Hansen's material was  $3\text{CaO}.\text{SiO}_2$  and his earlier work was contaminated with volatilized silica.

Bogue in his 1947 book, under the heading 'The Final Solution of the Alite Problem', thought that the controversy was concluded. But in 1952 J W Jeffery<sup>16</sup> described his 1949 study using large crystals of  $3\text{CaO}.\text{SiO}_2$ , alite produced by R Nurse, and  $3\text{CaO}.\text{SiO}_2$  from basic slag. He

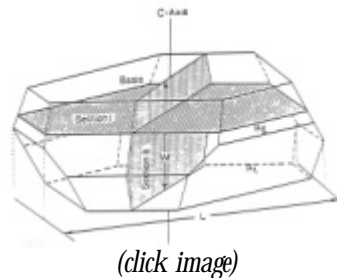
calculated the composition of alite to be  $54\text{CaO} \cdot 16\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{MgO}$  (abbreviated form  $\text{C}_{54}\text{S}_{16}\text{AM}$ ) which was equivalent to 18 molecules of  $\text{C}_3\text{S}$  with two  $\text{SiO}_2$  molecules replaced by one molecule of  $\text{Al}_2\text{O}_3$  and one molecule of  $\text{MgO}$ . So it appeared that whilst the majority of workers were correct in their correlation of  $3\text{CaO} \cdot \text{SiO}_2$  with alite, Janecke was not entirely wrong in attributing a small content of  $\text{Al}_2\text{O}_3$ .

Alite is found mainly as idiomorphic crystals in industrial clinker. Yamaguchi and Ono<sup>28</sup> (1966) have made an extensive crystallographic study of alite. Guinier and M Regourd<sup>29</sup> (1968) made a detailed study of the trigonal rhombohedral form and in 1992 (Ninth International Symposium on the Chemistry of Cement) M Regourd and Boikova<sup>30</sup> made a comprehensive review of the crystal chemistry of alite. Chemical additions may affect the solid solution during clinker burning markedly influencing polymorphism. For pure  $3\text{CaO} \cdot \text{SiO}_2$  the sequence of polymorphic transformations upon heating is as follows:-



Where letters indicate the formal crystallographic symmetry; T= triclinic, M = monoclinic, R = rhombohedral and the subscript numbers designate variants of a particular symmetry. The zoning of works' clinkers was examined by Uchikawa et al<sup>31</sup> (1992). Alite is mostly found as idiomorphic crystals in industrial clinker.

Having described the historical development of knowledge relating to alite it is now fitting that we should illustrate the crystal. The following sketch (Yamaguchi and Ono, 1966) of a single crystal illustrates the principal crystal sections, W and L denote the dimensions necessary to define the crystal size.



**Figure 6. Diagram of alite crystals with principal sections indicated**  
(W and L denote the dimensions necessary to define the crystal size)

Twinning may be observed in Section I of the sketch and Section II shows polarising properties. The optical vector  $\alpha$  is parallel to the C axis and the mineral is optically negative.

The crystal habit shown in the sketch (Fig 6) belongs to the trigonal system with basis and two rhombohedral faces developed. Polymorphic transformations are influenced by temperature and chemical environment. Solid solutions from naturally occurring minerals have been known for many years. Reflecting on the development of our understanding of the nature of alite over the years, we have surely achieved what Bogue described in 1947 as the "final solution". It was not as clear cut as was thought just over fifty years ago. The  $3\text{CaO} \cdot \text{SiO}_2$ , produced in a shaft kiln and

described in 1887 by Le Chatelier, is structurally similar to the alite from the rotary kiln of today, though the solid solution absorption may not be so profound.

### ***Journey to Tjuvholmen***

At the front of both editions of R H Bogue's book 'The Chemistry of Portland Cement' there is a dedication page. It states "*To my colleagues who, in nineteen thirty-eight on the occasion of the Stockholm Symposium on the Chemistry of Cements dedicated Committee Island*

*in the interest of a better understanding and continued co-operation among the scientists of the world.*

*Lennart Forsen, of Finland  
Thorbergur Thorvaldson, of Canada  
Fred Lea, of England  
Stig Giertz-Hedstrom, of Sweden  
Myron Swayze, of the United States of America.*"

The investigation of the background to this dedication revealed an interesting story. In 1897 the author, Jerome K Jerome produced a humorous novel "Three Men in a Boat" but in these reflections we move on 41 years, to 1938 to talk about six men in a boat. The story started in 1936 at the World Power Congress in Washington when four of the delegates (L Forsen, R Bogue, F Lea and S Giertz-Hedstrom), all cement chemists, planned the symposium on cement which then took place two years later in Stockholm.

In 1938 war clouds were building over Europe and a tense atmosphere was detected after the Munich appeasement. On Saturday 10 July 1938, immediately after the ending of the Stockholm Symposium, the five men mentioned in Bogue's dedication travelled to Finland, with Dr Bogue, as guests of Lennart Forsen. Each bought a little fir tree and the six rowed out to a tiny island that had no trees nor any name where each planted his tree and they dedicated the spot "Committee Island".

The next stage in the story was the dedicated page in Bogue's first edition (1947) and then the second edition (1955) of his classic text book. The story, so far, gives no indication of the location of this island and this year, some fifty-one years after Bogue's dedication, I decided to locate the island. This was accomplished with the help of the Concrete Association of Finland (Suomen Betoniyhdistys Finska Betongföreningen).

Committee Island was located about one nautical mile from the harbour of Parainen (also known as Pargas). The Island does have a name, Tjuvholmen, or Tjuven to the local inhabitants, the English translation of which is thief's island. Today Tjuvholmen is an island with small trees and bushes. The Concrete Association of Finland has planned, following the initiative of the author, to check the condition of the fir trees and arrange for a plaque beside the trees telling their history. The location of Tjuvholmen is 60° (17 mins, 10.1 sec) Northern latitude, 22° (18 mins, 50.2 sec) Eastern latitude.



### **Quality**

The early shaft kilns of 1850-1870 produced heterogeneous, meso Portland cement clinker. The chamber kilns of Johnson in the 1880's and the Hilton chamber kilns of the 1890s produced an improved meso Portland cement clinker. Setting characteristics of the hydrating cement was such that there was no need for the incorporation of a retarding component (eg gypsum).

The realisation of the need for quality was slow in Britain. Although the cement made by William Aspdin was contemporarily better in strength than that made by I C Johnson, it was less consistent. Johnson had realised the importance of proportioning his raw meal.

### **Quality – German history**

Despite the steady improvement in quality of cement in the UK from the 1870's, the German cement industry was gaining the reputation for consistent quality. Wilhelm Michaelis (1840-1911) was the founder of German research on Portland cement in chemico-technical aspects. His 1869 book, 'Die Hydraulischen Mörtel', based his treatment of the constitution of Portland cement clinker on the mean chemical composition of 12 cements obtained from various countries, the mean values of the analytical data is as follows:

	<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>CaO</b>
Mean value, %	24.3	7.5	3.3	60.8
Lowest value, %	22.9	5.3	0.5	55.8
Highest value, %	26.0	9.4	6.1	63.2

Despite the rather wide variation in the analytical values of these early shaft kiln cements Michaelis, in 1869, made some initial assessments on the nature of combination of oxides in kiln firing.

The first reported analysis of a Portland cement was in an article by Pettenkofer in 1849 (Dinglers Polytechnisches Journal Vol cxiii, 354–357) – the analyst being a Dr Anton Hopfgartner (Vienna). The lime content of this cement was low (CaO 54.1%) and it was probably a Roman cement. The same analysis was also reported in 'Praktisch Anleitung Zur Anwendung der Cemente' by W A Becker (1869) citing Pettenkofer as the analyst.

Rudolf Dyckerhoff introduced strict chemical control of raw materials in 1871. The oldest research laboratory, Zement und Mörteltechnisches Laboratorium, was established in Berlin in 1872. In 1877 the Association of German Portland Cement Manufacturers (Verein Deutscher Zement Fabrikanten – VDZ) was formed and the first German cement standard was published.

For a more detailed history of the development of the German Portland cement industry I recommend a paper 'A hundred years of German Cement Works Association' by G Wischers<sup>32</sup> and also a paper by W Locher<sup>33</sup>, 'A hundred years of research on the chemistry of cement in Germany' – both papers were published in 1977.

Some 8000 barrels of Dyckerhoff cement, were imported to America in 1884 for the base concrete of the Statue of Liberty in New York. When the statue was 'unveiled' on the 28 October 1886, it became the highest structure on the New York skyline. This was the year before Le Chatelier's doctoral thesis.

### **Quality – English history**

In reflecting upon the development of quality control in Britain, my first thoughts focus on the village in East Yorkshire where I live. Newgate House, Newgate Street, Cottingham was the home of John Hudson Earle in the 1890s. (His son George, later Sir George Earle, was born here 8 February 1890 and he became president of APCM and BPCM). Hudson Earle initiated quality control in his works. British cement manufacturers had been severely handicapped for many years by civil engineers who drew up their own specifications for cement creating a confusing and contradictory situation. In 1898, G & T Earle had the distinction of being the first manufacturer in Britain to publish “Standard Methods of Testing Cement”. It was so well received that two further, enlarged editions were published in 1901 and 1904. These predated the first British Standard for cement, BS12, published in December 1904.

In line with the new approach on quality, John Hudson Earle recorded the trade name ‘Pelican’ cement in September 1897. It is said that walking through St James Park he happened to see the pelicans fed and this reminded him of the rhyme:

*A wonderful bird is the pelican  
His beak will hold more than his bellican  
He can take in his beak  
Food enough for a week  
But I'm damned if I see how the hellican.*

The idea followed that the bird’s great bill was representing an ever-ready receptacle for orders and its lower quarters an untiring grinding mill. The name pelican became synonymous with Portland cement in the north of England until the mid 1960s when, in a major marketing rationalisation, it was superseded by the Blue Circle brand.



*(click image)*

**Figure 7. Title page of Earle’s ‘Standard Methods of Testing Cement’, third edition (1904)**

In 1889 Earle’s established a physical testing house and in 1897 Hudson Earle appointed F S Wood as chief chemist. It was F S Wood and his team that enabled Earles to publish their standard methods.

It is interesting to note that amongst the large committee preparing BS12 (issued December 1904) there was only one chemist – Bertram Blount. Since 1904, and up to May 1996, there have been some fifteen editions of BS12, *ie* fourteen revisions of the original standard. The tenth revision (July 1971) was the first metricated edition.

**Table 5. British Standard 12 Specification for Portland cement (ordinary and rapid hardening)**

First published	December 1904
First revision	June 1907
Second revision	August 1910
Third revision	March 1915
Fourth revision	August 1920
Fifth revision	October 1925
Sixth revision	November 1931
Seventh revision	July 1940
Eighth revision	November 1947
Ninth revision	March 1958
Tenth revision (published in metric form as Part 2)	July 1971
Eleventh revision	June 1978
Twelfth revision	April 1989
Thirteenth revision	November 1991
Fourteenth revision	May 1996

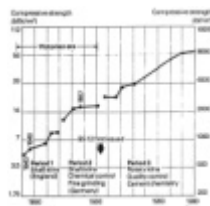
The fourteenth revision came into effect 15 May 1996 having been prepared by BSI sub-Committee B/516/6.

In 1966–67 BSI Panel CEB/1/1/6 comprising six members (two from the Cement Makers Federation, two from independent test houses, and one each from the Building Research Station and the Cement and Concrete Association) who deliberated and produced BS 4550 : Methods of Testing Cement : Part 2 Chemical Tests : 1970. It included both UK and ISO methods. This standard was replaced by BS EN 196-2 (1995) with additional methods in BS EN 196-21 (1992) and BS EN 196-5 (1995).

The progress of technical improvement of Portland cement may be illustrated by the steady increase of 28 day compressive strength in the period 1840–1980 as indicated in Fig 8.

Whilst the quality of German cement from the 1870s to the start of the twentieth century was the highest in Europe one wonders what was the state of the quality of English cement. W Harry Stanger and Bertram Blount addressed a meeting in New York<sup>34</sup> on 23 May 1902 regarding the ‘Proposed Standardisation of Cement Analysis’ and the following is a quote from their paper:

*“...It was not so long ago that the average English cement maker scarcely realised that he was a chemical manufacturer and he was apt to overlook the fact that a properly equipped laboratory under the control of a competent works chemist was the kernel and brain of his undertaking...”*



(click image)

**Figure 8. Stages of technological improvement**

Referring to the American cement industry, which was more quality conscious than the English cement manufacturers in 1902, they continued:

*“...It is peculiarly gratifying to learn that already, in one of the great cement producing countries of the world, the chemist has so completely established himself that he feels the time for self criticism has come, and is prepared to subject his conventional methods to a rigorous scrutiny....”*

This last quotation indicates that American cement chemists had appreciated the importance of collaborative analyses.

### ***Collaborative analytical work***

The function of collaborative analyses is three-fold:

- Validation of a technique
- Method acceptability for a standard specification
- Production of a master sample for method study or a certified reference standard

A report<sup>35</sup> on a meeting of the New York Section of the Society of Chemical Industry, 20 December 1901, entitled ‘A Report of the Sub-Committee on Uniformity in Analysis of Materials for the Portland Cement Industry’ described an early collaborative study. The survey was thorough, the analyses compared and methods evaluated. The survey was instigated in March 1901, 30 analysts were involved, and by 25 September 1901 17 analysts had reported on cement rock, limestone and Portland cement. Amongst the 17, who were mainly from cement works, was W F Hillebrand of the US Geological Survey, Washington.

The best known of all collaborative analytical studies was in the realm of geochemistry where two silicate rocks, G-1 (a granite) and W-1 (a diabase), were analysed by literally dozens of analysts, resulting in two well documented reports<sup>36</sup> in 1951 and 1960.

In 1951–1952 Canada Cement, Montreal involved twelve laboratories in Canada, USA and UK with twelve cement samples.

In the preparation of BS 4550 Part 2 (1970) there was a limited amount of collaborative work between the representatives of the Cement Makers Federation, independent and Government analysts in assessing the validity of the methods examined. For the preparation of BS 4027 (1966) various methods of alumina determination were evaluated before the oxine method was accepted.

In June 1969 the Bureau of Analysed Samples Ltd, issued a certified standard Portland cement, BCS No 372. The original bulk sample passing 124 $\mu$  was approximately 146 kg; the bulk sample was homogenised with mechanical sieving followed by mixing in an electrically powered large cone mixer for a period of time. BCS No 372 was replaced in February 1990 by BCS-CRM No 372/1. The cement from which BCS-CRM No 372/1 was prepared was donated by the British Cement Association; it was graded to pass 75 $\mu$ , and prepared in a similar manner as used previously for BCS No 372. The certified chemical analyses for these samples is shown in table 6.

**Table 6. BCS Certified analyses** (on ignited, 925<sup>o</sup>C sample)

Composition	Sample 372 (%)	Sample 372/1 (%)
SiO <sub>2</sub>	21.30	20.30
Al <sub>2</sub> O <sub>3</sub>	5.35	5.37
TiO <sub>2</sub>	0.33	0.27
Fe <sub>2</sub> O <sub>3</sub>	2.49	3.42
Mn <sub>2</sub> O <sub>3</sub>	0.06	0.074
CaO	65.80	65.30
MgO	1.30	1.31
Na <sub>2</sub> O	0.21	0.10
K <sub>2</sub> O	0.62	0.75
SO <sub>3</sub>	2.35	2.95
P <sub>2</sub> O <sub>5</sub>	0.19	----

Nine analysts were involved in the certification of the BCS samples.

The American National Bureau of Standards issue, in a powder form, ten certified reference materials (eight Portland cement and two high alumina cements) with a colour identification coding. The Portland cements are numbered 1880, 1881 and 1884-1889 with the high alumina cements being numbered 1882 and 1883. There are also three CRM - Portland cement clinker standards intended primarily for the determination of the abundance of major phases in cement clinkers, ie alite (C<sub>3</sub>S), belite (C<sub>2</sub>S), aluminat (C<sub>3</sub>A) and ferrite (C<sub>2</sub>(AF)); these are numbered 8486-8488.

There is a further SRM No 144-p for calibrating air permeability specific surface area meters and the Wagner turbidimetric specific surface area according to ASTM specifications

### ***The development of quality in Portland cement***

In retrospect it is possible to differentiate stages in the development of historic Portland cement through a study of the mineralogical assemblage comprising 'Portland' cements manufactured at different periods (Blezard<sup>12</sup> 1981)). This approach facilitates a classification with the following terminology:

- proto Portland cement:
- meso Portland cement:
- normal Portland cement.

By studying the unhydrated mineral assemblage in mortar using reflected light microscopy, the nature of the original cement may be ascertained.

Proto Portland cement has little evidence of CaO-SiO<sub>2</sub> interaction. Joseph Aspdin's original patent cement may be termed proto Portland cement. Meso Portland cement is an extremely heterogeneous material with definite evidence of CaO-SiO<sub>2</sub>. This is typical of shaft or chamber kiln cement pre-1900.

Meso-Portland cement was first produced at Northfleet in Kent, in 1843, by William Aspdin. Prior to this the so-called Portland cement was proto-Portland cement. Meso-Portland cement was then produced in France (Boulogne) 1853; Germany (Stettin) 1855; Austria 1860; Denmark 1868; Switzerland 1871; USA 1871; Belgium 1872; Sweden 1873 and Holland 1875.

Normal Portland cement, as we know it today, did not appear till the early 1900s as rotary kilns were introduced. It is a quality calcareous cement and consists of a mixture of calcium silicates formed in a molten matrix from a suitably proportioned and homogeneously prepared mixture of calcareous and argillaceous components. Unlike the earlier proto- or meso-Portland cement, normal Portland cement will contain a controlled amount of interground calcium sulphate to retard setting.

As the technical knowledge of normal Portland cement increased, by relating mineral components to performance related properties, special cements for specific applications were devised, and the name 'Portland cement' achieved the status of a generic term.

### ***The development of techniques or chemical analysis***

Cement chemists, as with other silicate chemists, express the elements analytically determined as oxides. For a century prior to the 1950s analytical silicate analysis based on Berzelius group separation procedure did not change much. This was the so-called classical period. Classical methods were slow and were essentially gravimetric techniques. The slowness of classical procedures led chemists to investigate more rapid methods – generally based on physical measurements – colorimetry, flame emission spectrography *etc.* A good review of classical analytical procedures for cement is to be found in SCI Monograph No 18 (1964) entitled 'Analysis of Calcareous Materials'. It also reviews a whole spectrum of state of the art techniques for the early 1960s, based on a two day symposium held 18–19 April 1963.

The philosophy of plant testing and analytical control changed in 1960–1970 from the analysis of period batch sampling to on-line analysis aided by computer control.

One of the slowest analytical techniques was the determination of sodium and potassium by the J Lawrence Smith method<sup>37</sup> (1865) which could take up to 3 days. The flame photometric procedure of Collins and Polkinhorne<sup>38</sup> (1952) with a commercial instrument (EEL Model 100) led the way for an accurate determination of alkalis within a couple of hours.

The development of complexometric methods for lime and magnesia<sup>39</sup> (1963) led the way for inclusion of EDTA volumetric procedures in a later British Standard BS 4550 Part 2 (1970).

Colorimetric analysis (static photometric and continuous flow absorptiometric methods) was a precursor to the more capital intensive X-ray fluorescence methods of the present time, which give rapid analytical data for record and control purposes.

### ***The microstructure of cement clinker***

The earliest work on the microscopy of cement commenced with the studies of Le Chatelier (1882, 1887) and Törnebohm (1897) who used the transmitted light mode. Slowly from the 1920s the use of the incident light technique was developed principally because of the high refractive index or opacity of the cement mineral phases. Polishing procedures and etching techniques were developed. The polishing procedures were based on standard metallographic techniques but to obtain a good polish a medium such as cerirouge (cerium oxide) is used. Etchants for specific phases have been developed<sup>40</sup> but for general study work on Portland cement clinker fabric hydrofluoric acid vapour etching of the polished surface is popular. The earliest illustration of HF-etched clinker that I can recall was an illustration used by T W Parker<sup>41</sup> in 1938 reproduced on a Dufay-Chromex film. Several good references are available for the study of clinker fabric *eg* Gille *et al*<sup>42</sup> (1965) and Hofmänner<sup>43</sup> (1973).

The academic study of clinker microstructure is an important adjunct to the chemistry of cement but from a practical point of view the maximum value of microscopy is only attained when the clinker fabric is correlated with technological anomalies, quality variation or the prediction of potential strength based on crystal characteristics from the kiln firing and cooling regime (Ono 1981).<sup>44</sup>

### ***Cement and chemical societies***

The Society of Chemical Industry has always had close links with industry and cement technology has been included in its involvement. The SCI, founded in 1881, comprises many groups. One of these groups, formed in 1933, was the Road and Building Materials Group, and a history of the first fifty years was given in a paper by D Broome [Chemistry and Industry, 5 December 1983]. In 1989 the name was changed to the Construction Materials Group. The first meeting of the Road and Building Materials Group was held on 8 December 1933. Since then the Group has held many cement themed symposia and meetings and many papers were published in the Journal of the Society of Chemical Industry (last published in 1950) and in Chemistry and Industry (the new format started in 1923).

The Royal Society of Chemistry was also concerned with the progress of cement technology over the years. Three monographs have been published:

- 'Lectures on Cement' by Bertram Blount 1912 (covering lectures given to the Institute of Chemistry 26 October 1911 and 1 December 1911).
- 'Lecture on Cement and Concrete' by F M Lea 1945 (Lecture given to the Institute of Chemistry 19 December 1944).
- 'The Chemistry of Cement' 1966. Lecture Series No 2 by H F W Taylor (Royal Institute of Chemistry).

It is interesting to record that an FIC qualification (now known as FRSC) was awarded by the Institute of Chemistry by examination to J C Blenkinsop on 20 November 1936. This award was unique in so much that it was the only occasion that a Fellowship was awarded in Branch G – Industrial Chemistry with special reference to Cement and Cement Manufacture. Figure 9 illustrates the certificate awarded to J C Blenkinsop. Mr Blenkinsop died in 1998 (a nonagenarian).



(click image)

**Figure 9. FIC certificate awarded to J C Blenkinsop**

## Conclusion

In concluding the reflections on the history of the chemistry of cement I am reminded of the enigmatic observation of an ancient philosopher who stated that “the only thing of permanence is change”.

When we reflect on the change of chemistry involved and the change of scale of working from the early nineteenth century to the late twentieth century we can appreciate the nature of progress. The basket scale operating as used in Joseph Aspdin’s works at Kirkgate in Wakefield with the primitive, handworked, intermittent operation bottle kiln is in strong contrast to the mountain moving machinery with computer controlled, continuously operating rotary kilns of the modern cement industry. There are no relics left of the Aspdin Kirkgate works which was closed in 1838 after a compulsory purchase of the land by the Manchester and Leeds Railway Company. Aspdin’s second works at the nearby Ings Road (Fig 10) operated until near the end of the century. No evidence of the works is to be seen today – the site is now a car wash station.

The cement industry on the north and south banks of the Thames estuary has been decimated. This was the cradle of the Portland cement industry – the source of the meso-Portland cement last century. On the north bank of the Thames all Portland cement manufacture has ceased. The Tunnel Portland Cement Co (West Thurrock), which was set up in 1874, grew and by 1950–1960 had become the largest cement plant in the UK, but in the late 1970s operations ceased. Like the Aspdin works in Wakefield no relics are left but the chalk quarry now houses Lakeside (West Thurrock) one of the largest out of town shopping complexes in the UK.

Yesterday’s technology is today’s history. We see this in the development of the chemistry of cement and these reflections have been considered in this paper. Progress is reflected by change and over the years the approach to quality control has changed with the increased knowledge of the chemistry of high temperature kiln reactions





(click image)

**Figure 10 Portland cement works Wakefield 1843**

Aspdin's second works can be seen through the trees behind the picnic party

## Acknowledgements

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