

LOOKING AHEAD FROM THE PAST: THE HERITAGE OF CEMENT CHEMISTRY

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The Proceedings of the International Congresses on cement chemistry document the important scientific advances in the field. This 12th congress is the latest of a line that stretches back to 1919 (see Table 1).

Table 1 – International conferences on the chemistry of cement

Conference	Place	Year
(1 st) General discussion	London, UK	1919
(2 nd) International Symposium	Stockholm, Sweden	1938
3 rd International Symposium	London, UK	1952
4 th International Symposium	Washington DC, USA	1960
5 th International Symposium	Tokyo, Japan	1968
6 th International Symposium	Moscow, USSR	1976
7 th International Congress	Paris, France	1980
8 th International Congress	Rio de Janeiro, Brazil	1986
9 th International Congress	New Delhi, India	1992
10 th International Congress	Gothenburg, Sweden	1997
11 th International Congress	Durban, South Africa	2003
12 th International Congress	Montreal, Canada	2007

A review of the proceedings of the successive conferences gives a comprehensive view of the development of the field. The large volume of published material in later conferences makes this a challenging task, but an extremely valuable one. I have regularly consulted many of the principal review papers and supplementary communications. In the short time available I would like to review some of the highlights of successive conferences, concentrating more on the earlier ones which may not be as widely available. This view must necessarily be subjective, reflecting my own research interests, but would be duplicated when concentrating on other topics

First International Symposium

The first conference was not designated as such, but a small group of delegates from around Europe gathered in London to participate in “a general discussion” on the setting of cements and plasters. The results were published in the Transactions of the Faraday Society, Vol. 16, pp. 1-68. Among the presentations were papers by Desch, Le Chatelier, Klein and Rankin.

The nature of the setting process was the first great debate of cement chemistry and has been reviewed in detail [1]. On the basis of his work with plaster, Le Chatelier proposed

that setting and hardening was due to the formation of small, elongated crystals of C–S–H which provides a high degree of local cohesion and strength. Michaelis, on the other hand, advanced the theory that it was caused by the dehydration of an initial hydrogel, which was dehydrated as water was consumed by further hydration. Crystallization processes (e.g. CH) only contributed to long term hardening. These two theories, crystals versus colloids, were the subject of intense debate for about 25 years until the first international symposium in 1919. In the end a compromise was reached that there was an element of truth in both points of view. Desch [2] summed it up as follows:

"I think it is very clearly established . . . that we are dealing largely with a difference in terms; that whether one regards the jelly as a mass of extremely minute interlacing particles or not is not of very much importance. At any rate, the essential point is that in the colloidal substance the particles are extremely small, and therefore the surface forces are very important. When you come to crystals of perceptible size, such as the crystallization of sodium sulfate, the surface forces are very small relatively to the forces of cohesion. In the case of the ultramicroscopic particles in the colloid, the surface forces are large in proportion to the forces of cohesion, and when that fact is fairly grasped it is seen that there is no great question of fact at issue between the two views."

Second International Symposium

19 years later the first specifically designated Symposium on the Chemistry of Cements was held in Stockholm in 1938 under the auspices of the Royal Swedish Institute for Engineering research and the Swedish Cement Association. The proceedings were published as a separate volume, but it was not designated as part of a series. At this meeting we can clearly see the elements of modern cement chemistry emerging. Bogue [3] presented an comprehensive paper on the constitution of clinker. He discussed equilibrium crystallization, introducing the Bogue equations, as well as the issues of non-equilibrium crystallization and the formation of glass in some detail. He also provided an extended discussion on the issues of unsoundness caused by expansions associated with periclase, free lime and C₃A.

Equally authoritative was Bessey's [4] summary of the progress that had been made in the systems CaO–Al₂O₃–H₂O and CaO–SiO₂–H₂O. In the former system the major sulfate-free hydrates had been identified and characterized compositionally, whereas in the latter system the confusion around the exact nature C–S–H was very evident even though there was some progress in characterizing crystalline hydrate phases. Linking these two contributions was a paper by Bussem summarizing the contribution of the new method of x-ray diffraction to understanding the structures of both anhydrous and hydrated phases.

Third International Symposium

London was again the site of the third International symposium, now recognized as part of the series started in 1919. The emphasis of this symposium, as judged by the number of review papers, was the composition of Portland cement and its phases (7 papers out

22) and the characterization of special cements (5 papers). The compositional and structural aspects of the principal components were discussed in detail. The proposed compositional model for alite put forward by Jeffery [5] was still referenced 20 years later [6]. It should be remembered that this work, and that on the other cement compounds, predated the advent of microanalysis, but despite this handicap the conclusions drawn were essentially confirmed by later experiment.

Fourth International Symposium

As we come closer to the present day the Proceedings become less historical and more relevant to contemporary work. For me the most significant paper in this symposium is that by Powers on the “Physical properties of cement paste” [7]. This is a condensed, yet comprehensive, version of his classical studies spanning a 15-year period. The quantitative relationships that Powers deduced from classical physical chemistry experiments, without the aid of a definitive description of the hydration reactions or the benefits of modern materials characterization techniques, have stood the test of time and, in recent years have been validated by sophisticated computer modeling.

Also of note in this symposium were the contributions on hydration of the calcium silicates (Brunauer & Greenberg), hydrothermal reactions (Taylor), and kinetics of hydration (Kondo). These were the first major contributions by these leaders of the modern era. However much of the work reported at Washington was largely overshadowed by the seminal work “The Chemistry of Cements”, edited by Taylor [8] and published only two years later.

Fifth International Symposium

As a young researcher starting out in the field I desperately wanted to go to Tokyo to attend this symposium. Although that wish was not fulfilled, it was to be the catalyst to bring me to the United States when the then President of the Portland Cement Association visited New Zealand, and our laboratory, on his way back from Tokyo. The Proceedings became one of my principal reference works for many years. It ran to five volumes, reflecting the increasing amount of research being done in the field, and reported in a much larger number of supplementary papers. (This trend has further developed in later conferences.) Taken together these papers provided a sharp focus on the directions the field was taking in critical areas. There were several reports of microanalysis of cement phases, which has now become a routine tool in experimental work. Easily overlooked was a supplementary paper by Frohnsdorff and co-workers [9], which foreshadowed the computer simulation modelling at NIST 25 years later.

Among the most thumbed principal papers in my copy of the Proceedings was the excellent review paper by Guinier and Regourd on the “Structure of Portland cement minerals”, and Taylor’s “Calcium Silicate hydrates”. Principal review papers by Schwiete and Ludwig [10] and Seligman and Greening [11], together with several supplementary papers, on the crystal structures, compositions and properties of hydrated calcium aluminates and ferrites firmly established the chemistry of the AFm phase in

hydrated Portland cement pastes. It was also at Tokyo that Kondo [12] first introduced his five stages of hydration of C_3S to an international audience.

Another review paper that I found very influential was that by Verbeck and Helmuth [13] on the “Structure and physical properties of cement paste”. This paper was less mathematical than Powers’ contribution in Washington, but offered some intriguing insights into how C–S–H behaved under different environmental conditions. Written discussion to this paper by Feldman and Sereda unveiled their ideas about the structure of C–S–H to a major international audience for the first time. During my first years at the University of Illinois every technical meeting in the USA could guarantee hours of animated debate about the nature of C–S–H and the relative merits of the Powers-Brunauer and Feldman-Sereda models. Twenty two years later Taylor [14] suggested that the two models were not incompatible if “.....*the nature of the gel porosity [in the Powers- Brunauer model] is reinterpreted[to assign] about one third of the gel porosity to the interlayer space, the remainder being microporosity or fine mesoporosity.....The boundary between interlayer space and micropores is ill-defined.*” In recent years modern materials characterization techniques applied to the study of C–S–H have the compositional variability of this phase and elements from both models have relevance in the interpretation of experimental data.

Sixth International Congress

The Proceedings of this conference were published only in Russian, which has reduced its impact upon subsequent research. The English texts of the papers were available only to delegates.

Seventh International Congress

There were several interesting themes developed at Paris. For the first time the rheology of cement pastes was explored in a principal paper by Helmuth, although no communications were presented on this topic. This congress also reported extensively on the many studies to link bulk paste properties with the microstructure of hardened paste and the properties of its constituent hydrates. Principal papers by Sereda, Feldman and Ramachandran and by Wittman highlighted an area of research on the properties of C–S–H that became increasingly important during the 1980s. About 40 communications were presented in this area.

Recent work on the early hydration of cement compounds was a small, but important, part of this conference, beginning an intense effort over the next decade to understand how setting, early hardening and microstructure are controlled by initial hydration. Of note was the use of electron optical and analytical methods to characterize these early processes, and the first presentations by Barret and co-workers on their extensive studies on hydrating suspensions. A principal paper by Skalny and Young [15] addressed the rival hypotheses developed to explain the mechanisms of early hydration of C_3S : the

control of the induction period by either the crystallization of calcium hydroxide or the formation of stable C–S–H. Subsequent work by Nonat and co-workers and by Gartner and Gaidis shows that the latter hypothesis is better able to explain experimental observations [16]. However, stable C–S–H and $\text{Ca}(\text{OH})_2$ both share the Ca–OH octahedral layer as a common structural element, so that yet again disparate viewpoints share some elements of commonality.

Eight International Congress

Several themes that were just touched upon at the preceding conference had a much higher profile in Rio. There is an increasing emphasis on the link between microstructure and properties: the paste–aggregate interface (Massazza), the microstructure of hardened cement paste (Diamond), and pore structure and its influence on transport properties (Feldman). Principal reports on all these subjects were presented together with several communications. Also, more attention was given to the chemistry and physics of deleterious reactions.

Ninth International Congress

An overarching theme at this conference was the sustainable production of cements and concretes, an appropriate theme for a developing country like India with its immense challenges relating to resources, energy and infrastructure. Congress reports covered the use of low grade fuels and and combustible wastes (Alhuwalia and Page), mineralizers and modifiers during clinkering (Moir and Glasser) and energy conservation and environmental control (Sprung and Delort). For the first time we encounter communications discussing silica fume and DSP cements (reactive powder concretes). MDF cements also feature and these new topics were introduced in a Congress report by Della Roy.

A principal report by Scrivener and Weiker on the “Advances in hydration at low, ambient and elevated temperatures” discussed for the first time results from solid state, magic angle spinning NMR spectroscopy to elucidate the evolution of hydration products. It also reviewed the remarkable progress made in characterizing and quantifying microstructure development using a combination of electron microscopy imaging and *in-situ* microanalysis.

Tenth and Eleventh International Congresses

The series returned to Sweden in 1997, but because of the lack of invited review papers giving a broad coverage of progress across the field, this conference has had less impact than others. Nevertheless there were some interesting contributions in submitted papers including several on the new hot topic of delayed ettringite formation.

The eleventh congress took place after my retirement and I was not been able to attend the conference and have not seen the published proceedings. Thus I am not able to offer any assessments on the impact of this Congress.

What will future Congresses report on?

I have been asked to offer my thoughts about will be the future directions in cements research. The only thing that I can confidently predict is that my predictions are most likely to be wrong. We now understand the complex processes of hydration of cement quite well and the application of modern materials characterization techniques are rapidly increasing the level of detail of that understanding. However I see three important areas where progress is already being made and will continue to advance.

The first area is sustainability in concrete construction and here the key is service life prediction, where we will continue to make significant progress. Designing structures for 50-year or 100-year service life is already a reality, although our approach is probably not optimal. Over the past ten years we have greatly increased our ability to probe and predict the internal conditions within hydrating concrete and to appreciate how the external conditions affect this. The relationship of pore structure to transport properties has been a major advance and I think there are similar advantages in relating C-S-H structure quantitatively to properties such as creep and shrinkage. The routine use of supplementary cementing materials, and the development of more complex ternary blends, demands this. While numerical and pixel-based modeling have become powerful predictive tools, there is a need to link these more closely to fundamental structure-property relationships. I don't believe that simple lab-based accelerated tests for durability can ever be a successful strategy and we must employ more sophisticated model-based approaches.

The ability to be able to quantify the extent to which concrete has responded to external conditions is crucial for the assessment of future life expectancy. I consider thermodynamic modeling to be key to this being done successfully and that further progress should be realized reasonably quickly. However, the kinetic aspects of chemical degradation processes have been largely overlooked, as has the relationships between microstructural breakdown and kinetics.

The second area is the need to reduce greenhouse gasses to try to reverse the alarming trends towards global warming that are accepted by an overwhelming majority of the science community. Although the manufacture of cement is now one of the most thermally efficient of high temperature processes it produces large amounts of CO₂ (~1 ton per ton of clinker). We will continue to see more extensive use of supplementary cementing materials to reduce the carbon footprint. I expect to see further development of modified Portland or non-Portland cements, and the pioneering of alternative manufacturing processes that sequester the evolved CO₂.

The third area is the evolution of controlled *in situ* production of concrete using field computers continually monitoring embedded sensors, which report on the progress of hydration and microstructure development. These same computers will predict the expected physical and engineering performance of the concrete for the medium and long term using computer simulation models, which have already been used to design the appropriate concrete mixture. The computer determines, as necessary, any changes to the curing regimen to bring properties back to required values for the predicted service life.

There is also a fourth area that I hope will flower in the future that will allow us to harness cementitious reactions to produce high performance materials using near-ambient processing temperatures. MDF and DSP cements are early examples of this, but this strategy has yet to capture the attention of the materials science community. I believe there is enormous potential in this approach to produce materials for applications where conventional ceramics are used, but where high temperatures are not encountered, but it will up to the next generations of cement scientists to take it to another level.

Whatever happens I can safely predict that the progress in the next 35 years will be as exciting, as stimulating and as challenging as in the past 35 years that it has been my privilege to enjoy.

References

1. RH Bogue, *The Chemistry of Portland Cement*, Reinhold, 1947.
2. CH Desch, Trans. Farad. Soc., 1918-19, **14** 1-7.
3. RH Bogue, Proc. (2nd) ISCC, pp. 59-98, Ingeniorsvetenskapsakademien, Stockholm, 1938.
4. GE Bessey, Proc. (2nd) ISCC, pp. 178-215, Ingeniorsvetenskapsakademien, Stockholm, 1938.
5. JW Jeffery, Proc. 3rd ISCC, pp. 30-55, Cement & Concr. Assoc., London, 1952.
6. FM Lea, *The Chemistry of Cement and Concrete*, 3rd edn/1st Amer. edn, Chemical Publ. Co., 1971.
7. TC Powers, Proc. 4th ISCC, Vol. II, pp. 577-608, Natl. Bur. Stds, Washington DC, 1962.
8. HFW Taylor, ed., *The Chemistry of Cements* (2 vol.), Academic, 1964.
9. GJC Frohnsdorf *et al.* Proc. 5th ISCC, Vol. II, pp. 321-7, Cement Assoc. Japan, Tokyo, 1968.
10. HE Schweite, U. Ludwig, Proc. 5th ISCC, Vol. II, pp. 37-66.
11. P Seligman, NR Greening, Proc. 5th ISCC, Vol. II, pp. 179-199
12. R Kondo and S. Ueda, Proc. 5th ISCC, Vol. II, pp.203-247.
13. G. Verbeck, RA Helmuth, Proc. 5th ISCC, Vol. III, 1-31.
14. HFW Taylor, *Cement Chemistry*, Academic, 1990.
15. JP Skalny, JF Young, Proc. 7th ISCC, Vol. I p. II-1/3, Editions Septima, Paris, 1980.
16. E. Gartner *et al.* in *Structure and Performance of Cements*, 2nd edn., J Bensted and P Barnes, ed., Spon Press, 2002.