Institution: University of Aberdeen

Unit of Assessment: 8 (Chemistry)

Title of case study: International Standards for Portland-limestone cements

1. Summary of the impact

This case study describes the impact on practitioners and services through the development of new international standards based on research at the University of Aberdeen on Portland-limestone cements undertaken in 2004-8. The findings of this research have been adopted into revised international specifications for Portland cement mixtures in the European Union, Canada and the United States. The findings have also been incorporated into an industry standard software package (CEMDATA) for modelling thermodynamic properties of cement mixture, now established as part of the GEMS software suite freely available.

2. Underpinning research

Cement research at Aberdeen began when HFW Taylor was appointed as a lecturer about 1950. A former student of the late J.D. Bernal FRS, Taylor took inspiration from Bernal's polymath approach to science and by demonstrating the application of crystal chemistry and structure to the hydration of cement, gave the subject new directions. Since Taylor's retirement about 1985 this work has been progressed by F.P. Glasser and D.E. Macphee. The importance of the work to science and industry has been recognised by (i) major research projects from the UK Environment Agency (at that time, HMIP and DoE) and the European Union, having as its objective providing a scientific basis for the immobilisation of nuclear waste in cement. This work is frequently cited today and forms an integral part of the safety case worldwide for radioactive waste immobilisation.

The specific example of more recent work which has influenced industry and which forms the basis of this Case Study relates to the use of limestone (calcium carbonate) as a reactive supplement for Portland cement. Since the 1970's, the cement industry has come under increasing pressure to reduce its carbon dioxide emissions: one tonne of Portland cement is responsible for emission of ~850kg CO_2 even with the best available abatement technology. By 1990 it was accepted on the basis of empirical evidence that adding c. 4-6% limestone to cement improved its strength and decreased product permeability. Up to 10-12% limestone by volume could be added without reducing properties to below those of equivalent mixes with 100% cement. The problem was that the evidence was statistical with a reasonable but not totally convincing probability. And it was insufficient to convince many sceptics of the need for change in an industry dominated by prescriptive specifications. Nevertheless, since limestone addition to cement reduces CO_2 emissions due to cement production (discounting the small energy cost of limestone production), the drive for the industry to reduce its CO_2 emissions meant that more convincing evidence for the value of limestone addition was needed.

In 2004 the Glasser group in Aberdeen began a research project dedicated to application of thermodynamics to cement hydration. The group had done pioneering work on the role of calcium carbonate in the hydration process [1]. However the lack of a good database meant that predictions were only semi- quantitative and only a coarse grid of relevant systems could be calculated. In 2003 Glasser successfully applied to Nanocem (a not-for-profit consortium financed by the European cement industry) to sponsor a project aimed at improving and applying a database for cementitious substances. As a demonstration example of the power of the new database and modern computation methods, calculations were undertaken and subsequently verified by targeted experiments, on phase relations in the CaO-Al_2O_3-SiO_2- $CaCO_3$-$CaSO_4$-H_2O system at 0-85ºC. It was highly relevant because the benefit, if any, of adding limestone to cement was being hotly debated at the time.

The calculations showed that the amount of $CaCO_3$ which could react with cement at a particular temperature was quantitatively related to the Al_2O_3/sulphate molar ratio of the cement. Diagrams were devised allowing the optimum amount of reactive carbonate to be predicted from a two-dimensional plot requiring as input compositional data obtained from elemental analysis of the cement. Experimentally, it was shown that the predicted equilibria were attained within a few days. This work was first reported at a conference [2] and in an industrial journal [3], which presented the results and explained the basis of the calculation without thermodynamic details, in a manner accessible to engineers and stakeholders. Two full papers in the journal Cement and Concrete Research then presented the details of the thermodynamic modelling [4, 5]. A subsequent paper has extended the modelling to include temperature dependence [6].

The key outcome of this work is that the addition of $CaCO_3$ can be optimised on a generic basis so as to shift most of the sulphate into ettringite, a low density calcium sulphoaluminate hydrate. This maximises conversion of liquid water to crystal water, thereby also optimising space filling by solids and reducing cement matrix porosity. This enables a win-win situation to be attained: reducing clinker contents, with their high CO_2 liberation, and also improving product durability in a wide range of aggressive service environments.

Such modification of the hydrate phase assemblage has mainly been used in the cement industry to maximise CO_2 reduction by increasing substitution of cement by limestone, while maintaining engineering properties such as strength and porosity, to those which would be obtained in cement-only formulations. This has led the industry to rely less on empiricism and more on science-based approaches to improve cement properties and reduce emissions. Thermodynamic treatments are now routinely being extended to optimise production parameters at the hydration stage.

3. References to the research

1. D. Damidot, S.J. Barnett, F.P. Glasser, D.E. Macphee, "*Investigation of the CaO-Al_2O_3–SiO_2–$CaSO_4$–$CaCO_3$–H_2O system at 25 degrees C by thermodynamic calculation*", Advances in Cement Research 16, 69-76 (2004)
2. T. Matschei, ; F.P. Glasser, D. Herfort,; B. Lothenbach, "*Relationships of Cement Paste Mineralogy to Porosity and Mechanical Properties*," presentation at *International Conference on Modelling of Heterogeneous Materials with Applications in Construction and Biomedical Engineering*, Prague, Czech Republic, 25-27 June 2007
3. T. Matschei, F.P. Glasser, "*The Influence of Limestone on Cement Hydration*", ZKG International 59, 78-86, 2006
4. T. Matschei, B. Lothenbach, F. P. Glasser, "*The Role of Calcium Carbonate in Cement Hydration*", Cement & Concrete Research, 37, 551-558, 2007
5. T. Matschei, B. Lothenbach, F.P. Glasser, "*Thermodynamic Properties of Portland Cement Hydrates in the System CaO-Al_2O_3–SiO_2–$CaSO_4$–$CaCO_3$–H_2O*", Cement and Concrete Research 37, 1379-1410, 2007.
6. T. Matschei, F.P. Glasser, "*Temperature Dependence of the Mineralogy of Portland Cement Paste in the presence of Calcium Carbonate*", Cement and Concrete Research 40, 763-777, 2010.

4. Details of the impact

The impact of the research undertaken at Aberdeen relates to practitioners and professional services, where professional and industry standards have been informed as a result of research findings. As stated by Professor R. D. Hooton, a world-leading contributor to the cement and construction industry in Canada: *"… the Chemistry Department at the University of Aberdeen has made the biggest contributions globally to our understanding of both hydration of cements and fundamental understanding of durability of cementitious materials for use in concrete*" [a].

The key outcome of the particular research project as described was to inform international standards beyond the EU. As verified by the Portland Cement Association, the industry trade association for North America, "*in the last several years, the US cement industry has made significant progress in its continuing efforts to improve the sustainability of the built environment, and a key component of that effort has been the development of specification requirements for Portland-limestone cements. After several years' effort, in 2012, US blended cement specifications were revised to include cements with up to 15% limestone. While other research has gone into this effort, a key component of the rationale supporting changes to both sets of specifications was results of your (Glasser) research related to the reactions that limestone undergoes during cement hydration, their volumetric changes, and the thermodynamic stability of the resulting phases. We continue to use the results of this research in the on-going educational efforts with specifiers, architects and engineers…*" [b]. Dr Kosmatka further clarifies the overall economic impact implied by the benefits derived from this research: "*It is difficult to estimate the economic impact of these changes for the concrete construction industry in the US. A roughly 10% saving with regard to CO_2 and other emissions and energy has made the industry more efficient as well as more sustainable, both of which help the competitiveness in the roughly $19 billion (US) cement industry*" [b].

The impact of Glasser's work on the North American cement industry is further supported by Al Innis, Vice President of Holcim (US), who states "…*The work you have done on limestone cements has been a key component in having the US standards accept blended cements containing up to 15% limestone. This change in standards gives our industry and Holcim (US) in particular the opportunity to provide our customers a higher quality product with a lower carbon footprint…"* [c].

In addition, to confirmation of new standards in the USA, specifications in Canada have also been developed. As Professor Hooton confirms: "*The work by Matschei, Lothenbach and Glasser has been important for the understanding of Portland-limestone cements that led to their adoption in cement specifications in Canada (CSA A3000) in 2008 and in the USA (ASTCM C595) in 2012. The use of these cements is now incorporated into the Canadian building codes, and their use is increasing*" [a].

Limestone addition to cement contributes to properties through three mechanisms: particle packing effects which reduce water demand, nucleation effects which accelerate hydration reactions, and production of carboaluminate phases which reduce porosity. According to a 2011 State of the Art Report from the Portland Cement Association, Glasser's work "*provided quantitative calculation of the phases that may be present…… a great step forward in understanding these systems"* [d]

The thermodynamic models derived from the research have now been incorporated into the GEMS suite (***G****ibbs* ***E****nergy* ***M****inimization* ***S****oftware for Geochemical Modelling*), originally developed by the Swiss Nuclear Organisation, and now managed by the Paul Scherrer Institute. Explicitly the research work has been fundamental to the CEMDATA07 database, included in the GEMS TDB software package (*GEMS* ***T****hermodynamic* ***D****ata****B****ase*) [e]. Empa, who co-supervised the research project, confirm that the Aberdeen research was a fundamental component to the cement database "*was published in 2007-2009 and based on work carried out at Empa (Lothenbach et al., 2008; Möschner et al. 2008, 2009; Schmidt et al. 2008) and a PhD carried out* *both at the University of Aberdeen and at Empa (Matschei et al, 2008*)" [f].

In overall terms, the economic benefit is hard to calculate, although the saving in CO_2 emissions is more straightforward. The world production of Portland cement is about 3 x10^9 tonnes per year. If one third of this production uses 10% limestone replacement, and assuming production in efficient equipment, the net saving in CO_2 emissions is of the order of 85 million tonnes per year. From this has to be deducted the energy input of quarrying and grinding limestone, but this is comparatively low (only a few million tonnes per year), Thus a reduction of the order of 80 million tonnes per year carbon dioxide emission is achieved, with considerable scope for greater reductions still realisable as the process continues to gain traction.

The International Energy Agency (IEA) has proposed strategies to reduce global CO_2 emissions by 52% from 2007 to 2050 [g]. The so-called Blue Map Scenario places different requirements on different sectors of the global economy. The cement industry is required to reduce its CO_2 emissions by 22.5% from 2007 to 2050. Limestone substitution in Portland cement at levels now shown by this work to be safe and reliable will achieve around 1/6th of the 450 million tonnes per year reduction in CO_2 emissions required.

Furthermore, the success of this project has led to financial support for bolder and more radical initiatives for reducing CO_2 emissions from the cement industry. The Qatar Foundation has awarded a US$5.3M grant to the University of Aberdeen (together with the University of Dundee) to investigate further reductions in the CO2 input to structural concrete and increased functional performance of products. This project, which commenced in September 2012, is focussed on indigenous Gulf region resources. The project has at its heart development of two novel cements: one being a low carbon-input cement base of calcium sulphoaluminate, and a second carbon-negative cement type.

5. Sources to corroborate the impact

a) NSERC/CAC Industrial research chair in Concrete Durability & Sustainability, University of Toronto, Canada.
This source corroborates the impact of the research findings towards the development of new cement standards in Canada

b) Vice President Research & Technical Services, Portland Cement Association, Illinois, USA
This source corroborates the impact of the research findings on the international cement industry, including reference to adoption in cement standards in Canada and the USA

c) Vice President for Quality and Product Performance, Holcim (US) Ltd.
This source corroborates the application of research findings and the impact to an international manufacturer of cement products

d) "State of the Art Report on the Use of Limestone in Cements at Levels up to 15%", P.D.Tennis, M.D.A.Thomas, W.J.Weiss, Portland Cement Association 2011 *(Chapter 2, pp11-16, relates to and cites Aberdeen research)*

e) Paul Scherrer Institute, Villigen, Switzerland: http://gems.web.psi.ch/publist.html
The GEMS website explicitly refers to the Aberdeen research publication (2007) in its Publications of Collaborators and Developers of Specific Databases

f) Empa, Switzerland: http://www.empa.ch/plugin/template/empa/*/62204/---/l=1
This site explicitly refers to the Aberdeen contribution to the CEMDATA07 database.

g) *"Energy Technology Perspectives 2010, Scenario and Strategies to 2050",* International Energy Agency Paris, ISBN: 978-92-64-08597-8
This source corroborates the impact of cement production on greenhouse gas emissions, and the impact of greenhouse gas reductions from a change in manufacturing processes.