Construction materials and structural technologies at the Institute for Research in Construction

Mitchell, L. D.

Publisher's version / Version de l'éditeur:

Proceedings of the Joint NSC-NRC Workshop on Construction Technologies: 26 April 2004, Taipei, Taiwan, pp. 1-10, 2004-04-01

Construction materials and structural technologies at the Institute for Research in Construction

Mitchell, L.

NRCC-47057

A version of this document is published in / Une version de ce document se trouve dans :
Proceedings of the Joint NSC-NRC Workshop on Construction Technologies, Taipei, Taiwan, April 26-27, 2004, pp. 1-10

CONSTRUCTION MATERIALS AND STRUCTURAL TECHNOLOGIES AT THE INSTITUTE FOR RESEARCH IN CONSTRUCTION

Lyndon MITCHELL[1]

ABSTRACT

A variety of projects and topics are under investigation within the cement-based materials group. The paper describes some important aspects of the work and then focuses on one project. The group has various tools and instruments to help achieve its goals. These include X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and thermal analysis, they are briefly described.

Quantitative phase analysis of cement using XRD using Rietveld analysis techniques will be discussed with emphasis on determination of amorphous content. The discussion concludes with suggestions for joint Taiwan-Canadian research projects, including the fire performance of high strength concrete and blended cements for climate change.

Keywords: *Concrete, Materials & X-Ray Diffraction*

INTRODUCTION

The study of cement and concrete science can be traced back to 1824 when J. Aspdin first manufactured modern Portland cement. In 1882 the famous French industrial scientist, Le Chatelier, published one of the first papers on its setting mechanism (Le Chatelier 1882). Since this paper the literature revolving around cement and concrete products has escalated exponentially, as has the production of Portland cement. Production has risen from 62.4 million tonnes in 1926 to 1.6 billion tonnes in 2000.

The Institute for Research in Construction (IRC) was established in 1947. Since that time the Institute has dedicated its work to safe and durable construction practises and concrete research has played a significant role. Early studies of concrete corrosion, in particular sulphate attack, led to the development of Type 50 cements (Mackenzie and Thorvaldson 1926; Swenson and Mackenzie 1968). Later work on alkali-aggregate reaction led to the first documented case of alkali-carbonate reaction (Swenson 1957), and advances in the knowledge of alkali-silica reaction (Grattan-Bellew 1987). This work still continues (Mitchell et al. 2004).

Previous work on the structure of CSH, the main binding phase of Portland cement, has lead to the publication of a structural model (Feldman and Sereda 1970).

More recent work has lead to the invention of conductive concrete (Pye et al. 2003) and the publication of several books (Ramachandran et al. 1981; Ramachandran et al. 2003; Ramachandran and Beaudoin 2000). Representatives from the materials group joined forces with the NRC's conference services office and the Palais de Congres de Montreal to successfully bid on the hosting of the 12th International Congress on the Chemistry of Cement (ICCC). This congress will be held in Montreal, Canada, in July 2007.

[1] *Research Officer,* ***Institute for Research in Construction, National Research Council Canada, email:Lyndon.Mitchell@nrc-cnrc.gc.ca***

FACILITIES

The group has direct access to a variety of advanced and routine characterization techniques. A list of the major equipment operated by the group is given in table 1. This equipment would be utilized as part of an international collaboration or partnership. A successful international collaborative project will build on the complementary strengths of the partners.

Table 1. Table listing prominent equipment

Description	Make and Model	Comment
X-Ray Diffraction	Scintag XDS 2000 (See figure 2)	Cu K alpha Radiation
X-Ray Fluorescence	Bruker AXS S4 Pioneer	Analysis of elements C through to U
Thermal Gravimetric Analysis	TA Instruments Q600 (See Figure 1)	Up to 1500°C Simultaneous TGA/DTA
Scanning Electron Microscopy	Hitachi S4800	Field Emission Gun electron source with EDS. Resolution to a few nanometres
Fourier Transfer Infrared Spectroscopy	Bomem MB100	Transmission, Photoacoustic, Attenuated total reflectance & solution spectroscopy
Atomic Force Microscopy	Jeol JSPM 5200	Low temperature & vacuum stages
Rheometer	Paar Physica MRC500	Low & High temperature vessels

The group, has a strong analytical base and access to both Institute and Council wide facilities. Cross-institute and council collaboration and co-operation is generally encouraged.

CURRENT PROJECTS

NANOMATERIALS

The profile of nanotechnology is growing and promises to be a key area of cross disciplinary research over the next 20 years. Major capital investment for nanotechnology is being approved both here in Canada and around the world. The construction industry has been identified as a large potential market. This would appear to be a fruitful topic of collaboration.

IRC has initiated a multi-researcher project to develop new technologies and products for the construction industry based on nanotechnology, with an emphasis on cements, cement-based products, admixtures and concretes. Cement is the most widely used construction material, making concrete and cement nanotechnology particularly important to the industry. Initial research has focused on the synthesis and use of reactive/non-reactive nanoparticulates; Figure 3 shows nanoparticulate monocalcium aluminate synthesised using “Chimie Douce” methods (Mitchell et al. 2002; Mitchell et al. 2003). The roles of nanoparticles in cement binders, novel investigations into layered materials (Raki et al. 2004), and new approaches to concrete reinforcement (Makar and Beaudoin 2003) are also areas of current study.

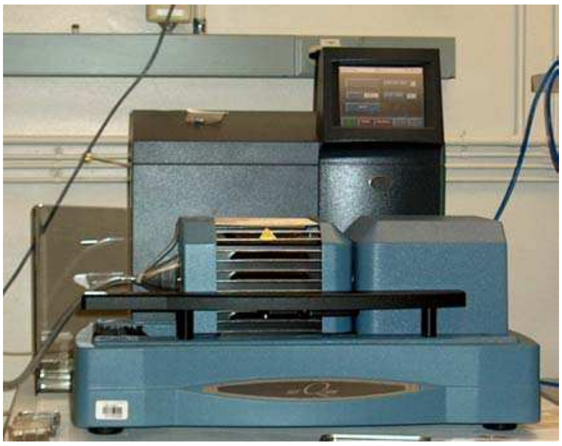

Figure 1. TA Instruments Q600

Figure 2. Scintag XDS 2000

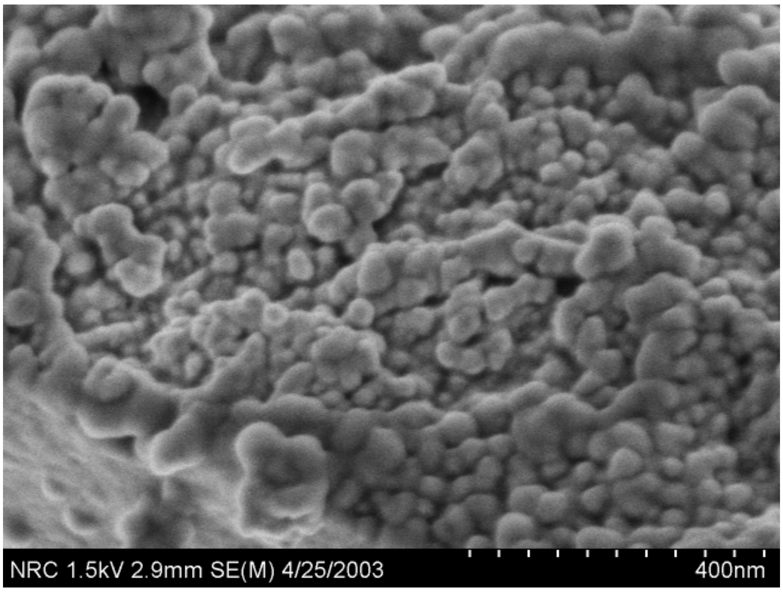

Figure 3. Nanoparticulate Monocalcium Aluminate Synthesised using "Chimie Douce" methods

ALKALI AGGREGATE REACTION

Alkali-aggregate reaction is a chemical reaction between certain types of aggregates and hydroxyl ions (OH-) associated with alkalis in the cement (1998). Usually, the alkalis come from the Portland cement but they may also come from other ingredients in the concrete or from the environment. Under some conditions, the reaction may result in damaging expansion and cracking of the concrete. Concrete deterioration caused by alkali-aggregate reaction is generally slow, but progressive.

In Canada, cracking due to alkali-aggregate reaction generally becomes visible when the concrete is 5 to 10 years old. The cracks facilitate the entry of de-icing salt solutions that may cause corrosion of the reinforcing steel, thereby accelerating deterioration and weakening a structure.

The best method for preventing premature deterioration of concrete due to alkali-aggregate reaction is to use aggregates that have a proven history of good performance in concrete, or have been shown by laboratory testing to be non-problematic.

Another method for minimizing the potential for expansion due to alkali-silica reaction in concrete is to replace a portion of the portland cement with a supplementary cementing material. Low-lime fly ash, ground granulated blast furnace slag, silica fume, metakaolin and natural pozzolans used in the appropriate quantities have been found to be an effective antidote for alkali-silica reaction.

In recent years much international effort has gone into demonstrating that the addition of lithium salts to concrete prevents or minimizes expansion due to alkali-silica reaction. Recent work at IRC has been aimed at investigating the mechanisms of this effect (Mitchell et al. 2004).

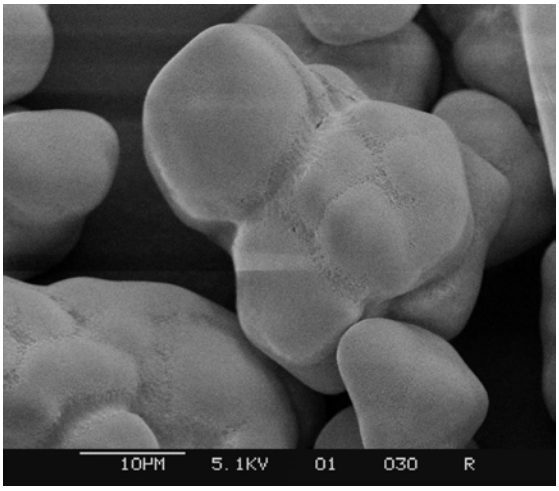

Figure 4. Opal after 28 days in $Ca(OH)_2$ and KOH (2000x magnification)

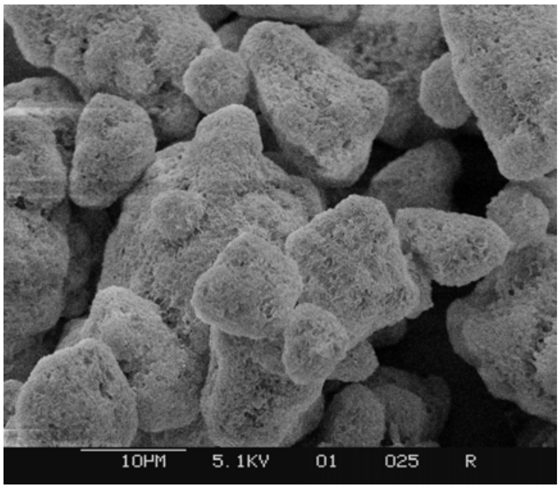

Figure 5. Opal after 28 days in $Ca(OH)_2$, KOH, and LiOH (2000x magnification)

Figure 4 shows the microstructure of opal (amorphous silica) after reaction with 1M potassium hydroxide for 28 days. Figure 5 shows the corresponding microstructure after reaction with 50:50 potassium hydroxide and lithium hydroxide. The particulate microstructure on reaction with potassium hydroxide is a smooth and rounded surface, with significant agglomeration. In contrast, the material reacted with blended potassium and lithium hydroxides appears to contain angular particles with a porous surface. This porous surface seems to inhibit agglomeration.

CLIMATE CHANGE & SUSTAINABILITY

As part of their five year strategic plan the IRC has created an initiative on sustainability. Sustainability has been defined by the World Commission on Environment and Development, (Brundtland Commission) 1987 as being "…..Development that meets the needs of the present without compromising the ability of future generations to meet their own needs……"

Many things we do affect the environment around us and it is impossible to construct a building without having some environmental impact on the world's environment. So architects, engineers, owners and developers are shaping the future of our communities. They have a responsibility to design and select materials and systems that will provide a durable foundation for sustainable communities. Materials choice can make a major impact on green building design. A full-life cycle assessment (LCA) must be undertaken when determining which material to select. Consideration must be given to extraction, processing, transport, construction, operation, disposal, re-use, recycling, off-gassing and volatile organic compounds (VOC) associated with the material.

Every 1 tonne of cement produced, produces 1 tonne of CO_2 (1998). For the year 2000, cement production accounted for ~1.6 billion tonnes representing equivalent levels of CO_2 by-product. Recently the climate change and sustainability communities within the construction industry have been focusing on the use of supplementary cementing materials (SCM) as a means of reducing green house gas emissions. The principle behind use of SCMs is that by replacing a fraction of the cement used in concrete with a SCM, a significant impact on CO_2 production can be realised. The concrete sub-program is leading a technology transfer project to explain the benefits and hazards of using SCMs. The project will create a website, and is funded by the Government of Canada action plan 2000 on climate change.

The IRC is also leading a project called "The Laurier Tache Car Parking Garage Phase Two – The East Wing" to address some of these issues. The primary aim of this work is to develop and test new concrete technologies in the laboratory and then transfer that knowledge to the field. In parallel with the materials installation a sophisticated embedded instrumentation grid will also be installed. Monitoring over a 5-year period will commence with the collected data being incorporated into a life cycle analysis prediction tool.

Five types of sensors are to be installed at the Laurier-Taché Parking Garage.

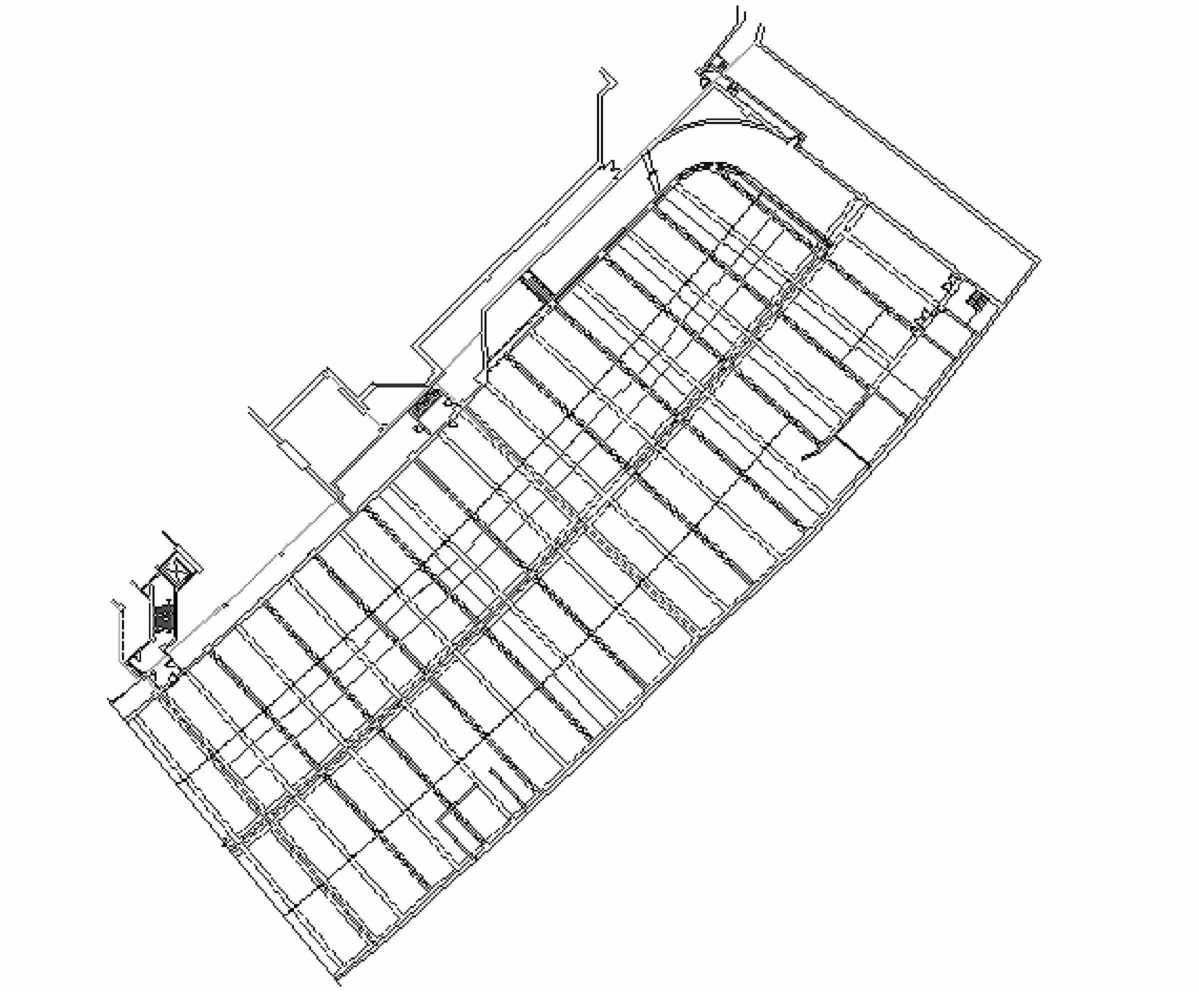

Figure 6. Drawing S221 from the Harmer Podolak Specification document (66% submission). Phase 2 Level P1 of the Laurier Taché car parking garage

<u>Sensor types:</u>

1. Weldable strain gauges on reinforcement (movement within the steel)

2. Manganese Dioxide Reference Electrodes in proximity to reinforcement (corrosion of the steel)

3. Relative humidity and temperature sensors embedded in concrete

4. Vibrating wire strain gauges, embedded in concrete (movement within the concrete)

5. Vibrating wire strain gauges, surface mounted on concrete (movement within the structure)

The cabling for these sensors will be routed through metal conduit in line with the safety regulations enforced in the garage. They will then run along the ceiling of the structure to the datalogger.

A successful outcome to this project would be the creation of a life-cycle analysis model for high-volume fly ash concrete, and the adoption of this model by Public Works and Government Services Canada (PWGSC).

PWGSC manages the real estate assets of the Canadian Federal Government, and are the largest property-owner in the world. The adoption of high-volume fly ash by this organisation would result in significant CO_2 savings.

HEAVY METAL IMMOBILISATION

Most hazardous waste is disposed of in expensive, specialized landfill operations. Stabilisation of materials to make them suitable for conventional landfill is an option, but the use of waste materials that have been rendered safe in value-added products is very attractive. Most current hazardous waste recycling uses high temperature techniques, notably vitrification, that transforms waste into durable and environmentally safe products. Vitrification has many advantages, including high volume reduction, destruction of organic compounds, immobilization of a wide range of oxides, etc. However, it does have a number of limitations:

1. A general intolerance of glasses for sulphur and chlorine
2. limited solubility of some oxides
3. loss of volatile metals during processing
4. high processing costs

Alternative ceramic processing routes have been examined for the treatment of waste. Certain mineral structure-types are known to be resistant to leaching of heavy metals. Such geo-mimics can provide a matrix for high concentrations of toxic metals that are potentially stable over geological timescales. A related process is the use of zeolite materials to trap metal ions within an aluminosilicate matrix before reaction at low temperatures (40-60ºC) to produce an amorphous 'geopolymer' (Raki 2004). This approach is particularly well suited for volatile heavy metals such as lead and cadmium, that can be lost during high temperature processing.

This project studies encapsulation of various metal ions in geopolymer materials, using natural alumino-silicates as reactants. The products are then studied using a variety of techniques to study the structure and stability of the geopolymer matrix to environmental degradation and leaching.

Collaborative project with Singapore

As part of an international collaboration with Singapore, the concrete subprogram will be working with researchers from the NRC's Institute for Chemical Process and Environmental Technology (ICPET) to turn a hazardous waste into a usable construction product.

Disposal of garbage is a worldwide problem, and involves the use of methods such as landfills or incineration. In densely populated places where space is at a premium, incineration is often the most popular solution. In some cases, such as in Singapore, it is the only solution.

But, incineration does not mean complete waste elimination. Facilities are forced to deal with the substantial accumulation of fly ash, lightweight particles entrained in the gases released during burning. Fly ash, which collects in the flues of incinerator smoke stacks, is classified as a hazardous material because of the range of heavy metals it contains, making disposal difficult and expensive. Chances for safe disposal, and even reuse, are much more promising if the toxic metals can be trapped in stable synthetic "rock-like" materials made from other non-hazardous minerals also found in the fly ash. The NRC-Singapore research project will focus on creating these new materials.

The project, which will begin in the next few months is made possible through an Memorandum of Understanding (MOU) between NRC and the Agency of Science, Technology and Research of Singapore, known as A*Star. Under the agreement, both sides provide funding for joint collaborations. Over 10 different NRC research institutes are currently involved in research projects under the agreement, which commenced in 1997.

QUANTITATIVE PHASE ANALYSIS OF CEMENT

Powder diffraction techniques for the analysis of cements and cement clinkers have been used for many years (Taylor et al. 2002). The emergence of the Rietveld method as a practical tool for quantitative analysis has allowed the study of increasingly complex systems. The recent advent of convolution-based profile fitting has brought this powerful technique to the verge of being a routine analytical tool for cement quality control.

However, in common with the more common diffraction techniques, Rietveld analysis only yields information on the crystalline phases present in the material. The possibility of significant amorphous content in a cement or fly ash cannot be ruled out, and this material may have a profound effect on the physical and chemical properties, e.g. the glass content in fly ashes.

The Rietveld method may be used to determine amorphous content by spiking the sample with a known quantity of a standard material. The difference between the calculated and known quantity of the standard material yields the amorphous content. The approach has many potential problems with regard to technique and sample preparation, and its application to systems as complex as cements and clinkers has only recently been reported (Suherman et al. 2002; Whitfield and Mitchell 2003). The potential benefits in knowing the amorphous content of a material are numerous, and as such, it is therefore worth expending considerable effort in developing these techniques.

Evidence published in 1937 by Lerch and Brownmiller (Lerch and Brownmiller 1937), indicates that cement clinkers can contain significant amorphous contents up to ~28%. In the context of modern-day quenching of clinker by forced-air cooling, this should not be surprising. Lerch and Brownmiller obtained their results by careful and skilful use of calorimetric techniques that would be rarely found in the modern laboratory. A study using a standardless X-ray technique known as the Ruland method, described a large variability in amorphous content for laboratory-produced single cement-phases (Yang 1996). Another paper stated a value of 19% for the amorphous content of monoclinic C_3S using the Rietveld method (De La Torre et al. 2001).

A study was undertaken to apply the Rietveld method of determining amorphous content to clinkers and ultimately cements. The experimental procedures used are explained in Whitfield and Mitchell (2003). An example of the diffraction data and the fitting obtained using the Rietveld method is shown in Figure 7. The raw results for this sample and the derived results for the cement are shown in Table 2. They show an amorphous content of 18% for the cement, which is consistent with the results previously obtained (Lerch and Brownmiller 1937; Suherman et al. 2002).

In order to test the validity of the results, a number of samples were prepared with an additional spike of an amorphous slag, as well as samples known to be highly crystalline. The cements spiked with slag yielded results as expected given the previously calculated amorphous content of the unspiked cement, as shown in Table 3. In addition, the alumina sample analysed did indeed yield low amorphous content, as one would expect.

This work has demonstrated the feasibility of using advanced X-ray diffraction techniques to determine the amorphous content in materials as complex as cements and clinkers.

FUTURE RESEARCH

Potential projects of interest include 1) development of various intumescent coatings for fire protection of concrete structures and 2) blended cements for climate change.

The first project, the study of high strength concrete's fire performance, would involve a number of IRC researchers and two programs: Building Envelope and Structure, and Fire-Risk Management. The project would involve designing concrete and concrete coatings for use in public areas, such as tunnels and subways. These types of structure require materials with non-toxic fire retarding properties to allow extended human evacuation times.

The second project will focus on making "green" construction products. The replacement of cement with supplementary cementing materials (SCMs), i.e. blended cements, within a mix is considered to be environmentally friendly from a climate change perspective. As the manufacture of one tonne of cement produces one tonne of CO_2, the replacement of 25-50% of the cement with SCMs can account for significant greenhouse gas (GHG) savings. This project would investigate the potential of new supplementary materials and attempt to remediate more traditional ones such as poor quality fly ash. Remediation can be achieved either with the development of a new accelerating additive or by changing the composition of the supplementary material itself. This project would also involve several researchers, but would only involve the Building Envelope and Structure program.

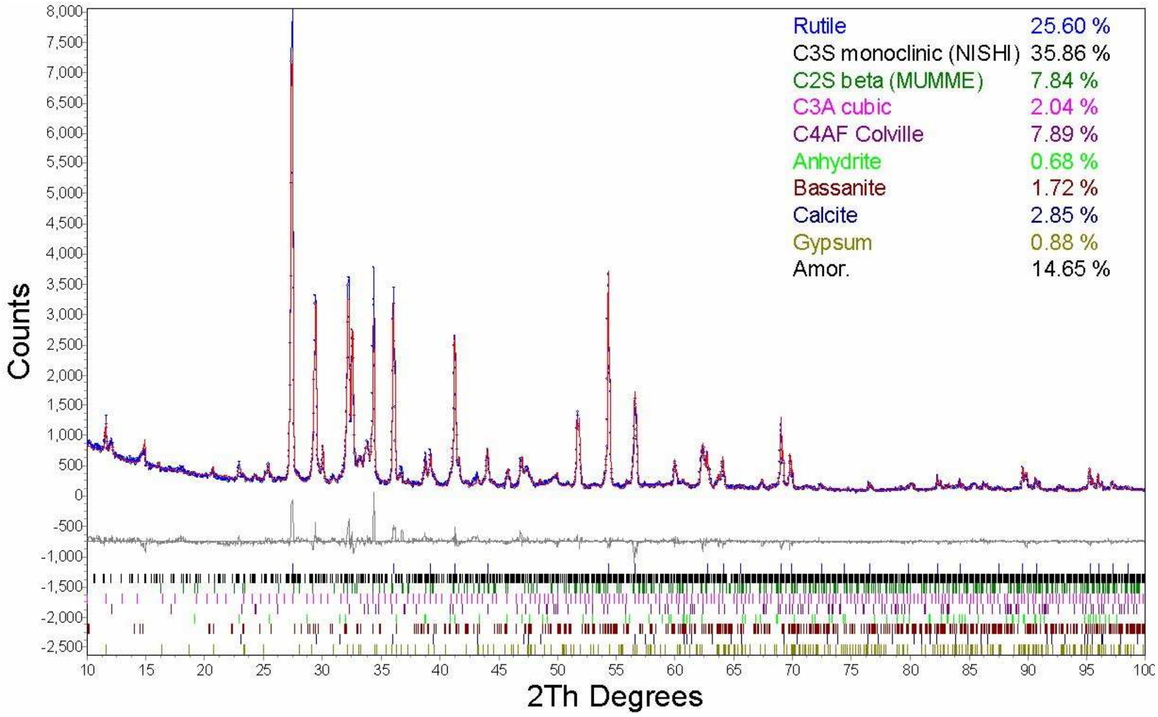

Figure 7. Rietveld difference plot of a type 10 ordinary Portland cement with addition of a 25 wt% TiO_2 spike (Whitfield and Mitchell 2003).

Table 2. Results of the analysis shown in figure 7 (Whitfield and Mitchell 2003).

Phase	**Percentage**	**Corrected Content**
Rutile	25.6	
C_3S	35.9	49.3
C_2S	7.8	10.8
C_4AF	2.0	2.8
C_3A	7.9	10.8
Anhydrite	0.7	0.9
Bassinite	1.7	2.4
Calcite	2.9	3.9
Gypsium	0.9	1.2
Amorphous	14.7	17.8
Total	100	100

Table 3. Calculated results for type 10 cements with and without a slag addition. The result of a analysis of a crystalline alumina sample additionally demonstrates that the method yields realistic results (Whitfield and Mitchell 2003).

Sample	% Amorphous content
TYPE 10 CEMENT	17.8 ± 2.2
Type 10 cement with 12.7wt% slag	25.8 ± 2.1 (expected = 28.2% assuming 17.8% amorphous content for cement)
0.3mm polishing Al_2O_3	2.3 ± 2.3

CONCLUDING REMARKS

This paper is a brief overview of historical and ongoing work carried out by the Cement based materials Group at the Institute for Research in Construction. The paper documents some of the expertise and instrumental facilities available for collaborative projects. Two possible project areas have been suggested, but other proposals for collaborative research from the Taiwanese scientific community will be most welcome.

ACKNOLEDGEMENTS

The author would like to thank Dr's Whitfield, Raki and Beaudoin for their useful discussion and reviews.

REFERENCES

De La Torre, A. G., Bruque, S., and Aranda, M. A. G. (2001), "Rietveld quantitative amorphous content analysis", *Journal of Applied Crystallography*, Vol. 34, 196-202.

Feldman, R. F., and Sereda, P. J. (1970), "The new model for hydrated Portland cement and its practical implications", *Engineering Journal*, Vol. 53, 53-57.

Grattan-Bellew, P.E. (1987), *Concrete alkali-aggregate reactions : Proceedings of the 7th International Conference, Ottawa, Canada*, Noyes Publications, Park Ridge, N.J., USA

Lea's Chemistry of Cement and Concrete, (1988) Hewlett, P. C. (Ed), Arnold, London, UK

Le Chatelier, H. (1882), "Recherches expérimentales sur laconstitution des ciments et la théorie de leur prise (Experimental researches on the constitution of cement and the theory of their setting)", *Acad.Sci.Paris*, Vol. 94, 867-869.

Lerch, W., and Brownmiller, L. T. (1937), "Method for Approximating the Glass Content of Portland Cement Clinker", *Journal of Research of the National Bureau of Standards*, Vol. 18, 609-622.

Mackenzie, C. J., and Thorvaldson, T. (1926), "Differentiation of the Action of Acids, Alkali waters, and Frost on Normal Portland Cement Concrete", *Engineering Journal*, Vol. 9, 79

Makar, J. M., Beaudoin, J. J., (2003) "Carbon Nanotubes and their application in the construction industry", 1st International Symposium on Nanotechnology in Construction, Paisley Scotland UK

Mitchell, L. D., Beaudoin, J. J., and Grattan-Bellew, P. E. (2004), "The effects of lithium hydroxide solution on alkali silica reaction gels created with opal", *Cement and Concrete Research*, Vol. 34, 641-649.

Mitchell, L. D., Margeson, J., Beaudoin, J. J., (2003) "Synthesis and Characterization of Nanoparticulate Calcium Aluminates", 1st International Symposium on Nanotechnology in Construction , Paisley Scotland UK

Mitchell, L. D., Whitfield, P. S., Margeson, J., and Beaudoin, J. J. (2002), "Sucrose Synthesis of Nanoparticulate Alumina", *Journal of Materials Science Letters*, Vol. 21, 1773-1775.

Pye, G. B., Myers, R., Arnott, M. R., Beaudoin, J. J. and Tumidajski, P. J., (2003) Conductive Concrete Composition. US Patent. 6,503,318 .

Raki,L. (2004) Turning wastes into building materials. *Construction Innovation*. **9**, (1):6

Raki, L., Beaudoin, J. J., and Mitchell, L. D. (2004), "Hydrotalcite-like Materials: Properties and uses in concrete", *Cement and Concrete Research*, Submitted

Ramachandran, V.S. and Beaudoin, J.J. (2000), *Handbook of Analytic Techniques in Concrete Science and Technology*, Noyes Publications, New York, USA

Ramachandran, V.S. Feldman, R.F. and Beaudoin, J.J. (1981), *Concrete Science*, Heyden & Son Ltd, London, UK

Ramachandran, V.S. Paroli, R.M. Beaudoin, J.J. and Delgado, A.H. (2003), *Handbook of Thermal Analysis of Construction Materials*, Noyes Publications/Williams Andrew, New York

Suherman, P. M., van Riessen, A., O'Connor, B., Bolton, D., and Fairhurst, H. (2002), "Determination of amorphous phase levels in Portland cement clinker", *Powder Diffraction*, Vol. 17, 178-185.

Swenson, E. G. (1957), "A Canadian Reactive Aggregate Undetected by ASTM tests", *ASTM Bulletin*, 48-51.

Swenson, E. G., Mackenzie, C. J., (1968) "Contributions of Thorbergur Thorvaldson to cement and concrete research. A historical review", E.G.Swenson (Ed), Performance of Concrete, pp. 3-17.

Taylor, J. C., Aldridge, L. P., Matulis, C. E., and Hinczak, I. (2002), "X-ray Powder Diffraction Analysis of Cements", In: Bensted, J., and Barnes, P. (Eds) , *Structure and Performance of Cements*, Spon Press, London

Whitfield, P. S., and Mitchell, L. D. (2003), "Quantitative Rietveld Analysis of the Amorphous Content in Cements and Clinkers", *Journal of Materials Science*, Vol. 38, 4415-4421.

Yang, R. (1996), "Crystallinity Determination of Pure Phases used as Standards for QXDA in Cement Chemistry", *Cement and Concrete Research*, Vol. 26, 1451-1461.