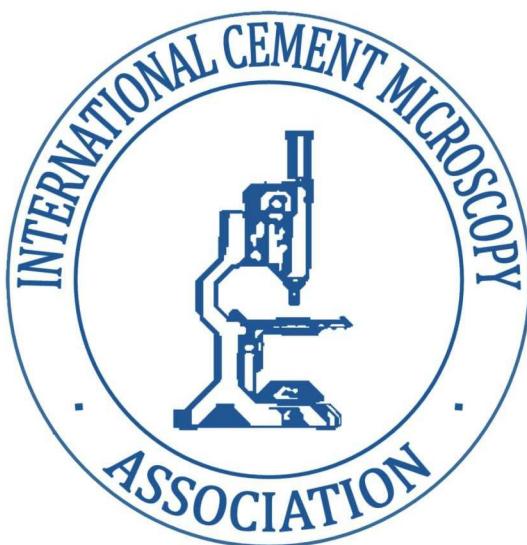


# **29th INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY**



**May 21 - May 24, 2007  
Quebec City, Quebec  
Canada**

**ISBN: 1-930787-02-2**

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## **Multi-Spectral SEM Imaging of Cementitious Materials**

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### ***Abstract***

Multi-spectral imaging of scanning electron microscope (SEM) images simplifies image processing of cementitious materials for quantitative measurements. This procedure utilizes an operator-designated training set of constituent phases and discriminant function analysis to classify each pixel into the group to which it most likely belongs. After classification, analysis of constituent phase features such as area, mass fraction, and surface areas may be performed. This new procedure has been adopted for processing clinker, and will form the basis for developing new standard reference material clinkers. It can also be used to explore the glass and crystalline phase distribution in fly ash and analysis of cement hydration products.

## **CLINKER CHANGES USING OXYGEN ENRICHMENT IN THE BACK END RISER DUCT OF THE NAZARETH KILN**

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### **ABSTRACT**

Mineralogical comparison is made of two clinker samples from the Nazareth kiln before and after an outage to replace the raw mill bypass line baghouse dust collector and burner pipe tip. An oxygen injection system was installed in the area of the auxiliary (riser duct) burners to facilitate combustion of fuel in the riser. Interpretation of mineralogical data and correlation with kiln process data is done based on the cumulative field experience of employees of Hamilton Technical Services, Inc.

**A ROUND ROBIN TEST ON MEASUREMENTS OF  
AIR VOID PARAMETERS IN HARDENED CONCRETE BY  
VARIOUS AUTOMATED IMAGE ANALYSES AND ASTM C 457 METHODS**

Dipayan Jana

**Construction Materials Consultants, Inc. and  
Applied Petrographic Services, Inc., Greensburg, PA 15601 USA**

Participants in the Round Robin Test and Coauthors on Descriptions of Image Analyses Methods used in this Study:

Karl W. Peterson<sup>1</sup>, Niels Thaulow<sup>2</sup>, Chris W. Baumgart<sup>3</sup>, Hisaaki Furuichi<sup>4</sup>, Mitzi Casper<sup>5</sup>, and Dipayan Jana<sup>5</sup>

1. Michigan Technological University, Dept. of Civil & Environmental Eng., Houghton, Michigan 49931 USA (**The Flatbed Scanner Method**).
2. RJ Lee Group, Inc., Monroeville, PA 15146 USA (**The RapidAir 457 Method**).
3. National Nuclear Security Administration – Kansas City Plant, USA (**The Automated Concrete Evaluation System**).
4. Fast Corporation Image Technology Division, Yamato, Kanagawa, Japan (**The HF-MAC01 Method**).
5. Construction Materials Consultants, Inc., Greensburg, PA 15601 USA (**The Modified Point Count Method of ASTM C 457**).

**ABSTRACT**

A systematic round robin study of five carefully prepared hardened concrete samples, having air contents from 2 to 10 percent was done by using four different automated image analysis techniques and the conventional ASTM C 457 method to compare the results obtained between various image analysis methods, and their variations compared to the average results from the C 457 method. The techniques used include image analysis of: (a) lapped sections of concretes as prepared for the C 457 tests, and (b) lapped sections treated with a black-and-white contrast enhancement step to highlight the air voids against the rest. All methods produced results of air void parameters that are more or less consistent with each other with expected reasonable between-method variability, and good agreements with the C 457 tests. This study demonstrates the ability and applicability of all these modern image analysis methods in rapid air void measurements of hardened concrete and particularly in rapid evaluation of freeze-thaw durability concrete at a fraction of time, with minimum operator-dependency, and with good reproducibility. All these image analysis methods have high potential for accurate assessment of air void spacing factor, the most important parameter for freeze-thaw durability, in concrete quality control and failure investigation.

## THAUMASITE IN CONCRETE - A CASE STUDY

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### ABSTRACT

An underground concrete structure in the midwestern United States exhibited a distress after about 10 years in service. The petrographic examination disclosed the presence of abundant amounts of cracking and secondary deposits, in addition to other alteration characteristics. A massive development of thaumasite was observed by SEM. Since the thaumasite development was similar to development of delayed ettringite formation - DEF - we would like to call this sulfate attack DTF - delayed thaumasite formation.

**Key Words:** Concrete, sulfate attack, ettringite, thaumasite (DTF)

## CONCRETE SCALING – A CRITICAL REVIEW

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### ABSTRACT

Scaling, i.e., local flaking or peeling away of the near-surface portion of a concrete slab is the most common type of surface distress, especially in areas exposed to cyclic freezing and thawing, and deicing chemicals. A comprehensive evaluation of factors responsible for concrete surface scaling is presented. The article gives a close look to the influences of: (a) concrete materials, proportions, and properties (air content, air void system, aggregate, cement paste, aggregate-paste interface, compressive strength, water-cementitious materials ratio, degree of saturation of concrete, and chemical admixtures); (b) construction practices (consolidation, finishing, curing, hot and cold weather protections, drainage, and surface treatments); (c) concrete maturity; and (d) deicing salts (salt type, concentration, timing of exposure) on scaling. The evaluation is based on numerous case studies on field reconnaissance and laboratory investigation of concrete scaling, where holistic approaches incorporating all possible factors for scaling were considered.

The results show that in a cyclic freezing and thawing environment, the most common causes of scaling are related to one or a combination of the following factors: (a) poor quality of concrete (e.g., having no or low air content, poor air-void system, unsound aggregates, etc.), (b) improper construction practices (e.g., improper finishing, inadequate curing), (c) exposure to corrosive (e.g., magnesium or ammonium-based) salts, (d) exposure to the common sodium or calcium chloride based salts at an early age prior to the attainment of maturity, and (e) exposure of an inherently poor quality and/or poorly constructed concrete to deicing salts.

Surface scaling in an apparently non-freezing environment can occur by improper finishing practices or, by reversible phase transformations of soluble salts (e.g., of sodium sulfate or carbonate) and zeolites (e.g., laumontite) between less-hydrous (or anhydrous) and more hydrous states during cyclic wetting and drying.

Fulfilling the common industry recommendations, e.g., of air content, compressive strength, and water-cementitious materials ratio may not necessarily guarantee the necessary scaling resistance unless a comprehensive evaluation of the influences of all possible factors related to concrete mixture, construction practices, and the environment on scaling are exercised, and, the concrete is accordingly designed, placed, finished, cured, and matured for the maximum durability.

## VIRTUAL HARDENED CONCRETE SAMPLE EXCHANGE PROGRAM

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### ABSTRACT

A set of digital images collected from a polished slab of hardened concrete has been made available on the world wide web. The images are provided in a format so that modified point counts may be performed remotely. Test results from participants will be posted on the web site. Names of companies or individuals will not be reported. The objective of the program is to isolate the influence of operator variation on test results from other variables, such as sample preparation, equipment used, and choice of grid or traverse line location. Recently, many different automated methods have been employed to perform ASTM C 457. Studies are emerging to compare test results obtained by various automated methods to test results obtained by manual methods. Often the results of a manual operator are used as a basis for comparison. A detailed look at manual operator variability will provide a background with which to evaluate variability in the automated procedures.

## DELAMINATION – A STATE-OF-THE-ART REVIEW

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Applied Petrographic Services, Inc., Greensburg, PA 15601 USA

### ABSTRACT

One of the increasing problems in concrete slabs is **delamination**, which is a plane of “separation,” usually forms within the top  $\frac{1}{4}$  to 1 in. (6.25 to 25 mm) of the finished surface, and orients parallel to the surface. Delamination can occur by a variety of reasons, such as: (a) the use of air entrainment in a concrete slab receiving a hard trowel finish; (b) machine-trowel finishing a lightweight aggregate concrete slab; (c) premature finishing of a slab prior to the cessation of bleeding; (d) top-down stiffening, or surface crusting of a concrete slab in a hot, windy, or dry weather, especially in a concrete undergoing slow and prolonged bleeding; (e) prolonged finishing operations on an outdoor air-entrained concrete slab, or, on a slab receiving a mineral or metallic surface hardener; (f) corrosion of reinforcing steel in concrete in the presence of chlorides and/or atmospheric carbon dioxide; and (g) cyclic freezing and thawing of a non-air-entrained, or poorly air-entrained concrete slab at critically saturated conditions.

Methods of detecting the delaminated areas in a slab include: (a) metal tapping, (b) manual or automated chain dragging, (c) electro-mechanical sounding, (d) impact echo, (d) infrared thermography, and (e) ground penetrating radar.

Among the techniques available for diagnosing the causes of delamination, petrographic examinations, along with detailed air void analysis of concrete cores from the delaminated areas are determined to be the most effective. After explaining factors responsible for delamination, and the techniques available for quantitative measurements of delaminated areas, the present paper provides case-study-based examples of detailed investigations of various mechanisms of delamination by diagnosing the evidence present in the delaminated concrete slabs. Finally, a list of common industry recommendations is provided to avoid such an increasing nuisance in the modern concrete slabs.

Increasing occurrences of delamination in both indoor and outdoor concrete slabs are, unfortunately, the results of modern fast track construction schedules, where inadequate design or, failure to follow a design causes the failure, such as either by accidentally incorporating air in a slab that will not be exposed to freezing during its service and will receive a machine trowel, or not incorporating air in an outdoor slab that will be exposed to freezing.

**A NEW LOOK TO AN OLD POZZOLAN:  
CLINOPTIOLITE – A PROMISING POZZOLAN IN CONCRETE**

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**ABSTRACT**

**Clinoptilolite**  $[(\text{Na}_4\text{K}_4)(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}]$ , the most common natural zeolite occurring as widespread tuffaceous lacustrine sedimentary deposits in the Western United States was used as a pozzolan at 0 to 40 percent by mass of portland cement replacements in concrete mixtures to investigate the effects of zeolite on fresh and hardened concrete properties, and durability.

Fresh concrete properties, e.g., temperature, air content, yield, unit weight were apparently unaffected by zeolite incorporation. A reduction in bleeding, and an accelerated initial setting at 10 to 30 percent cement replacement levels was noticed by zeolite. The main effect, however, was in noticeable reduction in workability, especially at greater than 10 percent level, which required addition of mid-range and high-range water reducing admixtures in the mixture.

Compared to the control mixtures, zeolite-blended concrete mixtures showed an improvement in compressive strength at 10 percent cement replacement level at 56 days, whereas 20 to 30 percent replacements caused a modest reduction in strength at the same age by approximately 10 percent. Pozzolanic effects of strength improvement are more pronounced at late ages (i.e., beyond 28 days) than at early age. Effects of pozzolanic reactions of clinoptilolite, however, are far more significant in improving concrete durability than compressive strength.

The most significant effects are in reduction in chloride permeability, a significant reduction in expansion due to alkali-aggregate reaction, and an improved resistance to acid and sulfate attacks, all of which are related to the overall densification of the microstructure, alkali-binding capacity of zeolite-blended cement pastes, and pozzolanic consumption of calcium hydroxide component of portland cement hydration in the paste. Drying shrinkage of zeolite-blended concrete mixtures having 10 to 20 percent zeolites are identical, and slightly higher than that of the control mixture. The benefits in durability far outweigh the slow rate of strength development at early age, or a modest strength reduction at 20 to 30 percent levels. The concrete industry should take advantage of this abundant “gold mine” in the Western United States as a promising pozzolan, especially when its importance in concrete durability is undeniable.

## THE GREAT PYRAMID DEBATE

### Evidence from Detailed Petrographic Examinations of Casing Stones from the Great Pyramid of Khufu, a Natural Limestone from Tura, and a Man-made (Geopolymeric) Limestone

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## ABSTRACT

Contrary to the well-known hypothesis of construction of the Great Pyramids at Giza by carving and hoisting quarried limestone blocks, in 1974 a French research chemist, Joseph Davidovits, proposed a radically different hypothesis that the pyramid blocks are not quarried stone but cast-in-place “concrete” prepared with the soft, marly kaolinitic limestone of Giza that was readily disintegrated in water and mixed with locally available lime and natron. The lime-natron combination, according to Davidovits, dissociates the kaolinitic clay from the limestone and forms an alkali-aluminosilicate (zeolitic) “glue”, which he termed “geopolymer”. The “man-made” hypothesis was proposed as an alternative explanation to the apparent mysteries associated with the “carve-and-hoist” hypothesis in regard to the methods of construction and observations of some “unusual” minerals in pyramid samples that are rare in natural limestone.

The purposes of the present study are to investigate: (a) evidence of microchemical signatures of the proposed lime-natron-clay-based geopolymeric chemistry in the binder phases of the pyramid samples; (b) textural, mineralogical, microstructural, and binder-microchemical comparisons among pyramid samples, natural limestone from Tura, and geopolymorphic limestone; and (c) the reported “unusual” constituents in the pyramid samples, if any, and their possible sources.

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<sup>1</sup> The Great Pyramid of Giza was the world's tallest building from c. 2570 BC to c. 1300 AD (from [http://en.wikipedia.org/wiki/Great\\_Pyramid\\_of\\_Giza](http://en.wikipedia.org/wiki/Great_Pyramid_of_Giza), with permission).

## WERE THE PYRAMIDS CAST IN PLACE?

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### **Abstract**

How the Great Pyramids of Giza were built has remained an enduring mystery. In the mid-1980s, Davidovits proposed that the stones used to build the pyramids were, instead of being quarried, cast *in situ* using granular limestone aggregate and an alkali alumino-silicate-based binder. Hard evidence for this idea, however, remained elusive. In a recent publication, we compared a number of pyramid limestone samples with six different limestone samples from possible quarries in the vicinity by means of scanning and transmission electron microscopy. The pyramid samples contained microconstituents with appreciable amounts of Si in combination with elements, such as Ca and Mg, in ratios that do not exist in any of the potential natural limestone sources. The intimate proximity of the microconstituents suggests that at some time these elements had been together in a solution. Some of the pyramid samples contained ingredients that were amorphous. Furthermore, between the natural limestone aggregates, the microconstituents with chemistries reminiscent of calcite and dolomite—not known to hydrate in nature—were hydrated. Apart from its implications for Egyptology, studying these materials also provides insight into an ancient concrete that might evolve into an affordable, environmentally friendly and durable building material.

## **GEOLOGIC ORIGIN OF EGYPTIAN PYRAMID BLOCKS AND ASSOCIATED STRUCTURES**

**International Cement Microscopy Association  
29<sup>th</sup> Annual Meeting, Panel Discussion, Quebec City, 21 May 2007)**

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### **ABSTRACT**

On-site examination of the pyramids in Giza and Saqqara in 1990, and laboratory analysis of a casing stone sample (EA 491) from the Great Pyramid of Khufu at Giza, supplied to the writer by the British Museum in 1987, reveal no evidence that the pyramid blocks were cast-in-place. *Cross sections* of delicate calcitic fossil shells, ripple laminations, numerous calcite-filled cracks, burrows formed by marine organisms, and many other on-site observations, clearly indicate a natural origin for the Khufu and Zoser blocks. Many features observed on the blocks indicate the activities of ordinary marine processes on Eocene-age sea-bottom sediment. Polished Aswan granite in the Khafre Valley Temple at Giza exhibits *cross sections* of xenoliths and mineral-filled veins that indicate typical igneous (magmatic) crystalline relationships. Examination of 10-micron-thick thin sections of casing stones has revealed conclusively that a geopolymeric binder (a matrix in which disaggregated limestone would have been embedded) is absent in the pyramid samples studied; the binder does indeed exist in a geopolymeric limestone made by Davidovits in July of 1982 and given to the writer. Sample EA 491 contains very little alkali or phosphorus, elements said to indicate a geopolymeric origin. Consequently, the geopolymeric cast-in-place method of ancient pyramid block manufacturing has no basis in fact.

## **NATURAL ORIGIN OF CASING STONE FROM THE PYRAMID OF CHEOPS**

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### **ABSTRACT**

Examination of a casing stone from the pyramid of Cheops using polarised light microscopy, scanning electron microscopy, energy dispersive X-ray micro-analysis, X-ray diffraction and infra-red spectroscopy indicates that it is a natural limestone. There are no features which support the artificial, geopolymeric origin advocated by Davidovits and co-workers.

## **MICROSCOPICAL EVALUATION OF NEARLY 100-YEAR OLD CONCRETE FROM GATUN LOCKS, PANAMA CANAL**

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### **Abstract**

The Petrography Laboratory at BASF Construction Chemicals had the opportunity to conduct a petrographic examination of a small portion of concrete from the Gatun Locks in the Panama Canal. A review of the Gatun Locks' history was performed and is presented as an introduction. Compared to the present day, concrete technology during the construction was in its infancy. The concrete was placed between 1909 and 1914 and shows unique characteristics. Optical microscopic, scanning electron microscopic and X-ray powder diffractometry analysis indicate an aggregate grading and portland cement characteristics unlike what is observed in present-day concrete. The aggregate appears to be gap graded, missing intermediate size aggregate fractions. Coarse aggregate particles composed of andesite show calcium enriched zones and silicon depleted zones at the aggregate peripheries. There is also an indication of loss of crystalline structure in these peripheries. Unlike what is experienced in modern concrete, the portland cement had a significant proportion of very large coarse particles (larger 100 microns). The central portion of some cement particles show relict cement phases (unhydrated phases) even though the concrete is nearly a century old.

## MICROCHEMICAL TESTS FOR CONCRETE PETROGRAPHY

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### ABSTRACT

Concrete petrographers often rely on a variety of reagents (stains, etchants, and other solutions) to quickly and fairly reliably provide microchemical information on the constituents of pastes and aggregates, contaminants in concrete-making materials, reactions between concrete constituents, and reactions between concrete and its service environment. This paper discusses the solutions used most frequently in our laboratories, and provides some directions concerning their use.

## Petrographic Evaluation of Fire Damaged Concrete

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Concrete petrography is a powerful and effective tool to be used to evaluate fire damages to concrete elements, including the maximum temperatures exposed and depths associated with various temperatures. Using different mineral thermometers, such as calcium hydroxide, quartz, and calcite, an experienced concrete petrographer can assess the temperature gradient quite accurately. This paper discusses how different mineral thermometers are used to assess the temperature exposed, as well as limitations and pitfalls of the method. Several case studies are presented.

## **Internal Sulfate Attack in Cementitious Materials due to Sulfate Imbalance**

*Derek X. Cong, Ph.D. and Matthew P. Carlton, P.E.*

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### **ABSTRACT**

Different forms of sulfate attack can cause damage to hardened hydraulic cement materials. The two most widely known forms include attack by environmental sulfate sources and delayed ettringite formation (DEF). DEF is an internal sulfate attack that occurs due to elevated temperature curing of some cementitious systems. This paper deals with another form of internal sulfate attack in hardened mortar, grout, or concrete that is unrelated to curing temperature of the freshly mixed materials, but rather due to sulfate imbalance of the cementitious materials, which often contain higher SO<sub>3</sub> contents than specified in ASTM C150. Many proprietary mortar and grout mixtures containing an intentional imbalance of sulfate are claimed to be suitable for use in exposed service conditions. Additional sulfate, in the form of gypsum, can also be added to cementitious grout to speed the setting process. However, when such systems are exposed to moisture during service, abundant secondary ettringite will form, resulting in expansion, cracking, and debonding of the affected materials. Remediation of the distress caused by this phenomenon can be very costly. By case studies, this paper discusses the mechanisms, identification, and remediation of internal sulfate attack, and how to avoid it.

**DETERMINATION OF WATER TO CEMENTITIOUS (W-CM) BINDER RATIOS BY THE USE OF FLUORESCENT MICROSCOPY IN HARDED CONCRETE SAMPLES: PART 1.**

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**ABSTRACT**

A method of accurately determining the water to cementitious ratio (w-c and w-cm) of hardened concretes by optical microscopy has become increasingly used by Concrete Petrographers throughout Europe and North America. This fluorescence technique has been shown to provide good reliable determination of the water to cement ratios of hardened concrete over a range from 0.35 to 0.70. Potential strength-related problems in field concretes often result from cement and / or mineral admixtures shortages / excesses, as well as the addition or shortage of extra free water added during mixing. These differences would cause changes to the paste to aggregate ratios, which may also affect the resultant localized and mean capillary porosity of the cement paste and therefore the determination of water to cementitious ratio obtained. A series of laboratory prepared concretes have been made up with reliably determined compositions and w-c ratios in order to assess a number of factors relating to this assessment method. These samples were well cured in a fog room prior to preparation as fluorescent resin impregnated thin sections. Concretes were prepared at both constant cement and variable cement contents, in order to see if any differences in apparent w-cm ratio were developed due to changes in the paste to aggregate ratio. Concretes of differing w-c ratios containing a selection of supplementary cementitious materials (SCM's) were also produced in order to see the effects that these materials have on the capillary porosity compared to normal Portland cement-based concrete over the range of w-cm ratios under investigation. Older reference sample fluorescent thin sections were compared with these new sets of standards in order to see if any deterioration in fluorescence developed in the samples with time. This investigation is on-going and so the results obtained so far are only partially completed.

## QUANTIFICATION OF ASR IN CONCRETE: AN INTRODUCTION TO THE DAMAGE-RATING INDEX METHOD

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### ABSTRACT

The information provided to managers, engineers, and owners of concrete construction that is thought to be affected by alkali-aggregate reaction (AAR) often relies on descriptive observations, typically generated by petrographers. Such data can be poorly understood by the recipients of the reports, due to the emphasis on qualitative descriptions of features viewed with the microscope and due to the use of unfamiliar jargon.

Procedures that have been developed to quantify the petrographic data, such that engineers, managers, and owners can more readily utilize this information, are considered an important advance in the field of the assessment of AAR, and, more specifically, alkali-silica reaction (ASR). The Damage Rating Index (DRI) is one such procedure. DRI is microscopy-based, and is rooted in the petrographic examination of concrete. It produces a numeric index of damage in concrete that is easy to understand.

This paper examines the use of the DRI on concrete specimens from structures and laboratory test samples that exhibited a range of ASR effects, from "Low" or "None" to "Highly-Affected". The method is examined as a potential tool to assist in ASR evaluation.

## PETROGRAPHIC EXAMINATION OF HISTORIC CONCRETE

By L. Brad Shotwell and W.G. Hime

### ABSTRACT

A sample of concrete received by one of the authors (W.G.H.) was known to have been removed from a decorative portion of a wall that was built before 1860. The wall surrounded the property where a grand house known as Portland Hall that was to be built by William Aspdin, the son of Joseph Aspdin, the inventor of portland cement. Although the house was never completed, the wall that surrounded the property stood for many years. The wall was reported to have had pilasters that were topped with elaborate capitols made of brick with a thick coating of cement and aggregate.

The sample was examined using petrographic methods outlined in ASTM C856 *Standard Practice for Petrographic Examination of Hardened Concrete* and ASTM C457 *Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete*. Significant features of the concrete detected petrographically include: 1) the presence of slag that was judged to be the by-product of copper smelting. 2) the presence of spherical air voids that are consistent with air-entrainment. 3) the lack of complete cement paste carbonation. At the time the concrete was produced, rapid detection of copper slag in either unused cement or in the hardened concrete would have been difficult or impossible without conducting a microscopic examination. This suggests the copper slag may represent a “trade secret” of the time. The current studies did not determine whether the spherical air voids represent a purposeful addition of a surfactant, or the presence of a serendipitous “workability” aid. As expected, the portland cement contained in the concrete was coarsely ground by modern standards. The lack of complete carbonation of the cementitious matrix is likely due to continued hydration of the coarsely ground portland cement while the concrete was in service.

# Use of Alternative Fuels in the Canadian and U.S. Cement Industry: Opportunities and Barriers

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## 1 Background - North American cement industry

The North American cement industry is diversified and primarily integrated with the construction aggregates and concrete products sectors.

### *Canada*

At the end of 2004, sixteen cement plants (27 kilns) operated in Canada, consisting of fifteen gray cement plants and one which produces white cement. Industry capacity was 16.63 Mt of clinker and 18.29 Mt of cement. (It has to be noted that this represents only about 0.75% of the total, global industry capacity.) Cement is produced in five out of ten Canadian provinces. Geographically, industry capacity is concentrated in the province of Ontario, with 50.3% of the total Canadian capacity, followed by Quebec with 16.8% capacity, British Columbia (16%) , Alberta (13.8%), and Nova Scotia (3.1%) accounting for the remaining output. It is a fairly modern industry, with 57% of its kilns built since 1980.<sup>4</sup> During the late 1990s and early 2000s, the construction industry in North America has been booming, and the Canadian cement industry, in 2005, has operated at 89.7% capacity utilization.<sup>3</sup> 2005 cement shipments were 14.27 Mt, worth \$1.66 billion.<sup>5</sup> About a third of the Canadian cement shipments are exported, primarily to the USA.

### *U.S.A.*

In the USA, 115 plants with a total of 186 kilns operated as of December 31, 2004. Cement is produced in 37 out of 50 states, and the industry has a capacity of 93.78 Mt clinker and 117.66 Mt cement.<sup>4</sup> California and Texas are the two states with the largest cement grinding capacities, 12.7% and 10.9%, followed by the states of Florida, Pennsylvania and Michigan. In 2005, U.S. cement consumption was 126.76 Mt (about 5.1% of the total, global production), while shipments by domestic producers accounted for a record 93.85 Mt.<sup>2</sup> Therefore, and this represents a rather typical annual volume, about 22% to 25% of the cement consumption has to be imported. Traditionally, Canada has been the main source of cement and clinker imports to the USA. Recently, however, imports from the Far East, especially from Thailand, China and Korea often approached those from Canada. Latin American countries, such as Columbia, Venezuela and Mexico, are also bringing significant cement volumes to the USA.

The Canadian and U.S. cement industries are well integrated into the global scene. Major multinationals and global leaders such as Lafarge SA of France, Holcim Ltd. of Switzerland, Votorantim Group of Brazil, Heidelberg Zement AG of Germany and Italcementi of Italy operate in both the US and Canada, with other players, such as CEMEX, Ash Grove Cement, California Portland Cement, Buzzi Unicem USA, Texas Industries Inc., and others involved only in the USA.

## From High Alumina Cement to Manganese Cement

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### ABSTRACT

Manganese can interact in several ways in High Alumina cements. By the addition of manganese sulphate to High Alumina cements a control of hydration similarly as by the use of gypsum can be obtained, despite other hydration products are formed.

A new method of introducing manganese in High Alumina cements can be obtained by using manganese raw materials already in mixing up the raw meal before sintering. By the use of elevated amounts of manganese (up to 30 %) some manganese cements can be obtained.

The addition of manganese can be performed by Mn-ore, Mn-bearing residues, Mn-wastes or Manganese fines from productions.

Different manganese-containing phases are formed during the sintering process. Also the hydration products can contain manganese.

The properties of manganese cements and the advantages are described.

## DURABILITY OF BLENDED CEMENTS – CAN ELEVATED TEMPERATURES BE USED TO ACCELERATE HYDRATION AND PREDICT LONG TERM PERFORMANCE?

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### ABSTRACT

It is well known that the cement matrix is a chemically reactive system that undergoes changes in mineralogy, microstructure and aqueous phase composition with time, temperature and in response to environmental influences. Durability studies that relate to long term engineering parameters such as strength and matrix stability are typically predicted on models based on studies of the cement matrix over a limited period of 2 to 3 years. This time period may be sufficient for neat cement systems but the blended cements continue to evolve. Blending agents such as fly ash and blast furnace slag have been reported to improve long term durability influenced by both internal (e.g. alkali-silica reaction) and external (e.g. sulfate ground waters, seawater, sewage, acid rain etc.) attack. Studies of solid and aqueous phase compositions both for neat and ordinary Portland cement blends cured at ambient temperature for prolonged periods are compared with the same blends cured at 55°C to accelerate hydration and establish phase equilibria. Results indicate that elevated the temperature modifies the hydration chemistry such that the mechanisms and products formed differ from that obtained over the long term at ambient temperature.

MICROSCOPY AS A POTENTIAL TOOL FOR EVALUATING SULFATE-RESISTANCE  
OF HYDRATING CEMENTS AND BLENDS  
PART II

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## ABSTRACT

This paper concludes a study in which microscopy (light and electron) was used to evaluate the sulfate resistance of various cements. In addition, this paper will show technologies that were useful in expediting detection of sulfate resistance or damage in hydrated cement. A discussion regarding the performances of various samples tested is also included.

The availability of API Class H, high sulfate resistance cement has decreased in the last few years as demand has increased and as many cement manufacturers have moved away from API cement production. An HSR cement is classified as a cement with less than 3% C<sub>3</sub>A. As manufacturers move away from API HSR cements, the C<sub>3</sub>A content of other cements may be upwards of 8% or higher. This reduction in HSR cements has lead to a compound problem: 1) a need for development of new cement blends that are sulfate resistant, and 2) a method for validating resistance to sulfate in a shorter time period—current ASTM requires one-year testing.

Various slurries were tested over a year-long period to determine their resistance to sulfate damage. These slurries (both conventional and experimental) were evaluated using the ASTM C1012 Sulfate Test. In addition to the standard ASTM test, other techniques and testing methods were evaluated as potential new protocols for expediting detection of sulfate damage and deterioration. Light microscopes and an environmental scanning electron microscope (ESEM) were used to examine test samples and measure expansion; the samples were then evaluated for cracking or other damage. Results obtained from the standard method and the deviations will be compared.

**CASE HISTORIES—  
SULFATE CRYSTALLIZATION IN A POWER-PLANT STACK  
AND LOW-STRENGTH CEMENT**

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**ABSTRACT**

Petrographic examination of mainly the interior ends of four cores from a coal-burning power plant stack reveals a wholesale replacement of the portland cement paste and limestone/dolomite aggregates in the zone of sulfatization (sulfate crystallization). Carbonation of the paste, measured from the interior ends of the cores, probably intensified at plant startup and has progressed to unusually great depths in each of the cores, up to 105 mm in Core 180, representing the 180-foot level in the stack. Therefore, paste alteration is interpreted to develop first with carbonation, followed by sulfatization, each process destroying the previous microstructure. Carbonation is normally not a deleterious process, except that it increases the corrosion potential of metal reinforcement. Sulfatization is extremely damaging to the concrete, progressively deepening the deterioration and spalling the effected concrete.

Two Type II cements, made from clinker derived from the same kiln, but at slightly different times, were studied to possibly explain a relatively low strength for one of the samples. The low-strength cement was seen to have a relatively large crystal size, a lower birefringence, and a slower reaction to 0.01% aqueous ammonium chloride. Therefore, at the time the clinker was produced representing the low-strength cement, the burning rate was slower and the temperature higher, decreasing the reactivity of the silicates. Larger crystal sizes, theoretically, would produce lower surface areas on a phase-by-phase basis in the finished cement, decreasing the hydraulic reactivity and strength-gain potential of the cement.

# **WATER TREATMENT PLANT SLUDGES ADDITION DURING CLINKERING: INFLUENCE ON MINERALOGY, PETROGRAPHY AND HYDRATION OF CEMENT**

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## **ABSTRACT**

The current use of fuels of substitution allows not only their energy valorisation but also contributes to the elimination of waste. Among, these alternate fuels, water treatment plant sludge (WTPS) were tested during the burning of clinkers. Their incineration brings minor and traces elements, being able to affect the formation reactions of clinker minerals and consequently the reactions of hydration and the quality of the end-products. The goal of this study is to assess the impact of the minor elements and traces (phosphorus, zinc, copper) - brought by the sludge co-incineration - on the mineralogy and petrography quality of an industrial clinker, and on the hydration of laboratory cements obtained from this clinker. Two industrial clinkers were studied: a reference (CK PILOT) burned with a coal/petroleum-coke mixture and a test (CK WTPS) burned with a coal/petroleum-coke/water treatment plant sludge mixtures. From the point of view of the chemical characterization (XRF, ICP-AES, EPMA), microstructure, mineralogy and petrography (XRD, SEM), the results show an enrichment in P, Cu & Zn without growth of new mineralogical phases, nor of major structural modification of the existing phases. Secondary belite appears, traducing reduced conditions of burning. If P could be detected at the crystal scale, Zn and Cu were not detected. The contribution of the TEM must confirm the absence or the presence of nanophases or interphases around or in minerals of the clinker. The microstructural characterization by ESEM on cements from fresh hydrated laboratory paste related to the morphology of the hydrates and their organization between 0 and 60 minutes. The first results show that hydrates (in particular set CSH) developed by the two cements (PILOT and WTPS) have different morphologies.

## **EFFECTS OF CARBONATION ON THE MINERAL COMPOSITION OF CEMENT KILN DUST**

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### **ABSTRACT**

Due to their relatively high calcium oxide content, industrial mineral oxide wastes are potential candidates for mineral sequestration of carbon dioxide ( $\text{CO}_2$ ). Cement kiln dust (CKD) contains 20-60% CaO making it a possible candidate for  $\text{CO}_2$  sequestration. In this study, three types of CKD are characterized, before and after carbonation, using environmental scanning electron microscopy and energy dispersive x-ray microanalysis to determine the mineralogical and morphological changes occurring due to carbonation. The reactants, products, and precipitation mechanisms were investigated to enhance understanding of the governing processes and allow better utilization of CKD for  $\text{CO}_2$  sequestration. The results of multiple independent analyses confirmed the formation of  $\text{CaCO}_3$  during carbonation. Examinations of the reaction pathways found that CaO and calcium hydroxide ( $\text{Ca(OH)}_2$ ) were the major reactants. Three types of  $\text{CaCO}_3$  precipitation mechanisms were observed: (1) diffusion of  $\text{CO}_2$  into  $\text{Ca(OH)}_2$  particles causing precipitation in the pores of the particle and the growth of a  $\text{CaCO}_3$  skin from the outside inward, (2) precipitation onto existing particles, and (3) precipitation from aqueous solution. The  $\text{CaCO}_3$  skin may slow further diffusion of  $\text{CO}_2$  into a particle, thus slowing the overall sequestration rate.

## High Resolution Cold Field Emission Scanning Electron Microscopy of Cements

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### **Abstract:**

Considerable attention has been paid in recent years to the use of environmental scanning electron microscopy and cryo-scanning electron microscopy for the study of hydrated cements. However, a different class of scanning electron microscopes (SEM), the high vacuum cold field emission (CFE) SEM also have applications in cement microscopy, having a unique set of advantages and disadvantages compared to other forms of SEM. CFE-SEMs are capable of operating at very low accelerating voltages and can thus produce very high magnification images without requiring coating of samples. However, sample preparation is a key issue for the use of these instruments, as the high vacuum environment of the CFE-SEM will draw free water out of the samples under examination. This paper discusses the use of CFE-SEM for tricalcium silicate and ordinary Portland cement microscopy, with an emphasis on both the early stages of cement hydration and unhydrated samples. The recent discovery of nanoscale structures formed at the end of the induction period is described.

**ICMA  
Denver CO  
May 3, 2006**

**Effects of a Glycol Type Grinding Aid on Finish  
Mill Production**

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**ABSTRACT**

A two week test was run at a cement plant utilizing a glycol type grinding aid at rates of 0.6 to 1.05 pounds per ton. The results show that there was an increase in production of approximately 7.5 tons per hour with very little effect on the Portland cement properties such as surface area, compressive strength, or air. Circulating load data indicated that efficiencies were obtained both in the mill as well as the separator when the rate reached 1 pound per ton.

**OIL WELL CEMENT TESTING  
COMPARING CEMENT CLASSES A, C, G AND H**

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**ABSTRACT:**

Oil well cement classes A, C, G and H are compared under similar conditions with a variety of tests; including specific gravity, particle size, rheology, thickening time, static gel strength, ultrasonic compressive strength and mechanical properties. Microscopic pictures of the cement powders are taken for potential analysis. There are pictures of the laboratory equipment used in testing and the outputs for class H cement are displayed.

## USE OF OPTICAL MICROSCOPY IN SOLVING WHITE CEMENT EARLY AGE STRENGTH PROBLEM

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### ABSTRACT

The properties of cement and especially early age strength are related to chemical and mineralogical properties of clinkers. In order to determine the cause of variation in early strength of white cement, seven samples of raw mixes and the corresponding clinkers have been collected.

Optical microscopy has been used to examine the microstructure of clinkers in order to assess the burnability of the corresponding raw mixes.

The comparison between the behaviour of seven raw meals and the corresponding white cement clinkers shows that the high silica modulus and the coarse grinding of quartz are the principle causes of concentration of belite clusters in the clinker and consequently low early age cement strengths.

### RESUME

Les propriétés du ciment et surtout les résistances à jeune âge sont intimement liées aux propriétés minéralogiques des clinkers. Dans le but de trouver les causes de variation des résistances à jeune âge du ciment blanc, sept échantillons de cru d'alimentation et leurs clinkers correspondants ont été prélevés.

La microscopie optique a été utilisée pour examiner la microstructure des clinkers dans le but d'évaluer l'aptitude à la cuisson des crus d'alimentation.

La comparaison entre les différents crus d'alimentation et les différents clinkers montre que le module silicique élevé et le broyage grossier du quartz sont les principales causes de la concentration de nids de bélite dans les clinkers et par conséquent des faibles résistances à jeune âge.