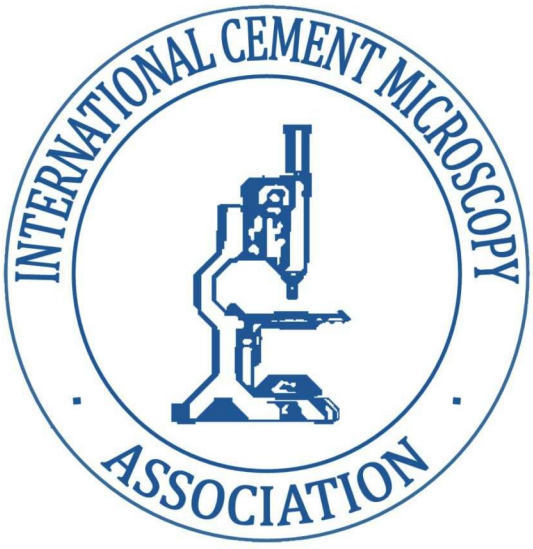
28th INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY



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AN INVESTIGATION INTO THE EFFECT OF VARIOUS FACTORS ON BELITE CLUSTERING IN PORTLAND CEMENT CLINKER

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ABSTRACT

Ash Grove Cement's Durkee, Oregon plant has an ongoing program of sampling and microscopic examination of the two types of clinker made there. Over the years, data has been accumulated regarding kiln feed fineness, free lime percentage, belite cluster size, and observed belite cluster ratio (clusters per nodule), as well as a host of other measurements based on the microscope. This data is used to evaluate the quality and grindability of the clinker, as well as evaluation of process changes, etc.

Belite clustering is a normal characteristic of Durkee's clinker, but observed cluster ratio can vary widely between samples. Finer grinding of the raw feed can sometimes mitigate clustering, but this is not always an option so other avenues are being explored. The study that is the subject of this paper involved an examination of the relationships between cluster ratio, cluster size, degree of burning as measured by free lime percentage, and kiln feed fineness.

It was found that degree of burning, as indicated by free lime percentage, appears to be the major factor determining the size and number of clusters in a clinker. It also appears that the fineness of the kiln feed can have an effect on both the clustering and the free lime percentage in a given clinker, and that this effect is more pronounced in Type I than in Type II clinker.

MICROSTRUCTURE OF EARLY AGE HYDRATION OF NATURAL ZEOLITE WITH PURE CEMENT PHASES

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ABSTRACT

Natural zeolites are mineralogical materials composed of aluminum and silica and are considered as pozzolanic in behavior when blended with cement. Literature on zeolite blended cements is limited, and tends to relate specifically to the effects on physical properties and durability such as compressive strength, porosity, sorptivity coefficients, degree of pozzolanic reaction, and influence on alkali aggregate expansion. Zeolites can significantly influence early age performance, particularly at elevated temperatures, and factors involved have not previously been characterized.

The effects on the microstructure of pure cement phases hydrated with two different natural zeolites were investigated at 85° and 185°F for periods up to 7 days. XRD data on selected samples were also obtained to provide further insight into the hydration chemistry mechanisms. Data was assessed with a view to explaining observed performance characteristics.

SAMPLE PREPARATION TECHNIQUES IN PETROGRAPHIC EXAMINATIONS OF CONSTRUCTION MATERIALS: A STATE-OF-THE-ART REVIEW[1]

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ABSTRACT

Appropriate preparation of a sample is an important step in petrographic examination. Over-preparation, inadequate preparation, or inappropriate preparation can reduce or destroy important information, or may provide wrong information. A state-of-the-art review of various sample preparation techniques for light and electron microscopy is provided. Techniques described are: cleaning, fresh fracturing, oil-immersion mount preparation, encapsulation, vacuum impregnation, sectioning, lapping, grinding, polishing, etching, staining, thin sectioning, fluorescent thin section preparation, half section preparation, staining techniques for rapid identification of alkali-silica reaction gel, sample preparation for air-void analysis of hardened concrete by conventional and image analyses methods, conductive coating for examination in SEM, ultra-thin-sectioning, sample preparation for x-ray diffraction, and a few modern techniques such as cryo-SEM, ESEM, and x-ray microscopy.

KEYWORDS: Petrography, Sample Preparation, Sectioning, Grinding, Polishing, and Microscopy.

Identification and Quantification of Components of Portland Cement

ICMA
Denver, CO
May 1, 2006

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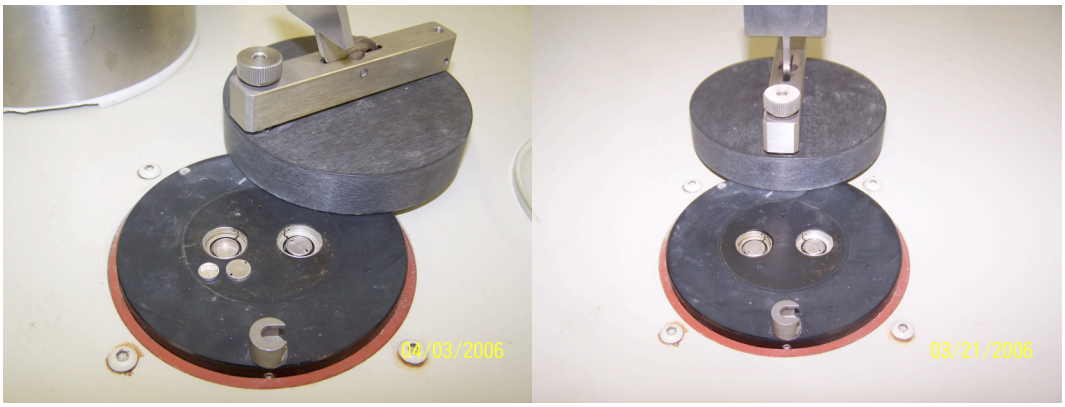
ROAN purchased a Perkin-Elmer, Model DSC 7 Differential Scanning Calorimeter (DSC) several years ago with the idea in mind of determining the different forms of sulfate present in Portland cement. Considerable work had been done on a leach test, [(1)] but that did not provide information other than the relative proportions of gypsum and plaster of Paris.

DSC differs from Differential Thermal Analysis (DTA) in that rather than measuring differential temperature, differential power consumption is measured. An ice bath is provided for cooling while electricity is used for heat in order to maintain a constant temperature on both the unknown sample as well as the reference, depending on whether the reaction exothermic or endothermic.



USING SCANNING ELECTRON MICROSCOPE REFERENCE BOOK "SEM-RB" FOR IDENTIFICATION PURPOSES

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ABSTRACT

A scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyzer can be successfully used to identify single particles, crystals or compounds in many complex materials. It is recommended that each SEM operator, researcher or investigator build her/his own personal scanning electron microscope reference book "SEM-RB" that can be used for such identifications. This paper presents a few examples of SEM-RB samples and their use for an identification of some aggregate particles in concrete.

Key Words: scanning electron microscope reference book "SEM-RB", BS images, X-ray elemental analysis, concrete, aggregate particles.

THE IMPACT OF SUPPLEMENTAL CEMENT ADDITIVES (SCMS) ON OILWELL CEMENTING ADDITIVE PERFORMANCE REVISITED

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and

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ABSTRACT

It is common knowledge that one of the main by-products of producing Portland cement is carbon dioxide (CO_2). Cement plants are under pressure worldwide to lower emissions of CO_2, and a simple, inexpensive way to lower CO_2 emissions is to add supplemental cement materials (SCMs) to the produced cement clinker. This process results in more finished product with less CO_2 produced and less energy consumed.

SCMs often include silica-rich materials such as fly ash, silica fume, ground blast furnace slag (GBFS), cement kiln dust (CKD), and metakaolin. These materials readily become part of the chemical matrix and often impart advantageous properties to the hydrating cement, such as reduced permeability, enhanced compressive strength, and increased sulfate resistance.

Another additive, raw limestone, is becoming increasingly popular in many parts of the world. Limestone is usually added in small amounts (less than 5%) and ground with the clinker. Limestone added in this manner is considered inert and appears to have little effect on the properties of the hydrated cement.

The authors presented a paper at the 2005 ICMA Conference entitled, "Adding SCMs to Portland Cement: Impact on Oilwell Cementing Additive Performance." That paper indicated that there was no apparent effect at temperatures up to 125°F. This paper examines temperatures up to 242°F.

This paper specifically compares an API monogrammed Class H cement to the same cement with 50% SCM added. Little difference was seen in retarder response up to 135°F, as was expected. As temperature increased, however, retarder response changed. It must be noted that a sodium lignosulfonate retarder was used in tests up to 186°F and a calcium lignosulfonate retarder was used for temperatures at 213°F and hotter.

Upgrading low quality natural and clay aggregates with modified cement coating paste for use in road materials

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Abstract

This paper examines the properties of low quality clay and natural gravel aggregates coated with a newly developed cement coating paste, and tests the effects of including these materials in a road pavement mixture. The investigation was divided into two main areas of study; the chemical and the testing of a road mixture containing the modified aggregate, namely a porous wearing road course.

The chemical testing involved a regime to show the affinity between cement coated and uncoated aggregates and bitumen in terms of adsorption, and desorption in the presence of water.
Porous wearing course pavement surfacing layer was chosen as a suitable road material for testing the effects of the modified clay and gravel aggregates on a road material behaviours under traffic loadings, as it is a stone matrix dependant mixture and is currently enjoying increased acceptance within Europe as a driver-friendly, high quality surfacing material. Tests applied included the repeat load axial tests, and the repeat load indirect tensile tests.

Observations made during the testing programme showed that the cement coated aggregates displayed an outstanding and useful improvement in their chemical and physical properties over uncoated aggregates in almost all the areas tested.

SOME USEFUL PETROGRAPHIC METHODS
Panel Session, ICMA, 1 May 2006

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Abstract

Some useful methods described in this contribution to the panel session on Sample Preparation are: (1) Sieving particles with tared polyester-mesh sieve cloths is helpful in determination of phase percentage variation. The sieve cloths are placed between stacked brass or plastic sieve frames, the assembly mounted on a 400-ml plastic container, into which a vacuum line connector has been inserted at the base. Particle sieving with polyester cloth to concentrate narrow particle-size ranges is required for quantitative work.

(2) For the polished grain mount, PGM, the glass slide is placed on a puddle of epoxy containing cement particles, instead of a puddle placed on the slide. The puddle is prepared on non-stick paper, for example, the backing from an adhesive-backed polishing cloth, and the excess epoxy is squeezed out with finger pressure on the glass slide. Grain mounts require no lapping with silicon-carbide papers, only coarse, medium, and fine polishing. If no transmitted-light observations are planned for the section, then a suitably cut ceramic tile can be used instead of a glass microscope slide.

(3) Gridded microscope slides, with the "x" direction labeled alphabetically and the "y" direction labeled numerically, can be used in making polished grain mounts. They facilitate the recording of the location of a particle of interest and returning to that grain after, say, staining or etching. With one-particle thick polished grain mounts one can examine the same crystal or grain in reflected and transmitted light. When changing from the polarized-light microscope to the SEM, one should keep in mind the possible inversion and rotation of images as an effect of reflection by the PLM lenses and mirrors.

(4) Use of "bumpers" for hand-holding slides during lapping and polishing, and similarly with beveled faucet washers for the load arm on the Minimet™, are highly recommended.

(5) Differential abrasion of hard and soft concrete components is promoted by the use of Buehler's Ultra-Pad™. The cloth can be used to develop topographic relief on a concrete surface, either on the concrete surface to be applied to the glass slide, or on the top of the thin section, or both, thus developing a thin section with preferentially abraded paste on the top and bottom surfaces, finally bringing the paste to a recommended thickness of approximately 20 microns.

(6) Microcrack detection and quantification with fluorescent epoxy, particularly in concretes undergoing alkali-carbonate reaction, can be accomplished by numbering the coarse aggregate particles on a lapped concrete specimen, and counting the microcracks originating within each aggregate particle, passing through the reaction rim, and terminating in the adjacent paste. The method is quite helpful in locating certain ACR-damaged aggregates for extraction and thin sectioning.

This presentation is in memory of Wase Ahmed of Buehler Ltd.

THE RIETVELD METHOD APPLIED: A ONE-YEAR CASE STUDY ON THE ACCURACY OF XRD VS. BOGUE FOR CLINKER PHASE ANALYSIS AT THE PLANT

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ABSTRACT

X-ray diffraction (XRD) has been slowly emerging in the cement industry in recent years, much like the manner in which x-ray fluorescence (XRF) analysis arose before ultimately becoming the prevailing method of chemical analysis in the industry during the 1960s. Standardless quantitative XRD analysis by the Rietveld method offers several distinct advantages over conventional techniques, most notably including rapid, direct measurement of true phase compositions and potential for better correlation to cement performance properties than Bogue calculations with its known, inherent deficiencies.

We compared results of clinker phase analysis by Rietveld refinement to traditional methods using the Bogue equation for a period of ~1 year at the Ash Grove Cement plant in Leamington, UT. The refinement strategy was developed in combination with independent characterization data obtained from a range of plant clinker samples in order to obtain robust performance with the highest possible accuracy.

Rietveld numbers for C_3S were found to be more accurate than Bogue C_3S values with appreciably better sensitivity to periods of kiln upset. Bogue C_3S values corrected for free lime content were on average 4% less than C_3S content determined by Rietveld. Bogue values also underestimated C_4AF contents by ~2-3% for clinkers higher in Fe_2O_3, but were more or less in agreement with Rietveld for clinkers lower in Fe_2O_3. Rietveld also measured orthorhombic C_3A levels that were consistent with observed Na_2O levels.

INTERNAL EXPANSION MECHANISMS AND DAMAGE IN CONCRETE: A CASE STUDY

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ABSTRACT

Concerns regarding the durability of concrete construction are increasing as our infrastructure grows and ages. The infiltration of environmental agents into the pore structure of concrete typically results in the deposition of secondary phases as a result of their chemical interaction with the original components of the material. While it is relatively simple to recognize these deposits in field concrete, investigators often mistakenly interpret their presence as indicia of damage to the concrete. However, in many cases secondary deposits may occur within concrete with no consequence to its performance. An investigation of a parking structure serves as a case study that illustrates the importance of recognizing mechanistic links between the presence of secondary alteration products, deterioration and/or distress in concrete, and damage in field concrete. The study showed that damage to the concrete was the result of stresses resulting from structural design and construction related activities such as erection, connection details and structural steel reinforcing details and not the result of any materials-related internal expansion mechanisms. The secondary deposits observed were the results of moisture penetration into the concrete mostly as a result of cracks associated with structural design and construction related activities. Recognition of the relevant damage mechanisms allowed the formulation of an economic and effective remediation and maintenance program. This exemplifies the need to obtain a thorough understanding of the significance of secondary reaction products in field concrete in order to technically justify and logically and economically prioritize any needed remediation of structures in service.

DELAYED SETTING OF CONCRETE – A PETROGRAPHIC AND CHEMICAL INVESTIGATION

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ABSTRACT

A comprehensive petrographic and chemical analysis was undertaken during the investigation of unusually delayed setting of a section of concrete placed during the repair of a bridge deck on a busy interstate highway. Reportedly, the final setting of concrete took more than 5 days and it was impossible to achieve the desired tyned surface finish within a reasonable period after the placement. Petrographic examinations determined a higher porosity, lower degree of portland cement hydration, and coarser size of calcium hydroxide component of portland cement hydration in the delayed set concrete compared to the normal set batch placed in the same day. The microstructural differences are consistent with the mechanism of delayed setting, which had kept many solution-filled pores empty for longer periods than the normal set concrete and allowed the development of relatively coarsely crystalline calcium hydroxide component of portland cement hydration in the open spaces. UV-VIS spectrophotometric analysis has determined approximately three times the dosage of the retarder in the delayed set concrete compared to that in the normal set. Concrete placed in hot weather usually contain a set-retarding chemical, whose dosage, if not controlled, can cause unusual retardation and associated early-age problems without necessarily affecting the design strength.

Quantitative mineralogical, chemical and application investigations on some High Alumina Cements from different sources

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Abstract
Different High Alumina cements from different companies and countries were collected and investigated on their chemical and mineralogical compositions qualitatively and quantitatively. Chemical measurements and also the quantitative mineral content was determined using different approaches. Besides optical measurements also Rietveld refinement procedures were used. The hydration behaviour was investigated using heat flow calorimetry.
A summary on the influence of mineralogical changes on hydration behaviour will be given.

EFFECT OF MINERAL ADDITIONS ON THE MICROSTRUCTURE OF HIGH CALCIUM FLY ASH

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ABSTRACT

Fly ash is a by-product obtained in thermal power plants burning pulverized coal. If the ash has the proper composition, it can be used in cement and concrete as a mineral additive, because of environmental, technological and economical reasons. TS EN 197-1, the standard for general cements, also allows the use of fly ash as a major constituent in several types of cement. According to their lime content and hydraulicity, fly ashes can be divided into high-calcium and low-calcium groups. Compared with low-calcium fly ashes, high-calcium fly ashes are known to have some disadvantages when used as an admixture in cement and concrete. Due to their relatively high lime content they may adversely affect some properties of cement and concrete such as shrinkage, sulfate resistance and freezing-thawing resistance. In Turkey, around half of the total amount of fly ash produced annually are the high-calcium fly ashes some of which do not completely conform to the relevant standards. They can not meet the minimum 25% SiO_2 limit and have high sulfate contents. Therefore, a study was designed to investigate the ways to improve the properties of high calcium fly ash including the one which is not conforming the standards, so that they could be used more efficiently in cement production. For this purpose, other mineral additions such as silica fume, ground sand, ground glass and ground granulated blastfurnace slag were mixed with high-calcium fly ash at various proportions to improve its properties. Microstructure of the resulting matrix and the strength development at 28 days have been studied.

Surface Morphology of Reactive Powder Concrete Containing Arsenic

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Keywords: Crystal structure; Scanning electron microscopy (SEM); Cement; Cement paste; Concrete

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

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and

Richard Ezeanyim

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ABSTRACT

This paper will consider the value of microscopy (light and/or electron) as a tool for assessing sulfate damage to various hydrating cements and blends that are being cured in aqueous sulfate environments.

Recent production changes at many of the oilwell cement producers in the United States shows that there will be a dramatic decrease in quantities of API Class H, High Sulfate Resistance (HSR) cements that will be available for oilwell cementing applications. Loss of this cement creates the need for evaluating performance of other types of cements/blends in aqueous environments and other "downhole" environments.

One of the standard evaluations for determining sulfate damage to hydrating/hydrated cements is based on curing the various cement pastes in a concentrated sulfate solution for one year and measuring test samples for expansion, cracking, or other signs of damage. This research study will utilize a standard method and some experimental methods to study a variety of different cements and blends containing various additives, in an attempt to determine sulfate resistance and also to try and develop accelerated test methods that provide useful information in a time frame less than the standard one year-long test.

Biomass fly ash in concrete:
Chemical and SEM analysis

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ABSTRACT

This document summarizes comparative tests of concrete prepared with eight types of cementitious material including neat Portland cement, cement combined with each of neat Class C and Class F coal-derived fly ash, and cement combined with each of these coal fly ashes with varying amounts of biomass fly ash [SW1: 80% Galatia coal co-fired with 20% switch grass; SW2: 90% Galatia coal co-fired with 10% switch grass]. Scanning Electron Microscopy (SEM), Electron Micro Probe Analysis (EMPA) and Energy Dispersive X-Ray (EDX) analyses show that both coal and biomass fly ash particles undergo significant pozzolanic reaction by one and two years after mixing, although biomass fly ash differs substantially from coal fly ash in its chemical composition. The results illustrate that fly ash derived from coal-biomass cofiring exhibits similar behavior and has similar advantages as fly ash from coal alone; indicating that biomass co-fired fly ash should not be precluded from use in concrete under conditions otherwise suitable for such applications.

Key words: Biomass fly ash; EDX; SEM, EMPA, ESEM.

CONTRIBUTION OF ELECTRON MICROSCOPY AND SPECTROSCOPY TO THE BEHAVIOUR OF MINOR HETERO ELEMENTS INTO CLINKERS

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ABSTRACT

For economical and ecological reasons, cement industry must face new challenges such to recycle industrial by products into the clinker kilns and by using co combustion of substitution fuels. Thus, these new practices induce the presence of hetero minor elements, in addition with the natural ones issued from quarries. These minor elements are supposed to be into the different phases of the clinkers. The object of this work is to present the contribution of a set of different tools such microscopy (optical and electronic) in association with spectroscopy techniques to identify, localized minor element like the phosphorus and evaluate its potential impact on the nature and structure of the different phases. Two different industrial materials with low and high phosphorus content have been study. The well-known phases (alite, belite, C3A, C4AF) have been identified at different scale. To determine the impact of the phosphorus on the crystallisation, the TEM/X-EDS have been used. The results show that the phosphorus is mainly trapped into belite and alite crystals, without noticeable structural modifications. On the other part, the existence of an amorphous phase around the crystals has been revealed. It supposed to be able to trap some phosphorus. The main result of this study is that only a set of different techniques working at different scale allow getting answers concerning the comportment of minor elements into clinker phases.

RESUME

Pour des raisons économiques et écologiques, les industries cimentières doivent relever de nouveaux défis tels que la réutilisation dans le cru de sous-produits industriels ou bien en employant la co-combustion de carburants de substitution. Ainsi, ces nouvelles pratiques induisent la présence d'hétéro éléments mineurs en plus des éléments majeurs provenant des matériaux des carrières. Ces éléments mineurs peuvent être inclus dans les différentes phases des clinkers. L'objet de ce travail est de présenter la contribution d'un ensemble de différents outils analytiques tels que la microscopie optique et électronique en association avec des techniques de spectroscopie en vue d'identifier, localiser et évaluer l'impact potentiel d'un élément mineur comme le phosphore sur la structure des différentes phases du clinker. Deux clinkers industriels différents avec de faible et forte teneur en phosphore ont été étudiés. Les phases traditionnelles (Alite, Bélite, C3A, C4AF) ont été identifiées à différentes échelles. L'impact du phosphore sur la cristallisation des différentes phases requière l'usage du MET/X-EDS. Les résultats montrent que le phosphore est majoritairement emprisonné dans des cristaux de Bélite et minoritairement dans l'Alite, sans modifications structurales détectables. D'autre part, l'existence d'une phase amorphe, susceptible de piéger du phosphore, autour des silicates a pu être confirmée. Le résultat principal de cette étude est que seul un ensemble de techniques complémentaires peut apporter des réponses quant au comportement des éléments mineurs dans les phases des clinkers.