

# ABSTRACTS

## THIRTY-FIFTH INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY



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## Table of contents

K. Luke and A. Silva	Advances in Particle Characterization: Benefits and Application
T. Witzke, T. Fuellmann, J.L. Anderson	Quantification of the M1 and M3 Polymorphs of C3S (Alite) in Clinker
J. Hajar, A. Sakulich, G. Keohane & J. Schiffman	Preliminary Investigations of Essential Oils as Corrosion Inhibitors in Steel Reinforced Cementitious Systems
J. Pacheco, O. Copuroglu & R.B. Polder	Optimisation of Chloride Quantification in Cementitious Mortar Using Energy-Dispersive X-ray Microanalysis
J. S. Lota, S. R. Farris, K. Luke	API Standard Class G Cement and Its Inconsistencies in Slurry Thickening Times
T. Sibbick, S. Garrity, & C. LaFleur	Determination of Water to Cementitious (W/CM) Binder Ratios By the Use of the Fluorescent Microscopy Technique in Hardened Concrete Samples: Part III
H. Al-Nageim & S. Al-Busultan	Stiffness, Axial Deformation and XRD Analysis of New Cold Mix Asphalt Containing Cementitious Waste Materials for Road Pavement
D. H. Campbell	Clinker and Cement – Microscopical Quality Control With Ono's Method
J.L. Wehby & M.D. Jackson	Evaluation of Mortar Microstructures in Ancient Roman Concrete From Ostia, Italy with PETROG Software
C. E. Buchanan, Jr.	Revisiting O'Hare Parking Garage: The successful Use of Expansive Cement
A. Lo Presti, T. Cerulli, A. Biancardi, E. Moretti, & D. Salvioni	Ettringite: A New Synthesis Approach
A. Sadangi, K. Suresh, & S. Chowdhury	Relative Evaluation of Microstructure and Phase Composition of Clinker Sintered With Bituminous Coal and Pet Coke
F. Amin, E. Moudilou & P. Le Coustumer	Nanopetrography Techniques Contribution to the Behaviour of Trace Elements Into Clinkers
A. Lo Presti, T. Cerulli, D. Salvioni, E. Carlini & S. Carra	A Phenomenon of Heterogeneous Coloration in a Self-Leveller: Not Only an Aesthetic Problem
S. Nezami, K. Peterson, K. J. Totty & R. Sibbick	Comparison of Hardened Concrete Air-Void Test Results from Rapid Air 457 and Flatbed Scanner Automated Analysis Equipment
S. Y. Lee, V. Jennings & A. Daugherty	Petrographic Evaluation of Deleterious Materials in Aggregates Used for Airfield Pavements in Accordance With UFGS Specification
A. Rodrigues, B. Fournier & J. Duchesne	Petrographic Characterization of the Deterioration Products in Concrete Containing Sulfide Bearing Aggregates: A Particular Case of Internal Sulfate Attack
S. Stoeber & H. Poellmann	Influences of Different Sulfonic Acids and Salts on the Hydration Behaviour of Cement Pastes

G.C. Anzalone & L. L. Sutter	Chloride Concentration Profile Collection With An Environmental Scanning Electron Microscope and X-ray Energy Dispersive Spectrometry
H. Poellmann, P. Sturm, R. Kaden & S. Stoeber	Hydration Control of Portland Cement and Calcium Aluminate Cement Using Different Earth Alkali Benzoate Hydrates
P. Du Toit & K. Feiner	Using Microscopy to Optimize the Manufacture of Oil Well Clinker
S.Y. Lee, A. Daugherty & D. Broton	Petrographic Examination of Iron-Ore and Colemanite Aggregates Used in Radiation Shielding Concrete
X. Hou, J. H. Shin, L.J. Struble & R.J. Kirkpatrick	Chemical and Microstructural Changes Associated with Alkali-Silica Reaction in Mortar

**ADVANCES IN PARTICLE CHARACTERIZATION-BENEFITS AND APPLICATIONS**

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**ABSTRACT**

Particle size and shape play a significant role in most chemical reactions that involve solid materials. Methods for determining particle size, and more specifically particle size distribution, are well documented. However, recent advancements in particle characterization can provide more detailed analysis that allow particles to not only be observed, but also individually characterized. A statistically significant number of particles (20,000 – 50,000) can be analyzed within minutes and each particle fully characterized using a number of morphological parameters. Additionally, chemical comparison of individual particles can be determined using a Raman spectrometer in conjunction with optical imaging. Particle size distributions based on number or volume calculations can also be determined from the statistical analysis.

This paper discusses the theories involved along with illustrative examples in defining particle morphological parameters, such as circle equivalent diameter, circularity, elongation, convexity, solidity, and both number and volume particle size distributions. One major advantage of optical imaging over the other techniques is the ability to classify particles in a mixture based on morphological parameters and Raman spectroscopy.

Particle characterization, particle size distributions and Raman spectra are given for cement and various additives. Analyses of two and three component systems are provided to show that not only the particle characteristics, but also the percentage composition of the individual components can be determined. The importance of particle characterization on performance is also illustrated where differences in particle characteristics of a retarder are shown to markedly affect the thickening time properties of cement.

The recent advances in particle characterization allow a much greater degree of understanding particle shape, distribution, and chemical comparison that can be used to define individual products and mixtures. This can be used to provide better understanding of performance, product composition, trouble-shooting and allow for improved QA/QC.

## QUANTIFICATION OF THE M1 AND M3 POLYMORPHS OF C3S (ALITE) IN CLINKER

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### ABSTRACT

A major component in industrial clinkers for cement production is alite, with the ideal composition  $\text{Ca}_3\text{SiO}_5$ , also written as C3S in the short cement notification. This compound can occur in at least seven different crystallographic polymorphs. Their formation depends mainly on the burning conditions (temperature, burning time, cooling rates) and minor or trace elements in the crystal structure, introduced by the raw material and fuels. Each of the different polymorphs may present different physical properties. The most relevant alite polymorphs in clinkers are two monoclinic polymorphs of alite, the M3 and M1 forms. Differences between the reactivity of synthetic M1 and M3 alite polymorphs have been cited in the literature in recent years. The careful identification and accurate quantification of these phases by full pattern Rietveld refinements, in an automated environment, is presented here.

**PRELIMINARY INVESTIGATIONS OF ESSENTIAL OILS AS CORROSION INHIBITORS IN STEEL REINFORCED CEMENTITIOUS SYSTEMS**

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**ABSTRACT**

Encapsulating bioactive agents in lightweight aggregate (LWA) is a method that shows promise as a corrosion mitigation technique in cementitious systems. LWA aggregates acts as a storage unit for the bioactive agent. Once hydration reactions in the cementitious matrix cause a drop in the internal humidity, the LWA will achieve pressure equilibrium by releasing the bioactive agent. In this way the bioactive agents, which normally severely retard hydration, will not interfere with the early age property development of the cementitious matrix. Desorption, compressive strength and calorimetric tests were conducted. It was found that expanded clay LWA absorbed more cinnamaldehyde than pumice LWA, however, the incorporation of bioactive agents severely retarded hydration and reduced the composite's strength. Significant future work that is needed, including microscopic studies, are discussed.

**OPTIMISATION OF CHLORIDE QUANTIFICATION IN CEMENTITIOUS MORTARS USING ENERGY-DISPERSIVE X-RAY ANALYSIS**

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**ABSTRACT**

Chlorides are responsible for initiating steel corrosion in reinforced concrete, the economically most important deterioration mechanism in concrete infrastructure. The quantification of chlorides is commonly performed by wet chemical analysis, e.g. acid dissolution and Volhard's titration. Energy-Dispersive X-Ray Spectrometry (EDS) is a powerful tool that can be employed in the detection and quantification of chlorides in cementitious materials. In order to provide fully quantitative analyses, a reference sample must be employed for calibration purposes. In this paper, commercially available microanalysis standard mount and a laboratory-made reference sample were used. Results show that the precision of the lab-made reference mount is suitable for cementitious analysis. Subsequently, chlorides were quantified in mortar specimens with concentrations of 1 and 2% wt cem. Results show that quantification of chlorides by employing different minerals was in the range of 0.8 and 1.6% for each sample, respectively.

## **API STANDARD CLASS G CEMENT AND ITS INCONSISTENCIES IN SLURRY THICKENING TIMES**

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### **ABSTRACT**

A Class G oil well cement conforming to API Standard Specifications was reported to give considerable variation, between batches, in the thickening time of a cement slurry formulation designed for well application. A fundamental study was undertaken on cement obtained from 3 separate batches in an attempt to determine the cause of the variability. The cement was characterized in terms of the chemical and physical properties and found to be within API Specifications: thickening times at 55°C, and 5200 psi give consistent thickening times of around 99 – 107 minutes and was well within the 90 -120 minutes limit. When used in a slurry formulated for a well having a bottom hole circulation temperature of 67°C, the 3 batches of cement give significantly different thickening times ranging from 1090 to 1400 minutes. A baseline was determined on the 3 batches of cements hydrated without additives, and properties of the hydration products determined using SEM, XRD, calorimetry, TGA/DTA and FTIR. The study was then extended to investigate the effect of the cement, first, in combination with the individual additives of the slurry formulation and second, with the complete additive composition. Additives of the slurry formulations included, lignosulfonate based retarder, sulfonated naphthalene formaldehyde condensate dispersant, hydroxyethylcellulose based fluid loss and polyether polyalcohol antifoam agent.

Baseline data indicated almost no difference in performance between the 3 batches of Class G cement. Variations in the thickening time observed in the formulated cement slurry were attributed primarily to the interaction with the lignosulfonate retarder though it was not the sole cause. Data suggests that the amount of absorption of the lignosulfonate retarder appear dependent on the specific surface area of the individual cement phases, in particular the alite phase. In addition the lignosulfonate influences the initial development of the ettringite and calcium hydroxide phases and alters the morphology of the C-S-H. Hydroxyethylcellulose component of the fluid loss additive also acts as a powerful retarder though its contribution to the variation between batches is minimal due to the physical rather than chemical process involved. The effects of the sulfonated naphthalene formaldehyde condensate dispersant and the polyether polyalcohol antifoam agent on thickening time were minimal and are only briefly discussed.

**DETERMINATION OF WATER TO CEMENTITIOUS (W/CM) BINDER RATIOS  
BY THE USE OF THE FLUORESCENT MICROSCOPY TECHNIQUE IN  
HARDENED CONCRETE SAMPLES: PART III.**

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**ABSTRACT**

The close relationship between the water to cement (w/cm) ratio of a cement-based matrix and its capillary porosity, and by association the intensity of fluorescent light in a particular sample, is well documented. The early part of this study confirmed similar relationships with various supplementary cementitious materials at differing w/cm ratios (0.35-0.70). However, this earlier work also showed the development of consistently higher fluorescence developed with the various SCM-containing mixes when compared to the equivalent Portland cement-only references. Either there truly is greater pore space available for the fluorescent epoxy to fill due to delayed hydration/ pozzolanic reaction, or the inherent light transmission characteristics of the SCM's allow light that is normally blocked by non-hydrated cement particles to shine through, or both.

In order to determine the impact of these alternatives a series of additional samples were produced at water to cementitious ratios of 0.35, 0.50 and 0.70 for mixes containing different levels of SCM. In addition samples were produced at water to powder ratios similar to these w/cm ratios, in which 25% and 50% replacement of the cement by non-reactive clear filler (quartz powder) and black filler (magnetite), to determine if any of the fluorescence differences exist relatable to the color of the original filler.

The same linear relationship between fluorescent light intensity and the water to cementitious ratio has been maintained for all the series tested so far- the higher the w/cm ratio, the higher the measured light intensity. The raised levels of fluorescence observed when supplementary cementitious materials (SCM's) are used in a mix appear to relate closely to the amount of cement replacement with SCM. The more SCM that is added to a mix, the higher the fluorescence measured compared to the equivalent Portland cement only sample. The replacement of 25% and 50% of the cement with the inert colorless quartz and opaque magnetite powder results in the expected increase (with quartz) and decrease (with magnetite) in the fluorescence level observed compared to the Portland cement only reference set, this being the result of the differing translucency levels of the two test materials. This would suggest that the color of the SCM will have some contributory effect on the resulting fluorescence developed. However, due to the relatively similar light color of the two SCM's tested here - slag and Type C fly ash-it was not possible to confirm that color and translucency of the SCM's is also contributing. This technique clearly still has great usefulness in the determination of w/cm ratios in hardened concretes in the range of 0.35 to 0.70. However, like all other techniques it should not be used by itself, but where possible in conjunction with a number of the other microscopic and physical methods where available. The need for relevant reference sets is paramount.

**STIFFNESS, AXIAL DEFORMATION AND XRD ANALYSIS OF NEW COLD MIX ASPHALT CONTAINING CEMENTITIOUS WASTE MATERIALS FOR ROAD PAVEMENT**

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**ABSTRACT**

This paper reports the stiffness, axial deformation and XRD analysis of a new cold mix asphalt developed for use in highway and airfield pavement structural layers including surfacing pavement. The main filler in the traditional Cold Mix Asphalt (CMA) is replaced with treated biomass waste fly ash materials. The waste or by-product materials were used as a modifier of the cold bitumen mixtures.

The new CMA has minimise the restriction imposed by road engineers on the use of cold bituminous emulsified mixtures by improving its mechanical and durability properties and hence provided a cheap products with less CO<sub>2</sub> emissions and less energy consumption compared with Hot Mix Asphalt (HMA).

Fly ash which is waste or by-product material was incorporated in the cold bituminous emulsion mixtures at five percentages 0-5.5% of aggregate weight in the mixture. The results have shown outstanding comparative improvement in the mechanical properties of the new cold mixtures compared with traditional cold mix asphalt. The reason for achieving these results was explained in this paper by the analysis of XRD of the fine mineral-emulsified mortar used in this study.

**Keywords:** cold bitumen emulsion mixtures, fly ash waste material, stiffness modulus.

CLINKER AND CEMENT-  
MICROSCOPICAL QUALITY CONTROL WITH ONO'S METHOD

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ABSTRACT

After a partial review of Ono's contribution to our industry, emphasis in this paper is given to the use of the microscope, studying grain mounts and polished sections in reflected and transmitted light, sometimes called "Ono's Method." The Ono Method emphasizes interpretation of kiln conditions, specifically, the heating rate, maximum temperature, time at high temperature, and cooling rate. A revised set of microscopical parameters for these interpretations of kiln conditions, based largely on Ono's microscopical work and that of the author, is offered. To this is added certain characteristics of raw meal, namely,  $Q_{45}$ ,  $C_{125}$ ,  $Q_{125}$ , and  $R_{45}$ . Improved methods of sample preparation, ranging from polished clinker nodules to powders, use of KOH-sugar solution residues, sieving with polyester cloth, and time-saving methods of particle counting are described. Other microscopical data that help to explain cement performance are: silicate crystal sizes, percentages of tightly packed belite nest fragments, alite-to-belite ratios,  $C_3A$  abundance and crystal size, added sulfate mineralogies and their percentages, free lime abundance, and many other items. Properly performed, according to Ono, the method provides a valuable prediction of 28-day mortar strength with a correlation coefficient of approximately 0.91, with a standard deviation of roughly 17.1 kg/cm<sup>2</sup>. This paper is based on the writer's Chapter 9.3 of the Portland Cement Association's "Innovations in Portland Cement Manufacturing" (2011).

**EVALUATION OF MORTAR MICROSTRUCTURES IN ANCIENT ROMAN  
CONCRETE FROM OSTIA, ITALY, WITH PETROG SOFTWARE**

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**ABSTRACT**

The ancient city of Ostia, at the mouth of the Tiber River 15 km downstream from Rome, is built mainly of brick-faced conglomeratic concrete structures that have remained largely intact for nearly 2000 years. Petrographic evaluation of volcanic ash–hydrated lime mortars from seven second century CE structures provides new insights into the builders’ selection of pozzolans and processing of lime and ash. PETROG software facilitated modal analyses of point counts through creation of a systematic catalog of diverse pozzolanic and cementitious microstructures, and a high resolution optical image of each point. A primary classification of each site was logged in the searchable PETROG database as pozzolanic aggregate, cementitious phase, or void space and further qualified in the software database with additional information. For aggregate, this includes lithological provenance of ash from the Roman volcanic province, authigenic clay or zeolitic surface textures, primary crystal fragments, and characteristics of ceramic fragments. For cementitious phases, this includes characteristics of the cementitious matrix and optical properties of discrete cementitious textures. For lime, calcite textures and purity of masses of relict putty were recorded and, for voids, the geometry of cracks, spherical, and sub-rounded spaces. The high level of detail recorded at each point allows in depth analysis of each specimen and quantifies comparisons among samples beyond what is possible with standard petrographic assessments. Results from modal analysis suggest three distinct mix designs containing zeolites and/or authigenic clays that functioned as natural pozzolans. Variations in these mixes represent specific technical decisions made by ancient builders. The empirical reasoning behind these decisions is an important but rarely explored area of archaeological research. Petrographic analysis with PETROG software has led to a better understanding of the construction industry in ancient Ostia by quantifying preferred or proprietary mixes apparently used by different groups of builders.

**O'HARE PARKING GARAGE**

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**ABSTRACT**

The O'Hare Airport Garage was constructed in 1971-73 utilizing Type K Expansive cement. At that time it was the largest expansive cement job in the world. It consisted of 6 decks, with 5 exposed both at top and bottom. When last inspected in the late 1990's, it had maintained its integrity, even though being exposed to extreme weather conditions. It is hoped to make another inspection prior to the talk to provide additional information.

## **ETTRINGITE: A NEW SYNTHESIS APPROACH**

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### **ABSTRACT**

To understand the development of mechanical and physical properties of cementitious systems,

it is crucial to investigate the critical rapid mineralogical changes that occur especially during early hydration stages. In particular in the really first minutes  $C_3A$  and  $C_4AF$  rapidly react with water producing typical hydration products (AFm, AFt).

Reactions that take place in real cement pastes are complex, so that to simulate these processes in laboratory a reliable and reproducible synthesis method has been developed.

This study has been focused on the synthesis of ettringite ( $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ ) that thanks to this technique has been obtained in a very short time and particularly free of impurities.

Evolution of particles size and colloidal dispersion stability were followed during the reaction performed under controlled conditions (pH, ionic strength, temperature, stirring and flow rate). Analyses have been performed with ESEM-FEG, Laser Diffraction Granulometry, Turbidimetry, Zeta Potential (ELS), TGA (c-DTA) and XRD.

This approach permitted us to understand which are the key parameters that rule the synthesis and hence it can be applied to other AFm, AFt-like systems.

**RELATIVE EVALUATION OF MICROSTRUCTURE AND PHASE COMPOSITION  
OF CLINKER SINTERED WITH BITUMINOUS COAL AND PET COKE**

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**ABSTRACT**

A comparative study has been carried out on plant produced clinkers made with 100% bituminous coal with that of coal plus pet coke mix fuel. The study aims to evaluate the influence of fuel mix, heterogeneity of kiln feed and occurrence of coarse calcareous and siliceous grains on the quality of clinker. The evaluation of texture, microstructure and phase composition of clinker was carried out by using polarized light and scanning electron microscope combined with energy dispersive x-ray.

The results show that increase of alite and belite crystal size with increase in  $SO_3$  content in clinker. The alite content also reduces when increasing pet coke percentage in the fuel mix. X-ray microanalysis show that  $SO_3$  is mainly concentrate on the belite and alite phases and some amount combined with alkalis.  $CaO/SiO_2$  molar ratio in examined clinkers is found to be varying in the range of 2.75 – 2.79 in alite and 1.80 -1.88 in belite phase. Inclusions of belite inside alite and the frequency of belite cluster is more in 65% pet coke plus 35 % bituminous coal fired clinker. From microstructural point of view it was found that the clinker made with 35 % pet coke plus 65% bituminous coal having better quality than others.

**NANOPETROGRAPHY TECHNIQUES CONTRIBUTION TO THE BEHAVIOUR  
OF TRACE ELEMENTS INTO CLINKERS AND MORTARS**

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**ABSTRACT**

Identifying heterogeneities within a clinker and understanding the processes leading to these changes are of major importance for cement makers. Indeed, the great diversity of the fuels used makes it usual to face microscopic particles whose mineralogical, chemical or structural properties are different from the matrix. Currently, the characterization of these phases is mainly based on optical microscopy, scanning electron microscopy, X-ray diffraction and electron microprobe analysis. The main advantages of these methods are their simplicity, the sample preparation (simple and normalized) and their scales which are micrometric. On the other hand the main limit, in relation with trace element distribution into the cement, clinker and mortar is the scale because trace element or minor phases act at nanometric level (concentration are lower than the percent, size of the potential neophases induced by the process and their distribution which has to be précised).

For this reasons additional techniques have to be faced like HRTEM/X-EDS or GDOES. They have been tested on the clinkers analysis, burned with alternative fuels, and on mortar doped with nanometric TiO<sub>2</sub>. These methods can be named micropetrographics should be able to precise the distribution of such trace elements like phosphorus or Ti, nature of the neo phases potentially generated into the manufactured products. A basic question quite difficult to answer is: are they trapped into the exiting phases without structural modifications or do they precipitated by creating new nanophases? Such question is of a great importance as soon as in the first case (trapping mechanism) long term durability is supposed to be not modified. In the second case (precipitation), how these news nanophases can act at long term on the durability or ageing or chemical reactions?

**A PHENOMENON OF HETEROGENEOUS COLORATION IN A SELF-LEVELLER: NOT ONLY AN AESTHETIC PROBLEM**

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ABSTRACT

Cementitious self-levelling formulations are probably the most complex and sophisticated among all building dry-mixed materials as the product must guarantee many different properties both during the application stage and during a floor's service life.

Particularly demanding is the use of a self-leveller as a floor's top: in this case in fact the self-leveller is only, and not always, protected by a thin coating layer, and therefore it must be overperforming not only in terms of mechanical characteristics and abrasion resistance, but also for what concerns surface appearance. In particular it is very important to be able to obtain a product the surface color of which is stable and homogeneous irrespectively from application procedures that might significantly change jobsite by jobsite.

In the case study presented in this paper we noticed that the residence time of the product in the bucket after it had been mixed with water, could significantly alter the surface color making it lighter, and thereby causing the floor's homogeneity to be unsatisfactory.

Samples of the product showing such difference have been initially described macroscopically and then characterized with mineralogical and chemical – physical techniques such as X Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and BET.

A fundamental rule has been played by the Electronic Microscopy (ESEM) coupled with EDS analysis. This technique gave us a key to understand the phenomenon, that happened to be not only esthetic but a complex mix of chemical and physical factors with an unexpected composition of the main hydration products.

**COMPARISON OF HARDENED CONCRETE AIR-VOID TEST RESULTS FROM  
RAPID AIR 457 AND FLATBED SCANNER AUTOMATED ANALYSIS  
EQUIPMENT**

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**ABSTRACT**

The air void parameters of 105 concrete samples are measured using a Rapid Air 457 commercial automated air void analysis system. The same concrete samples are also scanned with an ordinary desktop flatbed scanner and the images are analyzed using scripts written for a commercial digital image editing. The results of air content and spacing factor found by the two automated methods show very good agreement. Chord length distributions of the two methods are also compared, and the Rapid Air 457 found to detect higher numbers of very small (<10 μm) chord intercepts.

**PETROGRAPHIC EVALUATION OF DELETERIOUS MATERIALS IN  
AGGREGATES USED FOR AIRFIELD PAVEMENTS IN ACCORDANCE WITH  
UFGS SPECIFICATION**

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**ABSTRACT**

Foreign object debris (FOD) at airports can cause damage that is very costly to airlines, airports, and airport tenants. Some of the most common FOD are fragments and rocks from concrete pavement made with aggregates containing deleterious materials. FOD can injure airport personnel and damage airplanes. Thus, the presence of deleteriously expansive constituents in the aggregates used in airfield pavements is potentially hazardous. Due to these reasons, aggregates used in airfield pavements often require specifications and testing procedures different than aggregates for general use in concrete. The Unified Facilities Guide Specification (UFGS) has been specifically used in specifying airfield pavement construction for military services. Federal agencies have recently been adopting the UFGS specification for various airfield pavement construction projects.

This article will describe projects on which petrographic examination was performed in accordance with UFGS Section 32 13 11 for different types of coarse aggregate samples to be used in airfield pavement projects. Relatively large sizes of samples were collected to meet the minimum sample size requirements specified in UFGS 32 13 11, paragraph 2.2.2.5. The six step testing sequence of UFGS 32 13 11, paragraph 2.2.2.5 was followed. All particles in each sieve fraction were visually and microscopically examined for the presence of deleterious materials. Particles not fully identified by visual and microscopical examination were separated and analyzed by SEM-EDX and other chemical methods including acid digestion. The identified deleterious materials were separated by category as described/classified in UFGS 32 13 11, paragraph 2.2.2.4, and the weight percentage of each category was calculated and reported. The deleterious materials testing of aggregates in accordance with the UFGS specification requires a specialized testing sequence and a level/extent of examination different than the examination of aggregates for general use in concrete. The examiner (petrographer) of the aggregates used for airfield pavement concrete should be familiar with UFGS 32 13 11 and the sequential test procedure (6-step process) required by paragraph 2.2.2.5.

**PETROGRAPHIC CHARACTERIZATION OF THE DETERIORATION PRODUCTS OF A CONCRETE CONTAINING SULFIDE BEARING AGGREGATES; A PARTICULAR CASE OF INTERNAL SULFATE ATTACK**

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**ABSTRACT**

Iron sulfides are common minor phase in many types of rocks. When iron sulfide-bearing aggregates are used for concrete production, they can cause damages as it is the case in the Trois-Rivières area (Quebec, Canada). In this case, the concrete incorporating sulfide-bearing aggregates caused the deterioration of more than 1000 house foundations and commercial buildings. This is a particular type of concrete deterioration. This deterioration process presents special features, including the high speed of the concrete degradation. The first signs of deterioration appear about 3 to 5 years after construction. In all the cases, the deterioration is such that the concrete foundations have to be replaced.

In order to better understand the problem, concrete samples from the affected structures were analyzed using different petrographic tools including polarizing microscope and scanning electron microscope *coupled* with an *energy dispersive x-ray* spectrometer (SEM/EDS). Polished thin sections and fractured surfaces of damaged concrete were examined to determine the oxidation state of the sulfide minerals, identify the reaction products and observe their morphology and interrelationships.

**INFLUENCES OF DIFFERENT SULFONIC ACIDS AND SALTS ON THE  
HYDRATION BEHAVIOR OF CEMENT PASTES.**

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**ABSTRACT**

Alkenesulfonic acids and sodium salts as well as arenesulfonic acids can be used as cement admixtures. According to the modification of the molecular structure of the sulfonic acids and salts, the hydration processes of a cement paste can be retarded or accelerated.

Due to the increase of the chain length  $C_nH_{2n+1}$  until  $n=9$  of aliphatic sulfonic acid salts  $C_nH_{2n+1}SO_3Na$  the course of hydration of an OPC can be retarded at constant additive concentration. Furthermore the use of different benzene sulfonic acids with different numbers of  $CH_3$ -substituents in combination with high and low additive concentration makes it possible to apply the organic substances as accelerators or retarders. Detailed studies show that the influence of the used additives are responsible for the retarded hydration process of  $C_3S$  and  $C_2S$ . Moreover sulfonic acid ions will be fixed in the inter layer of in-situ formed AFm-phases.

**Keywords: Calorimetry, Sulfonic acids, Additives**

**CONCRETE CHLORIDE CONCENTRATION PROFILE COLLECTION WITH AN ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE AND X-RAY ENERGY DISPERSIVE SPECTROMETRY**

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**ABSTRACT**

A method for developing chloride concentration profiles from a series of elemental maps collected by an EDS-equipped Environmental Scanning Electron Microscope (ESEM) is reviewed. Analysis is performed on diamond-ground surfaces, requiring minimal preparation. Additional advantages are very good discrimination between paste and aggregate, significant automation and rapid turn-around. Standard preparation and instrument calibration is discussed along with examples of profiles produced by the method.

**HYDRATION CONTROL OF PORTLAND CEMENT AND CALCIUM ALUMINATE CEMENT USING DIFFERENT EARTH ALKALI BENZOATE HYDRATES**

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**ABSTRACT**

The use of different alkaline earth benzoates as additives to Portland cements and calcium aluminate cements was studied. Carboxylic acid salts can be used to control setting and hardening of cement. Various hydration mechanisms were described in literature for carboxylates. In this study Mg-, Ca-, Sr-, Ba-, Co- and Ni-benzoate hydrates were synthesized and characterized regarding their thermal stability and infrared data. Moreover, the crystal structure of  $\text{Co}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was solved and  $\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was found to be isotypic. The synthesized benzoates were applied as admixtures to cement pastes of an OPC and a CAC in form of aqueous solutions of different molarities. The influence of these admixtures on the setting behaviour are presented and compared to the setting of the cement pastes with pure water as a reference. Depending on the concentrations the admixtures mainly retard or in some cases accelerate the setting. In addition, a significant influence of the type of cation was found.

## **USING MICROSCOPY TO OPTIMIZE THE MANUFACTURE OF HSR CLINKER**

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### **ABSTRACT**

This paper describes the use of microscopy to optimize product quality which also improves energy consumption in the clinkering manufacturing process.

While the use of microscopy to determine the microstructure and phase composition of clinker is well known, it is often not integrated as a routine proactive optimization practice. Microscopy is commonly used during periods of new equipment start-up or for troubleshooting of performance issues. Today with heightened focus on focus on Green house gasses and performance based cements, pozzolan, slag and limestone addition, increased focus on measuring and predicting the properties of clinker hydration compounds is considered an essential technique.

Progression of the clinker hydration compounds from a highly reactive state to a low reactive state was followed by microscopy during a trial. In addition, correlations to real time sensors were established and kiln and raw mix control actions were made to optimize the clinker hydration compound reactivity by optically observing and measuring the crystal size, purity and changes to the microstructure.

The process of mastering clinker hydration compounds reactivity by combining microscopy with real time sensors and process control changes has proven to enhance cement consistency while reducing energy costs.

The clinker from the production trial described in the paper showed features consistent with good HSR well clinker and was confirmed by physical testing of the cement produced from the clinker.

**PETROGRAPHIC EXAMINATION OF IRON-ORE AND COLEMANITE  
AGGREGATES USED IN RADIATION SHIELDING CONCRETE**

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**ABSTRACT**

Radiation shielding concrete (RSC) is used in applications such as nuclear power plants, health care facilities, collegiate test reactors, national laboratories, and research facilities. The type and quantity of aggregates in RSC are important component for radiation protection properties of the concrete. Either natural heavyweight aggregates or synthetic aggregates are used in RSC. ASTM C638 Standard provides two classes of aggregates/materials used in RSC; (1) Class 1 - gamma ray shielding, and (2) Class 2 - neutron shielding. Iron ores are one of the most common Class 1 natural aggregates for gamma ray shielding. Colemanite is the most common Class 2 natural aggregate. Minerals with substantial boron content, such as colemanite, have been proven to be particularly effective in absorbing thermal neutrons without producing highly penetrating gamma rays.

Iron ore and colemanite aggregate samples were petrographically examined in accordance with ASTM C295 to detect potentially harmful (deleterious and undesirable) materials in RSC. Each sieve fraction of an aggregate sample was examined, and its constituents identified, classified, and tabulated into the following three categories: (1) particles consisting almost entirely of iron-bearing metallic minerals (or boron minerals for the "colemanite" aggregate), (2) particles of mixed iron-bearing metallic minerals and impure materials, and (3) particles of impure materials. Particles in each category were examined using different test methods and techniques (combinations of transmitted and reflected light microscopy, X-ray diffraction, and X-ray fluorescence) to determine potentially harmful materials in RSC.

Although ASTM C295 applies to aggregates for general use as well as for RSC, petrographic examination of these specialized aggregates for RSC involves in more stringent QA requirements, different levels and extent of examination, and proper experience and training of the petrographer performing the examination.

## CHEMICAL AND MICROSTRUCTURAL CHANGES ASSOCIATED WITH ALKALI-SILICA REACTION IN MORTAR

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### ABSTRACT

In previous studies of laboratory synthesized gels and model aggregate-solution reactions, we demonstrated that, under the conditions of those experiments, the alkali-silica reaction (ASR) proceeds by silica dissolution, reaction of silica with calcium hydroxide and Ca-rich calcium silicate hydrate (C-S-H) to form a Si-rich, polymerized C-S-H, and finally formation of an alkali silicate hydrate gel (A-S-H). In the present study, mortars undergoing ASR were examined using X-ray diffraction, <sup>29</sup>Si magic angle spinning nuclear magnetic resonance spectroscopy, and scanning electron microscopy to investigate more fully the microstructural relationships between expansion and A-S-H. Mortars for both expansion and microstructural examination were immersed in 1N NaOH solution at either 23°C or 80°C. The results show a direct connection between A-S-H gel formation and expansion. At 80°C, the reaction chemistry and microstructural changes in the mortars were similar to those we previously observed in synthesized gels and aggregate-solution reactions, and the A-S-H formation appeared to be strongly associated with the mortar expansion. At 23°C, the reaction chemistry and microstructural changes were somewhat different. We observed less reduction in calcium hydroxide, only a moderate increase in average C-S-H polymerization, and A-S-H gel was detected by scanning electron microscopy but not by nuclear magnetic resonance and only after the mortar had already exhibited much expansion.

**Keywords:** alkali-aggregate reaction, concrete durability, SEM-EDX, nuclear magnetic resonance, x-ray diffraction, crack, expansion