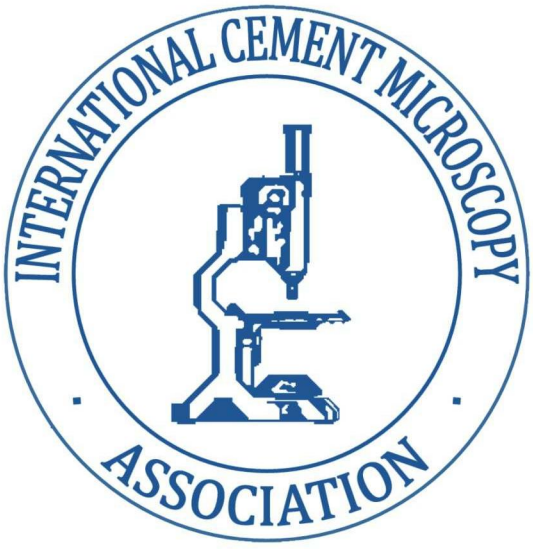
26th INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY



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Further Investigations in the Determination of Cement and Mineral Admixture Content in Hardened Concrete using X-ray Fluorescence Spectrometry

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Background

Concrete is utilized in construction projects worldwide. Its physical properties and ready availability make it an ideal building material. However, changes in proportions or types of cement, sand, coarse aggregate, fly ash, slag or water or other components may alter the properties of plastic and/or hardened concrete.

Furthermore, many factors influence the proper and complete mixing of these components. Batch plant vs. dry mix, aggregate shape and size, water to cement ratio, slump, air content, mixing speed, batch sequencing, truck blade condition and configuration and a host of other factors all may influence proper and complete blending of the materials. Owners and specifiers need assurance that all ingredients are combined as specified.

Determining the appropriate mix time for the material types and mix design in use is critical to producing the highest quality, uniform concrete in the shortest time possible. A sometimes overlooked but critical aspect of the ready mix operation, mix homogeneity can be determined by taking samples of the plastic concrete at various mixing times. The mass percentages each of the elements determined in the concrete sub-samples should be consistent throughout the discharge after the appropriate mixing time at mixing speed has been established. Total mixing drum revolutions as well as revolutions at mixing speed should be documented in all cases.

For some time now, ready mix producers and cement suppliers and property owners have had to rely on a select few standard procedures to determine the cement content in hardened concrete, which can have significant interferences, thus biasing results. In addition, the use of mineral admixtures such as fly ash and ground granulated blast furnace slag complicate the determination by standard methodologies and assumptions must be made regarding the compositions of these

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SEQUENCE OF CLINKER-PHASE CRYSTALLIZATION

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ABSTRACT

Microscopical relationships between different phases in cement clinkers can be used to interpret the sequence of crystallization, that is, which crystals formed before others. This paper lists some of the observations allowing the relative determination of crystallization sequence. Periclase, for example, can be shown to occur within alite, and the latter crystal is, therefore, younger. Periclase within belite indicates the existence of periclase prior to the crystallization of belite. Free lime, belite, and matrix within alite are all older than the enclosing alite. Aluminate (C_3A) can be shown to be younger than the adjacent ferrite, but the opposite relationship might apply under different conditions of cooling. These and other examples are selected to illustrate relative age relationships between some of the crystals occurring in portland cement clinker.

The subjects of crystallization from a solution or melt, or growth within the solid state, lie at the heart of physical chemistry. Interesting and fundamental as they are, they are beyond the scope of this presentation. The effects of minor elements and gases (fluorine , sulfate, and oxygen levels, for example) or other crystal-chemistry relationships make generalizations about clinker-crystal sequence somewhat speculative. I believe, however, that the microscopical criteria for determination of crystal sequence remain applicable, tempered with an understanding of their possible fallibility.

FINITE CHARACTERIZATION OF ASHES FROM A CIRCULATING FLUIDIZED BED COMBUSTION THERMAL POWER PLANT

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ABSTRACT

Fly ash and bottom ash from fluidized bed combustion power plants have limited use in the construction industry because of their high-inherited sulfate content. Therefore, most of these ashes are land-filled. Finite characterization, which included the determination of physical, chemical and mineralogical properties of such a land-filled ash from a circulating fluidized bed combustion power plant, was undertaken. The land-filled ash, which had been stockpiled for several years, was compared with freshly generated ash from this power plant. The tests performed included particle size distribution pattern, mineralogical, chemical, and water-soluble ions analyses, and morphological characterization using scanning electron microscope/energy dispersive X-ray analysis.

The results indicate that a significant amount of the sulfate component in stockpiled ash was consumed in a reaction, which involved the formation of ettringite. The sulfate (anhydrite) in fly ash and bottom ash also converted to gypsum when landfilled, and lime in fly ash and bottom ash was spent due to weathering.

The final objective of this research is to study if this stockpiled ash can be gainfully utilized in the production of a construction material. The characterization results suggest that the deleterious expansive reaction involving sulfate ions has been completed. Therefore, several potentials exist for utilization of the stockpiled ash; for example, in soil stabilization, road base construction and flowable fills.

CONCRETE PETROGRAPHY: CAPABILITIES AND LIMITATIONS

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ABSTRACT

Concrete petrography is a powerful tool to investigate concrete, mortar, stucco, aggregate, and other construction materials. It is capable of identifying different components, verifying mix proportions, and differentiating various mechanisms of premature concrete failures. However, there are also some pitfalls and limitations, and the data can be easily over-interpreted. Through case studies, this paper discusses what valuable information can be extracted from a petrographic investigation and what cannot.

KEY WORDS

Concrete petrography, carbonation, relative crack age, w/c, SEM, mix design

COMMON QUALITY PROBLEMS WITH OIL WELL CEMENT

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ABSTRACT:

Many would like to group oil well cement with the other common commodities used in the construction industry such as iron ore, silica sand, or bauxite. If in fact, well cement is made properly it is closer to being an industrial chemical than it is to a building commodity. Properly designed and produced well cement will have a consistent quality record, exhibit stable shelf life, and for the most part be free of the common well cement quality problems. This paper will investigate the more common well cement problems and recommend ways to avoid them. The paper will also stress the single most important well cement quality characteristic: consistency.

GYPSUM IN HARDENED CONCRETE - IS IT ALWAYS A SIGN OF CONCRETE DESTRUCTION?

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ABSTRACT

As observed by a scanning electron microscope (SEM), concrete may contain gypsum in the hydrated cement paste that does not create additional or unusual distress to a particular concrete structure. Sources of gypsum included silicate aggregates, fly ash particles, and carbonation of ettringite. The paper presents BS images accompanied by X-ray elemental analyses of gypsum in hydrated cement paste and in aggregate/fly ash particles.

Key Words: Concrete, SEM, gypsum, aggregate/fly ash particles.

SEM INVESTIGATION OF MICROBIOLOGICALLY REMEDIATED PLASTIC SHRINKAGE CRACKS IN CONCRETE

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ABSTRACT

This paper presents the results of a study on the effects of microbiologically induced mineral precipitation in reducing the plastic shrinkage cracks in concrete slabs by external remediation. External bio-remediation was done by soaking the slabs (made with and without bacteria) with plastic shrinkage cracks in a remediation tank filled with bacteria (*B. pasteurii*) suspended in medium (Urea-$CaCl_2$ solution). The crack areas before and after remediation were compared to determine the extent of crack area reduction and are presented in this paper. The plastic shrinkage crack area reduction capacities of concrete slabs (made with and without bacteria) by external bio and chemical (only medium) remediation are presented in this paper. The effect of dead bacteria and different concentrations of live bacteria on the plastic shrinkage crack area reduction capacity were also determined.

Microbiologically induced external remediation was found to be very effective in remediating plastic shrinkage cracks. External bio- remediations of the cracked slabs were found to be effective than external chemical remediation. X-ray diffraction technique was used to characterize the chemical composition of the crystals that grew on the surface of the concrete slabs. Scanning Electron Microscope (SEM) was used to conduct an elemental and compound analysis on the concrete samples to document the role of microbiologically induced calcite precipitation in plugging the plastic shrinkage cracks.

Hydration of Calcium Aluminate in Ettringite-based Binder – Investigation of Model Systems

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ABSTRACT

Calcium aluminate cements are normally sulfate-free, but blending with calcium sulfate-hemihydrate ($C\underline{S}H_{0.5}$) or gypsum ($C\underline{S}H_2$) can lead to formation of the sulfate-containing hydrate Ettringite ($C_6A\underline{S}_3H_{32}$).

CA and Fe-doped $CA_{1-x}F_x$ solid solutions were synthesized in laboratory furnaces at 1250°C from reagent grade chemicals. All phases were checked for minor phases and characterized by X-ray powder diffraction analysis. Structural parameter refinement by Rietveld-analysis with fundamental parameter approach (Topas 2.1) was employed for crystallographic characterization of the anhydrous phases.

Due to the wide technical importance of Ettringite-based binder systems model systems of $CA_{1-x}F_x$ with $0 \leq x \leq 0.1$ with admixtures of $C\underline{S}H_{0.5}$ were hydrated at 23°C in a heat flow calorimeter based on an quadruple arrangement as described before by [1] and fully revised by [2]. In accordance with calorimetric data the hydrating mixtures were investigated by X-ray powder diffraction analysis in order to interpret the recorded caloric effects of the first 48 hours of in-situ hydration.

Reaction of pure CA with water is beginning after 17-18 hours of induction period [3]. In contrast mixtures of CA and $C\underline{S}H_{0.5}$ are reacting immediately with water during the first minutes of hydration. This main phase of water absorption could be observed without induction period for all sulfate-containing mixtures. From XRD-investigations we could attribute this mainly to exothermic reaction of $C\underline{S}H_{0.5}$ (hemihydrate) transforming into $C\underline{S}H_2$ (gypsum). The following 2nd maximum of heat flow can be correlated

INFLUENCE OF A FINELY GROUND WASTE GLASS ON THE MICROSTRUCTURE DEVELOPMENT OF CEMENT PASTES

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ABSTRACT

Due to the number of environmental, technological and economical reasons, the utilization of finely ground waste glass as a component of cement based materials is an important alternative to the existing methods of glass recycling. It is known that a finely ground glass participates in a pozzolanic reaction, that provides an improvement of the properties of cement pastes at a hardened stage. Therefore, the realization of the pozzolanic potential of waste glass requires better understanding of the hydration mechanisms involving waste glass.

The current study was designed to evaluate the effects of different types of waste glass (window glass, monitor glass and two types of bottle glass) on the microstructure and strength development of cement. For this purpose, the cement pastes incorporating a large amount (50 % by weight) of waste glass were investigated by scanning electron microscope at different ages. The study was focused on the microstructure development of pastes containing waste glass and also on the effect of waste glass on cement performance. SEM investigations were useful to detect the changes in C-S-H, CH and interface between the paste matrix and waste glass particles. Finally, the main differences between the hydration products of the reference cement and the cements containing waste glass were identified using SEM.

IN-SITU XRD INVESTIGATION OF OPC HYDRATION

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ABSTRACT

Rietveld+ calculations of XRD pattern of hydrated OPC pastes are leading to repeatable results with true quantitative approach. The first hydration product after stirring cement powder with water (after 5 min) is Ettringite, with about 10 ma.-% with respect to the wet cement paste. C_3A, C_4AF, and sulfate carriers are decreasing at the same time. During the next 2.5 h no significant change in quantitative phase composition could be observed. After about 8.1 h a significant content of Portlandite was observed. Consequently an increasing amorphous content of CSH phase and a decreasing content of Alite was determined. At the same time C_3A and Anhydrite are decreasing due to formation of more Ettringite. Until 19 h hydration is continuing and leading to an Ettringite content of about 18 ma.-% together with increasing Portlandite and CSH contents. Belite content is not changing during the hydration until 19.1 h. Approximately 45 ma.-% of the paste are hydrated after 19 h. The development of the phase content is correlating very well with heat flow from calorimetric investigations. The first heat flow maximum correlates with hydration of calcium sulfates and calcium aluminates/ferrites. The second heat flow maximum indicates the simultaneous hydration of calcium sulfates, calcium aluminates/ferrites and Alite. Crystallinity of Ettringite is improved during hydration time. Lattice parameters of Ettringite show a shift from $CO_3^{2-}/OH^-/Fe^{3+}$ containing solid solutions towards pure $C_3A*3CaSO_4*32H_2O$ during hydration time.

MICROSTRUCTURE AND CHEMICAL RESISTANT PROPERTIES OF RESORCINOL FORMALDEHYDE RESIN SAND CEMENT CONCRETE

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ABSTRACT

Resorcinol - formaldehyde resin (RF), the phenolic resin chosen for the preparation of the polymer sand cement composites is characterised by its high heat and chemical resistance. It also combines the advantage of being cost effective and crosslinking without the help of external agents that could have adverse effect on the properties of the cement concrete. The following study focuses on the changes in the microstructure and chemical resistance properties of the resorcinol formaldehyde resin cement sand composite with varying proportions of sand and cement. It was found from the study that the *in situ* synthesis of the resin facilitated easy mixing of the components during preparation of the composite. Investigations into the microstructure and chemical resistant properties of the composite were done after immersion of the hydrated and cross-linked polymer cement composites in different chemical environments. The compressive strength and chemical resistance properties of the composites were found to be better than those of cement concrete. The SEM revealed a more compact structure in case of the RF cement concrete and RF sand cement mortars.

OILWELL CEMENTS AND CALCIUM HYDROXIDE FORMATION

Bill Caveny, Halliburton

ABSTRACT

Calcium hydroxide formation and reactions are an important mechanism during the hydration process of Portland cements. This paper presents a brief study of some causes and effects of calcium hydroxide in oilwell cements as they undergo hydration in varying conditions of temperature and pressure relative to the downhole environments of oilwells. Light microscopy and electron microscopy methods utilizing cryogenics, environmental scanning electron microscopy (ESEM), and high-vacuum systems are all used in examining the formation of calcium hydroxide as the cement hydrates under varying conditions.

CEMENTS OF THE 21st CENTURY*

Shondeep L. Sarkar[1] and Jean-Claude Roumain[2]

ABSTRACT

This paper provides a brief historical perspective on the development of cement, a look at common problems and solutions, and a statement of the current status of cement production and applications. The authors further give their assessment of the need for performance-based cements and offer a look forward to characteristics that the cements of the future will need.

As we move into the new millennium and portland cement reaches its 178 anniversary, global cement consumption stretches over the 1.5-billion-ton mark. Although cement strength has increased significantly since the Aspdin era, new challenges for the cement industry loom as we enter the new millennium. One of these is to abide by the Kyoto Agreement to reduce atmospheric CO_2 emissions. Binary-, ternary-, and quaternary-component blended cements appear to offer viable solutions for achieving this environmental target. There is an imminent need to make provisions for performance-oriented blended cements to deal with the key issue of the low-clinker-factor cement.

Ductal® - Ultra-High Performance Material with Ductility:

The Technology, Material Properties and Examples

By Vic Perry, FCSCE, MASc., P. Eng. And Bill Carruthers, PE

ABSTRACT

Ductal® is a new material technology offering a unique combination of superior characteristics including ductility, strength and durability, while providing highly moldable products with a quality surface. The materials provide compressive strengths up to 30,000 psi and flexural strengths up to 7,200 psi.

The material's unique combination of superior properties enable the designer to create thinner sections, longer spans and higher structures that are lighter, more graceful and innovative in geometry and form while providing superior durability and impermeability against corrosion, abrasion and impact. This technology provides opportunities to improve many existing products and manufacture new products that will compete with materials such as stainless steel, cast iron, ceramics and others.

This paper presents the material technology, mechanical properties, solutions and the manufacture, installation and assembly for specific example projects including: roof panels and canopies, five-sided boxes and anchor plates.

Many economies gained from this new technology are a result of engineering new solutions for old problems. By utilizing the unique combination of superior properties, designs can eliminate passive reinforcing steel and experience reduced global construction costs, formworks, labor and maintenance. Additionally, this relates to benefits such as improved construction safety, speed of construction, usage life and others.

CemPro Analytics Ltd	**On-line analysis of raw-mix with SOLAS in a cement plant in Lengfurt (Germany)**

Executive Summary

SOLAS (Schnelle On-Line Analyse von Schüttgüternon) is a proven technology for analysing bulk materials and is employed in coal industry in many power plants and coal mines. This rugged analyser is designed to work under harsh conditions and engineered to high degree of reliability for control applications. SOLAS can also be used in the cement industry for analysing the raw materials. SOLAS was EDXRF was installed and evaluated Lengfurt cement plant (Heidelberg) in Germany for analysing raw meal.

- The principle of SOLAS combines a patented pneumatic sampling system combined with energy-dispersive x-ray fluorescence analysis (EDXRF).
- Techniques for raw mix control for raw mills are reviewed.
- SOLAS was put into operation from January 2004. During the evaluation period nearly 2.600 samples were sampled and analysed. Every hour routine Lab samples were automatically taken and analysed in order to compare with the results. The plant had automated laboratory system with extensive robotics and with ARL laboratory analyser.
- The SOLAS results were in excellent agreement with the Lab samples for the measured concentrations of SiO_2, CaO, Fe_2O_3, Al_2O_3, K_2O and SO_3.
- The results show that the on-line analyzer SOLAS is well suited for monitoring t raw-mix and for implementing raw mix proportioning scheme.
- Due to the high sampling and analysing frequency of SOLAS, the instrument is particularly suited for quality control of raw mix after vertical mills with a high throughput.