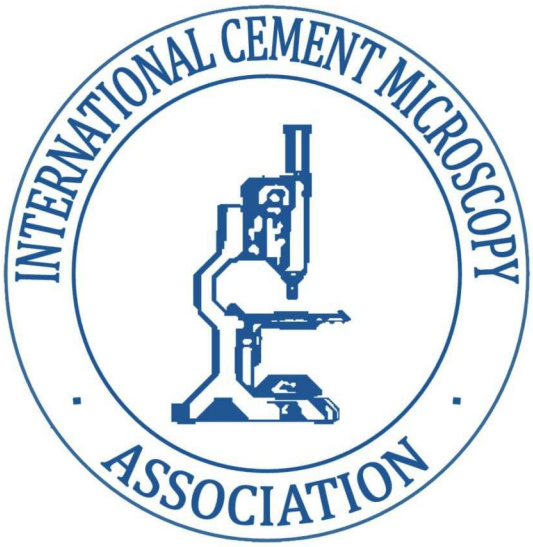
25th INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY



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CLINKER MICROSCOPY 101: WHAT THE PLANT MICROSCOPIST IS LOOKING FOR AND WHY

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ABSTRACT

Clinker is the basic foundation of both cement and concrete. Without good clinker, it is difficult, if not impossible, to make either good cement or good concrete. At the plant level, where the equipment available for analysis is generally far below the level of research labs or other facilities, the quality control manager can use the microscope as a tool to improve his cement by improving his clinker. There are a few key factors the plant microscopist can use to determine how good the clinker is, and to determine the potential future performance of the cement from that clinker. Above all, the plant microscopist needs to have some history of his clinker, so that he will know whether or not a change is necessary in the clinker, or what effect a process change has had on the clinker.

SOLVING RAW MATERIAL CHALLENGES

By
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F. MacGregor Miller, Senior Principal Scientist

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Abstract

A comprehensive understanding of the chemical and physical aspects of raw material transformation into clinker is an important foundation to increasing production, reducing costs, and improving quality at the cement plant. Clinker formation relies on numerous kiln feed properties and pyroprocessing conditions. Understanding the influential properties of the feed (chemistry, fineness, uniformity, and mineralogy) can lead to improvements in its burnability and therefore in the efficiency of plant operations. The paper discusses clinker formation, its relation to kiln feed properties, and the importance of optimizing burnability by careful mix control, good mix homogeneity, and tailoring the burning process to the raw mix. The burnability and kiln feed are discussed in relation to specific fuel consumption.

When the raw materials available make it hard to achieve burnability goals, the use of fluxes and/or mineralizers may be helpful. Fluxes and mineralizers indirectly affect burnability by promoting clinker phase formation to occur earlier; their effect on clinker formation and cement quality is briefly described. Fluoride-containing compounds have proven to be the most effective mineralizers in cement clinkering reactions. However, an excessive amount of fluoride may delay cement setting time.

Emphasis is placed on the effects of changes in raw material burnability and clinker formation on kiln operations, finish mill productivity, and the properties of the resulting cement.

PARTICLE SIZE,
CAN WE ALL SING OUT OF THE SAME BOOK?

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Particle size, and its measure, has always been an elusive parameter in the cement industry. Sieving was initially used, and the sieves were of cloth and relatively coarse. The first specifications for cement, written in 1902, required that the cement have a given sieved fineness.

In 1933, Wagner developed a turbidimeter, which became standard in the cement industry, and is still used. The biggest problem is that it is very operator dependent, and is time consuming. In addition, the surface area results are low, primarily because an average diameter of 3.75 microns was taken for the material smaller than 7.5 microns. Portland cements of normal fineness were around 1800 Wagner surface area.

Later, R. L. Blaine at the National Bureau of Standards developed the air permeability apparatus which has proven to be a work horse as far as surface area is concerned. However, when running Portland cements, it is markedly affected by contaminants and exposure to moisture. It presented results of 3600 to 3800, about double the Wagner value.

Other methods have been used, but it was not until the laser beam apparatus was developed in the late 70's that a rapid method for particle size distribution was found.

However, different instruments gave widely varying results, and all produced data which had different micron sizes, so therefore no comparisons could be made, sometimes even between different models of equipment from the same manufacturer.

Task group 1, of ASTM sub-committee C01.13 has been diligently working for several years to provide some standardization. Three series of round-robins have been run, and some things are apparent which are:

CAUSES OF HIGH EARLY VISCOSITY PROBLEMS IN WELL CEMENTS

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ABSTRACT:

One of the worst problems a cement chemist faces when working with well cements is commonly referred to as viscosity problems. To the well cement chemist working in a cement plant viscosity is interpreted to mean the degree of set in the cement slurry system. This short paper will address some of the known causes of early viscosity. Viscosity problems of retarded cements and neat cements will be discussed. It will soon become evident that viscosity problems are a result of many factors and are seldom caused by just one change of parameter. The idea that only a change of gypsum hydration state could cause viscosity problems is quickly dashed.

DURABILITY OF CEMENT MORTAR MADE WITH DIFFERENT CONCENTRATIONS OF BACTERIA

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ABSTRACT

This paper presents the results of a durability study on cement mortar beams with bacteria, exposed to alkaline, sulfate and freeze-thaw environments. Different concentrations of bacteria were used for the investigation. Using Scanning Electron Microscopy (SEM) the influence of bacteria in improving the durability characteristics of cement mortar was investigated. The cement mortar beams with bacteria performed better when compared to beams without bacteria. It was also found that the effects due to alkaline, sulfate and freeze-thaw attack reduced with increase in concentrations of bacteria.

Keywords: Calcite precipitation, cell concentration, *bacillus pasteurii* (bacteria), durability, alkali-aggregate reactivity, sulfate attack, freeze-thaw

MICROSTRUCTURE OF PHENOLIC RESIN CEMENT CONCRETE

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ABSTRACT

Studies on cement concrete microstructures are carried out in order to explain experimentally observed phenomenon and for constitutive modelling of concrete at the macroscopic level. Many investigations have already been conducted to investigate the structure property relationships before and after the addition of external agents to the cement concrete. This paper describes the study and analysis of the microstructures of phenolic resin cement concrete and their effect on the macroscopic properties. Resorcinol formaldehyde and m-cresol formaldehyde resins were used to form the composite. The cementatious phase of the cured phenolic resin cement concrete samples were etched and the resulting polymer network was analysed under a Scanning Electron Microscope. Thermal and chemical analyses of the phenolic resin cement concrete were also carried out to determine the interactions between the polymer and cement concrete phases and the extent of hydration after the addition of polymer into the composite network. Investigations on resorcinol formaldehyde cement concrete revealed that the interactions between resorcinol and the Ca^{2+} ions in the cement concrete resulted in a strong chemical bond between the resin and the cement. The final composite had mechanical and chemical resistant properties far better than virgin cement.

The X-ray Microscope: A New Tool for Concrete Analysis

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Abstract

The x-ray microscope is a new tool for characterizing the microstructure of portland cement concrete. It provides a means of imaging density and chemical variations in the concrete by means of transmitted x-ray and fluorescence x-ray mapping, respectively. It also offers a new method of extracting x-ray diffraction measurements from small volumes and mapping crystallographic variations of large crystals.

Preparations of Samples for SEM Investigations – The Less the Better!

by

Stella L. Marusin

Key Words: SEM of concrete failure, sample preparation, DEF, Na_2SO_4, ASR, gypsum, shrinkage cracks

Abstract

After using SEM for investigations of failure of building materials for several decades, I consider the best sample preparations for this purpose to be a cut (sawn), broken (fractured), or simply a naturally obtained, air cleaned surface without any alteration by casting, grinding, vacuuming or temperature treatment, or use of epoxy or fluorescent dye. This paper presents a few examples of erroneous or misleading conclusions based on investigation of "laboratory prepared" surfaces of concrete samples.

ALKALI-SILICA REACTIONS (ASR) IN CONCRETE AND AGGREGATES

By

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ABSTRACT

Alkali-silica reactivity (ASR) is a major cause of deterioration of highway structures, pavements, bridges, and airport runways in the United States, particularly in the Western States such as California, Colorado, Idaho, Nevada, and New Mexico. With the increasing difficulty in locating high quality of aggregate sources due to environmental regulations and restrictions, it is imperative to understand its: (a) detection, (b) test methods of identifying potentially reactive aggregates for use in concrete and related construction materials, and (c) general methods used in preventing ASR problems. Case histories are described to illustrate ASR damage in concrete structures utilizing petrographic techniques and analysis.

STATISTICAL DETERMINATION OF CEMENTITIOUS MATERIALS CONTENT IN HARDENED CONCRETE, PART II

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ABSTRACT

This paper is a continuation of a paper entitled "Statistical Determination of Cementitious Materials Content in Hardened Concrete" that was presented in the twenty second ICMA in Montreal, Canada. In that paper, a regression equation was developed based on paste contents determined by point count of twenty concrete samples with known mix proportions. Using the regression equation, the cementitious materials content can be calculated once the paste content is determined via traditional point count method, and the water-to-cementitious materials ratio (w/cm) is estimated. However, in pursuing a better mathematical fit to the data, the equation used a cross term which is the product of paste content and w/cm. Consequently, the resulting equation is a curve having a limit w/cm value. This would result in errors in the calculation of the cementitious materials content around the limit value.

In this paper, a new linear regression equation is developed based on the point count data of thirty one concrete samples with known mix proportions. No limit value can be reached from the equation. The new equation has a coefficient of determination (R^2) of 0.96 and a standard deviation of 23, and is equally effective for portland cement concrete and concrete containing fly ash. Total cementitious materials content can be readily calculated using the equation. In addition, the effect of fly ash, and the relationship between the cementitious materials content and the paste volume determined by point count method are further discussed.

KEY WORDS

cementitious materials content, fly ash, paste volume, point count, regression equation

COMPARISON OF HYDRATION PRODUCTS OF DIFFERENT POZZOLANIC SYSTEMS

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ABSTRACT
Hydration of different pozzolanic materials results in hydration products with varying amount and properties. Consequently, properties of cements with different pozzolanic materials are considerably changed. Therefore, to understand hydration mechanisms and the properties of hydration products of different pozzolans is of main importance. To evaluate these differences, the current study is designed. In the study, four types of pozzolan representing wide range of such materials (C and F Class fly ashes, granulated blastfurnace slag and natural pozzolan) were used and mixed with lime. Lime- pozzolan mixtures were investigated for quality and quantity of hydration products, pozzolanic activity and microstructure points of view. For this purpose , scanning electron microscopy with energy dispersive analyser, thermogravimetric analyser and physical-mechanical testing techniques were used. In the studies by these equipment and techniques, morphology of the hydration products, pozzolanic activities of pozzolans were investigated in a detailed manner.

ÖZET
Farklı tiplerdeki puzzolanik maddelerin hidratasyon ürünleri miktar ve özellikleri açısından birbirinden farklıdır. Buna ba_lı olarak, farklı tiplerdeki puzzolanik maddeler ile hazırlanan çimentoların özelliklerinin de önemli ölçüde birbirinden farklı olacaktır. Bu nedenle, farklı puzzolanların hidratasyon ürünlerini ve hidratasyon mekanizmasını anlamak oldukça önemlidir. Hidratasyon ürünleri ve hidratasyon mekanizması farklılı_ının tespit edilmesi, bu ara_tırmanın amacını olu_turmu_tur. Bu çalı_mada, dört farklı tipte (C ve F sınıfı uçucu kül, granüle yüksek fırın curufu, do_al puzolan) kullanılmı_ ve kireçle karı_tırılmı_tır. Kireç –puzolan karı_ımları, hidratasyon ürünleri,puzolanik aktivite ve mikroyapı açısından de_erlendirilmi_tir. Bu amaçla, EDS sistemli tarama elektron mikroskobu, termogravimetrik analizör kullanarak ve fiziksel-mekanik testler yapılarak, puzolanların hidratasyon ürünleri ve puzolanik aktiviteleri incelenmi_tir.

ASSESSMENT OF POZZOLANIC REACTIVITY OF CLASS-F FLY ASHES THROUGH MINERALOGICAL & MICROSTRUCTURAL CHARACTERIZATION.

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ABSTRACT:

The effectiveness of low lime fly ash used in cement is determined to a large extent by three parameters viz. fineness, carbon content (Loss on Ignition) and the glassy phase content of the fly ash. In this work, typical Indian class-F fly ashes have been characterized for their physico- chemical and mineralogical properties. While the particle size distribution vary widely among the samples, the chemical and mineralogical characteristics vary with in a narrow range. The reactive silica content of the fly ash was determined following chemical treatment as per EN-196-2 method. The microscopic examination of the residue left after the chemical treatment reveals that this treatment attacks preferentially the glassy portion of the spherical particles of the fly ash. This observation was supported by the XRD analysis carried out on the fly ash before and after the chemical treatment. The XRD of the residue shows total disappearance of the amorphous hump and enhancement of crystalline quartz and mullite peaks. The SEM examination of classified fly ash fractions reveals that these glassy, spherical particles are predominantly present in the -45μm fractions. This is further confirmed by higher reactive silica content obtained in this fraction. Also, the mortars containing -45μm fraction of the fly ash show superior flow property as compared to the one with +45μm fraction, due to the 'ball bearing effect' of the small spherical particles.

In order to determine the pozzolanic reactivity of the Class-F fly ash in cement and concrete, the samples of fly ash were aged up to 28 days in different solutions viz., 1 N NaOH, saturated solutions of $Ca(OH)_2$, and $CaSO_4.2H_2O$ corresponding to the pH of around 13.5, 12, and 6.5 respectively. The treatment was aimed at simulating the pH of the pore fluid normally encountered in concrete/ cement paste matrix at different ages. Information from analyses for various elemental oxides in the solution suggests that the fly ash reacts with in 7 days in 1 N NaOH, at 28 days in case of $Ca(OH)_2$ and very little reaction is observed for $CaSO_4.2H_2O$ solution. The SEM examination of the treated fly ash reveals that these reactions preferentially occur on the surface of the spherical glassy particles, which corroborates the earlier result that the spherical particles are indeed more reactive and contributes to the pozzolanic reactions of the fly ash. The above characterization studies on fly ash have been found useful in evolving directions for optimizing its use in blended cement and concrete.

MICROSTRUCTURE OF CEMENT AND ALITE PASTES DOPED WITH LEAD CONTAINING COMPOUNDS

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ABSTRACT

In this work the microstructure of pastes produced by mixing of commercial cement and alite with different Pb containing compounds was observed under SEM and the hydration products were analysed by EDS. The setting and hardening of cement is strongly retarded in the presence of PbO which is easily soluble in pore liquid, or in the presence of soluble Pb salts. But, what is surprising, PbO does not hinder the heat evolution process of alite; PbO gives a significant growth of heat output – presumably it plays a role of nucleating agent. Many experiments were arranged to explain this effect. The sets of calorimetric results indicated the role of sulphate ions, producing insoluble $PbSO_4$ thin coating rather than the formation of hydroxide (or calcium salt with Pb in anion). However, the intensive formation of calcium silicate hydrate product after so-called induction period was evidenced in each case when Pb compounds were present as components of hydrating alite mixtures.

In microscopic observations different forms of very compact dense C-S-H occur as a dominating component of alite pastes with Pb-bearing compounds. Some of them are composed of small grains, plates or fibres with more or less Pb. In some areas C-S-H occurs as continuous, “dense” mass. Calcium hydroxide does not form well shaped crystals, as observed in typical, pure alite paste, but very small, poorly crystallized particles. Small rods or bars containing Pb, S, Ca are also visible in samples hydrating with gypsum addition..

Effect of Partial Substitution of Gypsum by Cement Kiln Dust on the Physico–Chemical and Microstructural Characteristics of Slag Cement Pastes

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Abstract

In this investigation, cement kiln dust (CKD) is used both as a set –retarder and as an activator for Portland blast furnace slag cement. The hardened slag cement pastes were tested for their physico-chemical, mechanical and microstructural properties. It was found that the partial substitution of gypsum by CKD results in an increase in the water of consistency, an acceleration of the setting time (initial & final), an increase in the rate of hydration, higher bulk density and compressive strength as well as lower apparent porosity. The results of phase composition and microstructure of the formed hydration products could be related as much as possible to the development in compressive strength of the hardened cement pastes.

MICROSTRUCTURE OF MORTARS AT DIFFERENT STAGES OF HYDRATION

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ABSTRACT

The microstructure of mortar specimens prepared from two different cements was studied at different stages of hydration. It was found that the formation of the microstructure up to one day is mainly due to the hydration of cement particles less than about 10 μm in size. For one of the cements, cement particles tend to dissolve and form mostly outer product C-S-H at early ages, leaving many empty pores of the sizes of the original cement paricles in the matrix. A gap of varying width seems to exist between the larger residual unhydrated cement particles and the matrix around them, but no obvious individual hydration shells are found. The other cement exhibited a quite different hydration pattern. Most cement particles seemed to hydrate quickly, with hydration products deposited relatively close to them. An individual hydration shell about 1 μm in thickness was observed around most cement particles, with a narrow gap between some, but not all, cement particles and their hydration shells. Heat curing increases the rate of hydration and seems to make hydration products deposit closer to the original cement particles.

MICROSTRUCTURE OF CEMENT AND ALITE PASTES PROCESSED WITH CONCENTRATED SOLUTIONS OF SODIUM CHLORIDE

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ABSTRACT

In this paper the microscopic observations and analyses relating to the processes in well cementing are reported. The cementitious materials for this purpose are mixed with highly concentrated brine and used in underground works as the so-called salt cements.

The microstructure of pastes produced by mixing of diluted and concentrated sodium chloride solutions with commercial cement as well as with the synthetic alite was observed under SEM and the hydration products were analysed by EDS. Apart from the samples produced at w/c=0,5, the solid residue separated from suspensions (w/c=10) was also examined.

NaCl affects the silicate phase hydration both in cement and in alite paste hydrated within a few days, giving the C-S-H phase extremely compact and dense, with no individual particles. One can observe the cracks surrounding the densified C-S-H gel. The NaCl crystals are present at high NaCl concentration in cement paste and seem to strengthen the structure The Friedel's salt crystals are not observed at early age but after 28 days maturing or more. In alite pastes there are very characteristic snail-like, compact forms of C-S-H, similar to those observed in calcium silicate hydrates produced from alite and silica and put in the salt brine. These forms are relatively poor in Ca and rich in Cl. The products formed at excess of water show quite different microstructure. The needle-like forms of C-S-H are visible. At high NaCl concentration the highly saturated with NaCl , flexible, long fibres are seen.

Hydration and microstructural Characteristics of Portland Cement Pastes Containing Cement Kiln Dust as Partial Substituent of Gypsum

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Abstract

In this investigation, the effect of partial substitution of gypsum by cement kiln dust (CKD) on the physico- mechanical and microstructural properties of the hardened ordinary Portland cement (OPC) pastes was reported. Such substitution results in an increase in the standard water of consistency and a decrease in the setting time of the fresh OPC pastes. The results obtained indicated that the partial substitution of gypsum by CKD causes an increase in the bulk density and compressive strength of the hardened OPC pastes due to the acceleration of the rate of hydration. The results of scanning electron microscopy (SEM) could be related to the development of compressive strength of the hardened cement pastes.