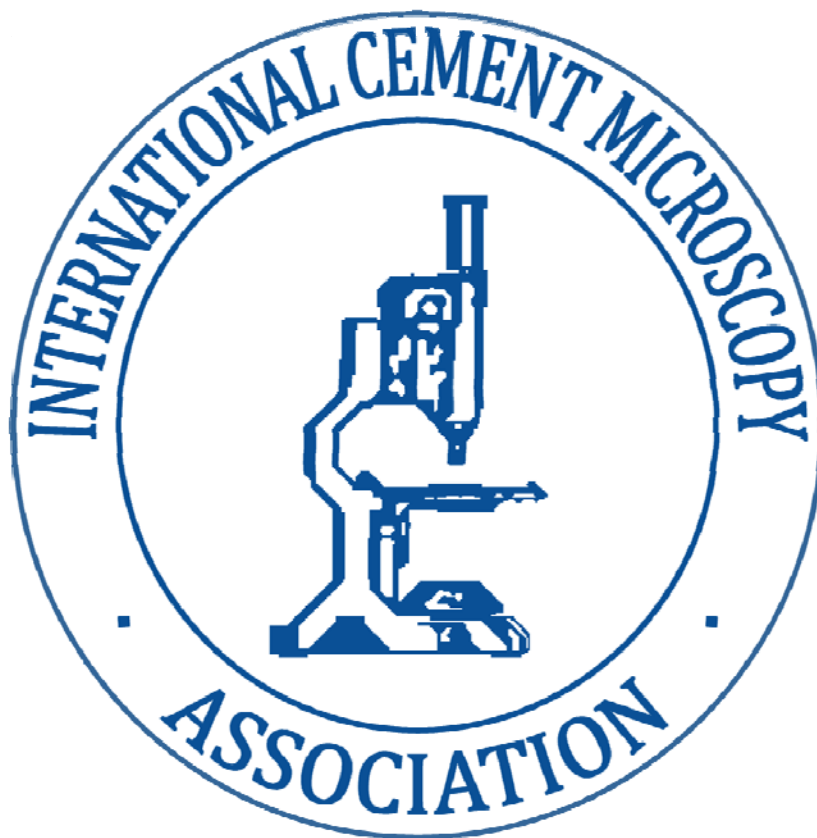


ABSTRACTS

THIRTY-SIXTH INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY



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Melia Milano Hotel

Milan 20149 Italy

**Sponsored and Organized by
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**PROGRAM OF THE THIRTY SIXTH
INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY
SPONSORED & ORGANIZED BY INTERNATIONAL CEMENT
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Melia Milano Hotel, Via Masaccio 19, Milan 20149, Italy

April 13 – April 17, 2014

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APPLICATION OF ADVANCED X-RAY MICRO-TOMOGRAPHY TO THE CHARACTERIZATION OF THE 3D MICROSTRUCTURE IN CEMENT PASTES

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ABSTRACT

Laboratory-based and synchrotron radiation (SR) X-ray computed micro-tomography (X- μ CT) is a very effective non-invasive tool for the investigation of the microstructural features and evolution of portland cement. The 2D and 3D virtual reconstructions of undisturbed samples at different hydration ages can be used to obtain a direct assessment and visualisation of the spatial and temporal relationship between the different cement components (Fig. 1). With respect to laboratory CT scans, modern synchrotron radiation-based X- μ CT systems offer the advantage of relatively short measurement times as well as improved contrast, so that the hydration process can be effectively monitored through the absorption-contrast radiographic images that are normally used. This can be achieved using several experimental solutions, including box beams, pencil beams, and energy dispersive configurations. It is shown that the XRD-based tomographic techniques can be successfully employed to map the spatial distribution of each phase in the hydrating paste.

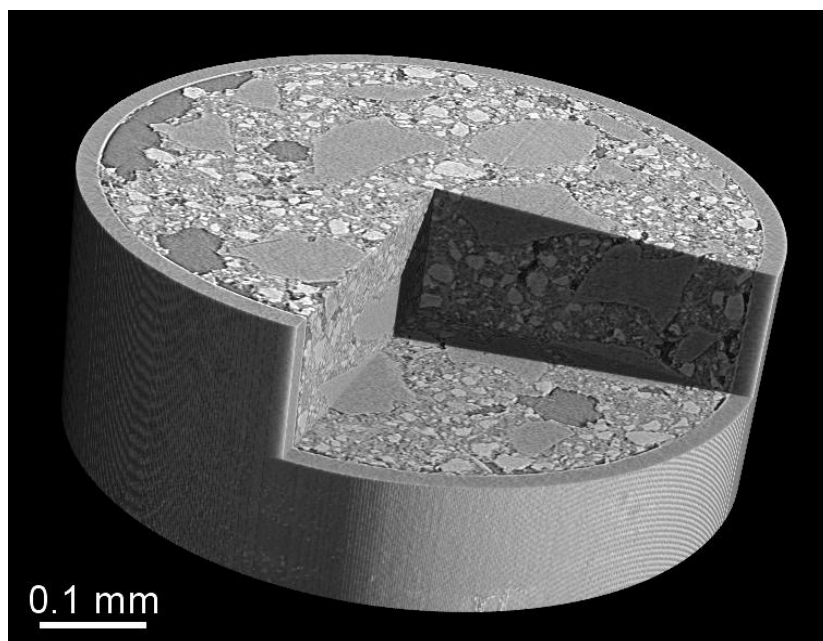


Figure 1. Virtual reconstruction of the 3D microstructure of the hydrating cement paste through absorption contrast computed X-ray micro-tomography

INVESTIGATION

ABOUT THE EFFECT OF CHEMICAL GRINDING AIDS ON CEMENT MILLING AND SEPARATION EFFICIENCY

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ABSTRACT

Cement manufacturing involves a grinding process of clinker, gypsum and secondary mineral additions, usually carried out in ball or roller mills. Efficiency of grinding (in terms of energy actually used to increase cement fineness over total energy) is usually very low and reported to be in the range 10-30%. Due to increasing interest in energy savings and high fineness cement production, it is mandatory a better understanding of physico-chemical processes involved. Chemical grinding aids are organic compounds used as process additives during cement grinding that allows to increase milling efficiency. Their mechanism of action (that may involve the formation of a monomolecular organic layer on cement surface or the neutralization of electrostatic forces) is still unclear. The effect of grinding aids is particularly evident in closed circuit grinding systems, in which a specific device (the separator or classifier) separates coarse particles from fines fractions. The addition of suitable chemical additives normally improves the efficiency of separation by reducing agglomeration and modifying the behavior of material processed by separator. In this paper an investigation on the morphology of cement particles ground in a typical ball mill with and without chemical grinding aids is described. Results are discussed considering the evaluation of separator and mill efficiency as well as physico-mechanical properties of cements.

INFLUENCE OF MINERALISERS ON THE CLINKER BURNING TEMPERATURE AND ITS MORPHOLOGY

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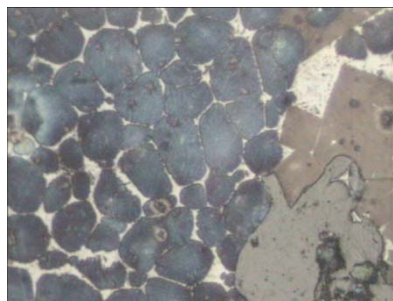
ABSTRACT

In a laboratory process of cement fabrication, the influence of mineralizes addition to three industrial raw materials on the clinkering process as well as on the morphology of the produced clinker is examined.

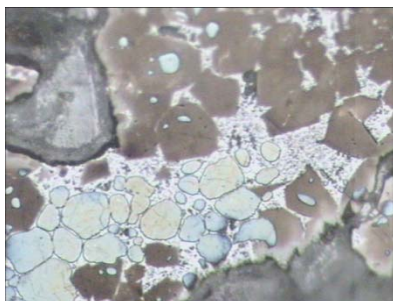
The industrial raw material used in this study comes from the Cement Society of Gabes. These raw that have been prepared in accordance with the production procedures followed by the cement's plant of Gabes, were named raw 1, raw 2 and raw 3. These later were variable at fineness. The mineraliser added to these mixtures, with varying percentages (0%, 1% and 2%) is fluorspar. It is added to the raw meal to prepare 5 g of a homogeneous mixture. Clinkers were synthesized in a kiln type Nabertherm. The burning temperatures varied between 1300 and 1450°C. The basis of assessment of raw materials was the estimation of free lime and C₃S content. Chemical, physical and mineralogical characterizations were made by using XRF, X-ray diffraction (XRD), thermogravimetric and differential thermal analysis (TG- DTA) and optical microscopy techniques.

The experimental results can show that the addition of small amounts of fluorspar (2%) to cement raw material accelerates the formation of C₃S phase and intensifies the process of the free lime combining during the clinkerisation.

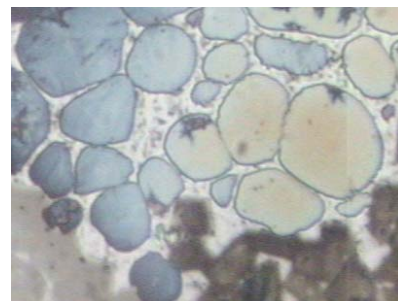
Key words: *fluorspar, mineraliser, clinkers, X-ray diffraction, optical microscopy.*



Clinker 1 (CK1),
T2=1350°C (1% fluorspar,
x100)



Clinker 1 (CK1),
T0=1450°C (2% fluorspar,
x100)



Clinker 3 (CK3),
T0=1450°C (2% fluorspar
x200)

EFFECT OF MINOR ELEMENTS ON CLINKER MINERALOGY AND REACTIVITY

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ABSTRACT

The role played by minor elements, such as alkalis, sulphur and magnesium in the clinker mineralogy has been widely discussed in the past literature [1]. The presence and quantity of these minor elements in the clinker lead to the stabilization of different polymorphic forms of C3A , C2S and C3S. Nevertheless the influence of the different polymorphs on the cement properties (both at the fresh and hardened state) has not yet been fully clarified. In the present study, both laboratory and industrial clinkers have been properly selected and analyzed by XRD, SEM and microprobe-WDS techniques for assessing their mineralogical composition and the chemical and micro-structural features of the clinker phases. Moreover the early hydration reactions of the related cement pastes have been monitored by in situ XRD and the results correlated to heat flow curves and to the mechanical properties of the related mortars. Sulphur containing clinker showed a different sulphate solubility and an improved C3S reactivity, leading to a higher degree of hydration and, as a consequence, to higher mechanical strengths especially at the early ages.

Keywords: Minor elements, hydration, cement reactivity, in situ-XRD

[1] Taylor H.F.W. (1990), “Cement Chemistry”, Academic Press Ltd.

**PETROGRAPHY OF BUILDING MATERIALS DETERIORATED
BY SULFATE ATTACK**

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ABSTRACT

Nowadays due to a growing demand for sustainability, building materials should be high-strength, more cost-effective, environmentally-friendly and durable. However, building materials are often in contact with aggressive environments that can significantly reduce their service life. One problem often encountered is the presence of sulfate from different sources that leads to premature deterioration of building materials by sulfate attack.

In fact, structural or material damages of buildings associated to the presence of sulfate are commonly reported in the scientific literature. Sulfates are contaminants that may come from different sources. Sulfates may come from external sources such as: ground or surface waters, solution of sulfuric acid, industrial waste waters, seawater, bacterial action in sewers or in agrofood effluents and oxidation of sulfide minerals in clay adjacent to construction. Sulfates may also come from internal sources such as: excess of sulfate in constituents (filler, supplementary cementing material), oxidation of sulfide-bearing aggregate, sulfate-rich aggregate or excess of added gypsum. Internal sulfate attack of concrete may also be due to heat-treated concrete responsible for delayed ettringite formation called DEF.

Damage due to sulfate attack may come from different actions including expansion, cracking, loss of strength, spalling and delamination. The role of petrography comes important to identify the source of possible sulfate attack or to diagnose the origin of the deficiency. Here, different cases of sulfate attack on building materials are presented including pyrite-induced heave in compacted backfills or in bedrock, concrete attack by external sulfate coming from industrial waste waters and finally an internal sulfate attack of concrete from the oxidation of sulfide-bearing aggregates. For each case, examples of petrographic studies are presented.

DETECTING THE CLINKERPHASES OF PORTLANDCEMENTCLINKER

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ABSTRACT

The knowledge of cement clinker composition is of great importance because of different reactivity of clinker phases. Thus the clinker composition influences different technical properties. This composition is affected by different factors like composition of the raw mix, burning temperature and different derived fuels. The amount of different clinker phases in Portland cement can be measured by X-ray powder diffraction (XRD) or by point counting under optical microscopes. Another way to obtain information about the composition is the automatic detection of the clinker phases by modern software. The aim of these investigations was to check if it is possible to detect these phases and which parameters need to be improved.

In a first step a polished section of the clinker has been prepared. Epoxy resin was tested for its ability to assist in the preparation of these sections. It was discovered that it is not possible to etch the sections constantly and that the used epoxy resin leaves a thin film on the clinker. That was found by atomic force microscopy (AFM) and micro-Raman spectroscopy. So another matrix had to be found. A melamine based resin has been applied and it worked out much better. The preparation process had to be optimized in some parameters.

In the next step different ways of etching have been compared. Direct contact with acid media and vapor etching could be used. Hydrofluoric acid vapor is a very good etching substance because the different phases get colored differently. The disadvantage is the complex handling of hydrofluoric acid. Acetic acid can also be used and brownish and grey colors can be obtained but it does not etch constantly. Water can also be used but it only causes different grey scales for every clinker phase.

These water edged phases were detected using a *BX 61 Olympus*TM optical microscope and the software *AnlaySIS five*TM from *Soft Imaging Solutions*. Some different synthesized clinkers have been detected by X-ray powder diffraction and quantified by Rietveld-analysis and the point counting method which is described in standards. For C_2S and C_3S we get a different result by use of the different quantification techniques of 3% or less. The C_3A and $C_4(A,F)$ were detected as one phase within the point counting and the detection method. In order to detect them individually the technique has to be improved. A specialty of the detection technique is the possibility to detect the amount of belite inclusions in alite.

HYDRATION PROPERTIES OF NATURAL CEMENTITIOUS PHASES BEARING ROCKS

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ABSTRACT

Unusual rocks from the Hatrurim basin, Israel, contain natural analogues of cementitious phases, such as larnite (\square -C₂S), \square -C₂S, hatrurite (C₃S), gehlenite (C₂AS) or mayenite (C₁₂A₇). The geological phenomenon at their origin is combustion metamorphism of impure marls and chinks that occurred 16 to 1.5 M.y. ago. The mineral assemblages of these rocks could give some valuable information in order to imagine new kinds of cements. Thus samples mostly containing larnite (\square -C₂S), \square -C₂S, mayenite and gehlenite (C₂AS) were studied as it could be an interesting phase assemblage to produce some low CO₂ clinker. After a brief review of the parageneses and occurrences of those natural cementitious phases bearing rocks, their textural characterization with respect to an industrial clinker was reported. Furthermore, hydration was studied by calorimetry, optical microscopy, SEM-EDX, SEM-SE and XRD. The calorimetry results emphasized a moderated kinetics following a sequence of 3 steps: mayenite quicker (0 - 4h) than gehlenite (4 – 14h) and then larnite (24-40h). The impact of impurities content of phases, namely the P content of larnite (C₂S) and \square -C₂S is discussed relatively to their reactivity. The main hydration products were C-S-H and hydrated gehlenite (strätlingite).

HYDRATION CONTROL OF PORTLAND CEMENT AND CALCIUM ALUMINATE CEMENT USING DIFFERENT METAL NAPHTHOATE HYDRATES

Pöllmann, H., Fischer, K. & Kaden, R.

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ABSTRACT

The use of different metal naphthoates 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-naphthoate hydrates were synthesized and characterized regarding their thermal stability and infrared data. The crystal structures of $\text{Sr}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ba}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Fig. 1) were solved and found to be isotypic with $\text{Ca}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The synthesized naphthoates 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 were examined by isoperibolic heat flow calorimetry 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, too.

For the examinations of the influence on the setting of OPC and CAC the following alkaline earth naphthoates were used as admixture:

magnesiumbenzoate pentahydrate	$\text{Mg}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 5\text{H}_2\text{O}$
calciumbenzoate dehydrate	$\text{Ca}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 2\text{H}_2\text{O}$
strontiumbenzoate dehydrate	$\text{Sr}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 2\text{H}_2\text{O}$
bariumbenzoate dihydrate	$\text{Ba}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 2\text{H}_2\text{O}$

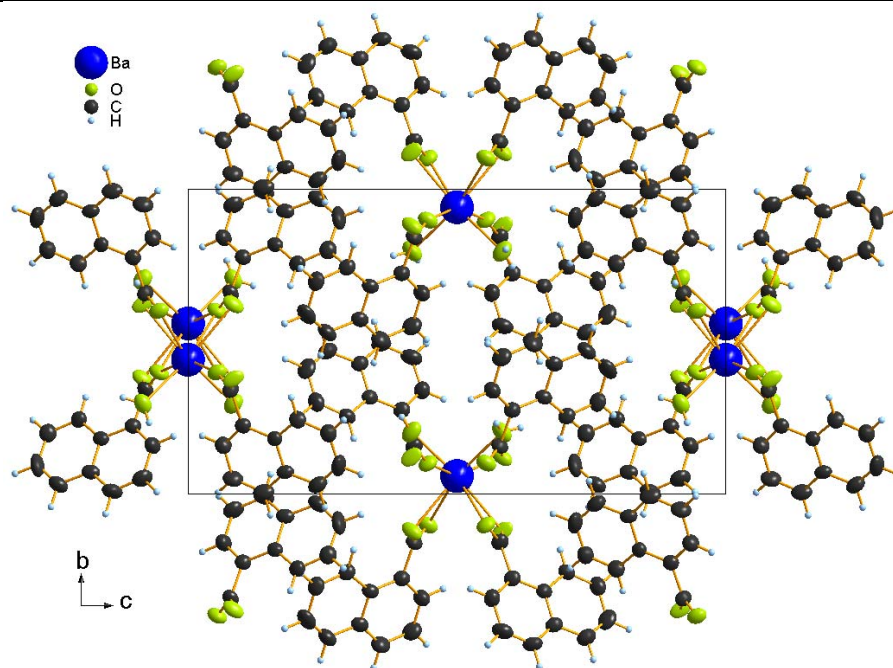


Fig. 1. Crystal structure of $\text{Ba}(\text{C}_{11}\text{H}_7\text{COO})_2 \cdot 2\text{H}_2\text{O}$ projected along $[100]$.

NEW SILICA FUME FROM RECYCLED WASTE GLASS

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ABSTRACT

Utilizing nanoparticles is one way that could stimulate the hydration reactivity and improve the rheological properties of concrete due to their fine size and spherical shape. Based on its high content in amorphous silica (SiO_2), waste glass represents a good material to valorize into glass nanoparticles ("glass fume"). "Glass fume" possesses a spherical and amorphous morphology with a bi-modal size range: composed of 97-98% of nano-size particles of 25-2500 nm in diameter and the balance of micron-size particles of 1-10 μm in diameter. In a situation where the use of silica fume is limited due to its scarcity and high cost, "glass fume" is presently tested in construction material to evaluate if it is a valuable alternative to silica fume.

When mixed in a cement paste, "glass fume" offer nucleation sites for portlandite and has both a pozzolanic and "filler" behaviors. Well-dispersed, "glass fume" improves slump of the cement pastes and mechanical properties of mortars. Moreover, it has been tested in high performance concrete (water-to-binder ratio (W/B) of 0.35). The evolutions of the compressive strength and of the permeability of the "glass fume" concrete are comparable of those of a high performance concrete mixed using silica fume. The SEM observations of paste, mortar and concrete show that nano-glass densifies both the cementitious matrix and the interfacial transition zone.

**CEMENT VARIABILITY – IMPACT ON R&D AND WELLBORE CEMENTING
OPERATIONS**

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ABSTRACT

Well cements are manufactured, in general, to conform to API standard specification, and provide the user with standardized cements. These cements, classified as Class A, B, C, G and H provide different properties that allow their use in a variety of wellbore applications. However the complexity of the wellbore, type of rock, stability of the rock formation, the temperature and pressure, require a robust cement system that can only be achieved by modifying the cement hydration and performance by using additives or blending components specific for the required application. Subtle variations in the cement from one supplier to another or between batches from a given supplier, that are not detectable in the API standard test can be significantly enhanced on addition of an additive and even more so when several additives are used.

This panel session, discusses how these subtle variations can impact the R&D process from fundamental studies to product development and slurry design as well as operational concerns and field implications.

CO₂-STABLE WELL CEMENTS: A REVIEW OF THE STATE OF ART

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ABSTRACT

Carbon capture and storage (CCS) is considered to be one of the most effective ways to dispose of anthropogenic CO₂. Cementing such CCS wells presents a technical challenge since ordinary Portland cement (OPC) is known for its corrosion potential with CO₂. Such corrosion involves formation of CaCO₃ from Ca(OH)₂ and potentially subsequent leaching as Ca(HCO₃)₂. This process may create channels in the cementitious matrix and allow migration of CO₂ to the surface. Moreover, the formation of CaCO₃ can cause cracks due to volume expansion during crystallization, resulting in pathways to the surface. In the present paper, a review on the state of art of cementing systems suitable for CCS wells is given.

A radical concept includes to completely eliminate all cement constituents which are potential reactants for CO₂. This approach was introduced by *T. Sugama* in 1992 and involves the use of a special calcium aluminate-phosphate cementing system which ultimately hydrates to apatite-like minerals which are fully CO₂-stable. The main drawback of this binder is the lack of suitable admixtures to control the slurry properties, and incompatibility with silos, pumping lines etc. holding Portland cement. As a result, this system has found limited application in the field so far and is currently used on geothermal wells only.

To overcome these problems, a slag Portland cement has been formulated with a reactive fly ash filler in such way as to minimize the release of Ca(OH)₂ during its hydration. This concept is based on reducing the CaO : SiO₂ weight ratio, thus binding most of the portlandite through the pozzolanic reaction and thereby producing additional C-S-H phases while only little portlandite is left which can undergo carbonation. Owing to the low amount of CaCO₃ present in this system, the crystallization pressure from CaCO₃ is minimal. As a consequence, crack formation does not occur. Also, leaching of CaCO₃ as Ca(HCO₃)₂ will be minimal because of the minute amount of CaCO₃ formed.

Recent laboratory testing and experience from the *SACROC* CO₂-flood field in South Texas has shown that surprisingly also OPC can resist CO₂, provided that the slurry is formulated at a higher w/c ratio (~ 0.55). Under these conditions, the hardened cement matrix contains sufficient capillary pores which provide enough space for expansion of the crystallizing CaCO₃, thus avoiding crack formation. At present, this approach seems to present the most attractive solution for sealing CCS wells.

Finally, a two-component organic resin system (Thermaset[®]) based on epoxy has been proposed as an alternative to inorganic cementing systems. This polymer can be expected to be inert against CO₂, rendering it an alternative candidate for sealing CCS wells. However, such polymeric binders are rather expensive and no lab or field data are available at present for its CO₂ tolerance.

**THE USE OF CEMENT CLINKER MICROSCOPY AS AN AID TO DETERMINE
THE PERFORMANCE DIFFERENCES IN THE PRESENCE OF CHEMICAL
ADDITIVES.**

Dr. Ted Sibbick and Dr. Josephine Cheung

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ABSTRACT

It has been noted that certain cement clinkers perform better with chemical additives than other clinkers regardless of the resulting cement's other performance criteria, such as strength, set time, grindability and water demand. Comparison of these different cements by bulk chemical analysis (XRF) and compositional phase analysis by QXRD do not appear to show any obvious or consistent performance related relationships. These chemical cement additives are generally added at the grinding stage to improve grinding, accelerate or retard hydration, or as in most cases studied here improve strength development of certain components of the cement (aluminate, ferrite, silicate phases etc.). In this study, we use optical clinker microscopy (and on occasions supporting SEM-EDX analysis) to identify if any consistent characteristics could be established to explain the performance differences observed in a series of forty-nine clinkers.

The morphological and compositional characteristics of the clinkers which might explain the differences in chemical additive performances observed in the clinkers studied will be highlighted. In addition, a comparison of the XRF and QXRD analysis will also be presented to highlight the characteristics identified by clinker microscopy that would otherwise have been missed by XRF and QXRD.

Keywords: Clinker Microscopy, Chemical additives, performance improvement, clinker quality.

**MICROSCOPY TO EVALUATE THE PROPERTIES OF CEMENT AND
ALTERATIONS IN THE HISTORIC MORTAR/CONCRETE – OLD NOBIRU
PORT PROJECT, NORTHEAST JAPAN**

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ABSTRACT

The remnants of old Nobiru Port structures were originally projected as a key spot near Sendai, but abandoned in 1884 before completion, due partly to a typhoon. They represent Japan's civil engineering and cultural heritage. This paper presents a result of petrographic examination of the historic mortar and concrete from the abutments of a brick masonry bridge. Detailed polarizing/reflecting microscopy, SEM observation and quantitative EDS analysis have been performed of polished thin sections of mortar/concrete specimens to reveal the properties of the cement clinker phases manufactured in the early Meiji era, along with cement hydrates and their alteration products.

Cement particles were much coarser and less homogeneous than those of modern Portland cement, retaining unhydrated clinker phases. The occurrence of large alite, varying shaped belites with parallel to cross lamellae, sporadic gehlenite, plus extremely coarse interstitial aluminate and ferrite, suggests slow heating of coarse-grained raw materials along with highly extended burning and annealing, typical of the batch-process kiln (bottle kiln) without a cooling apparatus. Magnesium silicate gel and ettringite characterized the footing concrete under sea water. In tracing back the technological history of Portland cement and its long-term durability, the above petrographic approach is useful.

INFLUENCE OF FLY ASH IN SUPPRESSING AAR EXPANSION IN A DAM WALL

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ABSTRACT

Alkali aggregate reaction (AAR) is a well-known mechanism of concrete expansion and cracking. Supplementary cementitious materials (SCMs) are also generally well known to suppress the AAR expansion and cracking. This paper presents the results of a case study in which concretes from two structures have been investigated and compared. In one case, a reactive aggregate, which in the early 1970s was incorrectly assessed as innocuous, was used in combination with Portland cement in the construction of a bridge structure. This bridge has developed serious AAR-induced cracking. In the second case, the same aggregate was used in combination with Portland cement and a fly ash which contained 10 % CaO and about 70 % ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$). The fly ash was apparently primarily used to improve the strength gain and reduce hydration heat, whereas the possibility of AAR was dismissed, as the aggregate was erroneously considered to be innocuous. The concrete that incorporated fly ash has not developed AAR after some 40 years in service.

EFFECTS OF FLUORIDES ON THE MECHANICAL STRENGTH DEVELOPMENT OF MORTARS ADMIXED WITH ALKALI-FREE ACCELERATORS

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ABSTRACT

Flash setting accelerators are chemical admixtures commonly used for sprayed concrete during tunnel excavation. They allow an immediate set of concrete which can bind to the substrate without dangerous collapses. Such a coating layer prevents the section convergence that is its tendency to squeeze. Today, the wet method is becoming more diffused. This technique requires the use of liquid flash setting accelerators which are pumped to a nozzle and immediately projected onto the rock wall. Recently the demand of alkali-free accelerators is growing very rapidly. They are water oversaturated solutions of aluminium sulphate with a total alkali metal content (expressed as equivalent of Na_2O) lower than 1%. In order to increase the storage life of those accelerators, several complexing agents for aluminium are used like fluorides, formic acid, diethanolamine. In this paper, the effects of fluoride on the performance of an alkali-free accelerator were studied. Therefore, mechanical strength development of cement paste samples added with an alkali-free accelerator containing several amounts of fluoride was measured. It was observed a reduction of the mechanical strength at increasing fluoride concentrations. In order to clarify this phenomenon, the influence of fluoride on accelerated hydrating cement paste was followed through morphological (ESEM-FEG) and crystal-chemical (TG/DSC, XRD) analyses.

INTERSTITIAL PHASE HYDRATION – IMPACT OF RETARDER AT 90 - 120°C

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ABSTRACT

Discontinuities in the retardation of cement in the temperature range around 90 – 120°C using conventional thickening time techniques for well cementing have been documented. The discontinuities result in unexpectedly long thickening times that are non-linear in relation to retarder concentration and in some cases are exponential between 90 and 100°C. At 120°C there is a notable threshold for some retarders the concentration has to be increased almost 5-fold to achieve a reasonable thickening time. These discontinuity effects have serious implications in formulating slurries for use in this temperature range.

Previous studies have indicated that these discontinuities are related to the interstitial phase. It is reported that at about 114°C ettringite is unstable and converts to monosulphate and gypsum or anhydrite, at least in the pure phase. The present study was performed to elucidate on the interaction between interstitial phase extracted for a Class G cement with conventional retarders to determine if this was in fact a reason for the discontinuities in thickening time at 90- 120°C. Conduction calorimetry, SEM and XRD techniques were used to follow the interstitial phase reaction with and without retarder present.

DISCOLOURATION OF FAIR-FACED CONCRETE – A CASE STUDY

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ABSTRACT

Fair-faced concrete has not only a technical function to fulfil but also an esthetical one. The appearance of such a concrete surface depends as well on the building site conditions as well on the materials and production methods of the concrete itself.

Within the framework of a research on the appearance and colour acceptance of different finishing building materials, funded by the Belgian FPS Economy, a case of discoloured fair-faced concrete was studied by petrography. As colour and texture differences of finishing materials have major impact on the human acceptance, the understanding of the fair-faced concrete discolouration could lead to control the causing parameters in the production phase and deliver concrete of good quality both on terms of performance and appearance.

A petrographical examination combined with ESEM-EDS analyses showed that the observed dark discolouration has its origin in the concrete microstructure. Our findings fit the model, proposed by D. Strehein and P. Schiess (2008), which state the large climatic conditions dependency of the transport and crystallization processes during drying of the fair-faced concrete after demoulding. In weather conditions of low temperatures and high relative humidities, the evaporation rate will be low which result in deposition of calcium hydroxides near the surface due to capillary transport and crystallization at the concrete surface. These depositions create a difference of surface structure, which in turn leads to a difference in reflected light when observing the surface. The irregular surfaces of the depositions lower the reflected light in regarding to the smoother surfaces and they do appear to be darker.

DAMAGE EVALUATION OF TWO DIFFERENT CONCRETE MIX DESIGNS CONTAINING SULFIDE BEARING AGGREGATES

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ABSTRACT

Since the first reported cases of concrete deterioration due to sulfide bearing aggregates in Trois-Rivières area (Quebec, Canada), a lot of questions have been raised. One of them was if a better concrete quality would have prevented or minimized the damage. This year an interesting case related to that question was presented to us. The house foundations of a 2 storey building with 8 apartments show the same problems that we have seen previously in Trois-Rivières area. The particular interest of this case is that the concrete utilised for the house foundations and the stairs and balconies were different mix designs. The house foundations were made with a 25 MPa concrete, while the stairs and balconies were made with 35MPa concrete. In this case, it was expected that the 35 MPa concrete would better resist damage than 25 MPa concrete which is actually much more porous. However, visual inspection of the two concretes showed us quite the opposite. The 35 MPa concrete was much deteriorated with presence of large open crack network, a brownish coloration of the walls and traces of rust.

In order to qualify and quantify the deterioration observed in the two types of concrete, core samples were extracted and submitted to DRI petrographic analysis (damaged rating index), compressive strength and SDT (Stiffness Damage Test). DRI method was adapted to reflect the damage observed in the case of deterioration due to the oxidation of sulfide-bearing aggregates. This study focuses on changes proposed to DRI test to properly reflect the damage caused by oxidation of iron sulfide mineral and sulfate attack of the cement paste and on the case study where two concretes of different quality were used for the same construction and presented different level of damage.

NANOPETROGRAPHY TECHNIQUES CONTRIBUTION TO THE BEHAVIOUR OF TRACE ELEMENTS INTO CLINKERS

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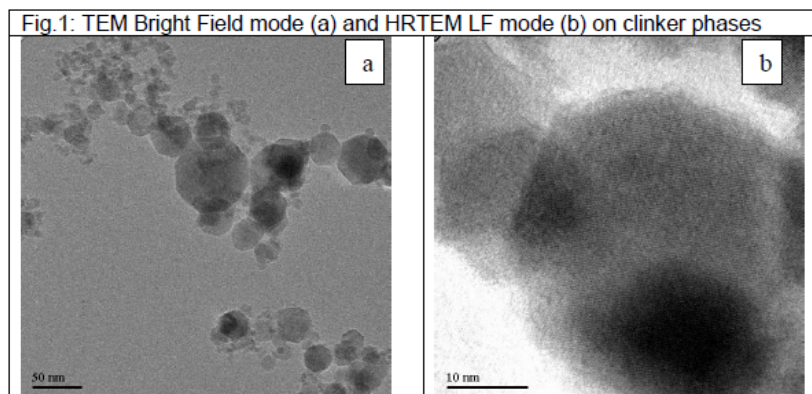
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ABSTRACT

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 or to generate microscopic (or smaller) particles with a mineralogy, chemistry or structure which differ from the current phases (C3S, C2S, C3A and C4AF). Currently, the characterization of these phases is mainly based on optical microscopy, scanning electron microscopy, X-ray diffraction and electron microprobe analysis. The advantages of these methods are their scale which is micrometric, their flexibility, fast and with short sample preparation. On the other hand their limit is their scale which cannot identify and analyze at nanoscale the potential heterophases.

The results obtained in the example of the clinkers analysis, burned with alternative fuels, do not allow fine identification of the trace elements, provided by these alternative fuels, in the nanocrystals. These methods named micropetrographies assume that the distribution of such trace elements like phosphorus is heterogeneous and form independent domains or nanodomains included into the main clinker phases (C3S, C2S, C3A & C4AF) but without specifying what chemical form and crystallographic properties. Second main problem deals with their localization and which mechanisms conduct to their formation: 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?

High Resolution Transmission Electron Microscope (Fig.1) is adapted to this type of problem because it allows access both to the chemistry (using X-EDS nanoprobe) and crystallography (nanodiffraction and high resolution modes). Tests were done on the C3S phase synthesis (pure and doped with phosphorus) and phases C3S and C2S extracted in industrial clinkers burned with alternative fuels. The results show the ability of MET to be imaged HR phosphate phases precipitated in the form of nanoscale clusters of less than one micron for the biggest ones.



QUANTITATIVE XRD-ANALYSIS OF HYDRATED CEMENTITIOUS SYSTEMS

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ABSTRACT

XRD analysis in combination with the Rietveld method enables the quantification of hydrated cementitious systems containing cement, blast-furnace slag and fly ash. The aim of the analysis approach is to determine all occurring crystalline phases and to distinguish between the amorphous contents originating from blast-furnace slag, fly ash and amorphous or ill-crystalline phases formed during the hydration reaction. The investigation of the time dependent decrease of the amorphous blast-furnace slag and fly ash content enables to follow the reaction of these materials and to determine the overall degree of reaction. In order to quantify the different amorphous contents, internal and external standard methods as well as hkl-approaches can be applied. In this study different multi-component cements including clinker, blast-furnace slag, fly ash and limestone were investigated at hydration times of up to 91 days.

INVESTIGATION OF THE HYDRATION OF HEMIHYDRATE WITH MICROSCOPIC METHODS

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ABSTRACT

Calcium sulphate based binders are used for different technical applications like floor pavements, plaster board or as casting material. For all these uses different technical properties are necessary. For floor pavements a high porosity and suitable strength is needed and for casting materials a high casting accuracy is the most important property. These properties are influenced by the morphology of the created dihydrate crystals, which depend on different facts like applied additives, reaction temperature or the reactant hemihydrate.

To investigate the reaction process with and without additives and to examine the crystal morphology during and after the reaction optical microscopy (OM) and environmental scanning electron microscopy (ESEM) were used. The kinetics of the reaction were measured by heat flow calorimetry (DCA). One main aim of the investigation was to determine the processes taking place during the different reaction steps which were analyzed by DCA. It has been found out that in the first step only hemihydrate is solved and during the next minutes seed crystals of dihydrate are formed. At the beginning of the main reaction these crystals are growing and no new seed crystals are formed. When most of the hemihydrate is dissolved the retarding period starts. The ion content of the liquid phase was analyzed by ion chromatography (IC) and it was proved that the highest Ca^{2+} and SO_4^{2-} ion concentration is measured during the first minutes when the seed crystal formation is taking place, because the Ostwald Miers range is exceeded then. If ESEM is used for the investigation water should not be condensed and evaporated *in situ* in series because different generations of crystals would be formed. These different crystal generations are formed because in every evaporation step some ions of the solution will precipitate and the ion concentration in the residual solution gets that high that the Ostwald Miers range is exceeded again and new seed crystals were formed.

The expansion of the specimen during hydration could also be explained using OM. It could be investigated that the growing dihydrate crystals are poshing each other during the hydration process. At higher temperatures longer crystals were formed. That is caused by the degree of saturation at the beginning of the reaction which is lower because of the lesser solubility of hemihydrate at higher temperatures. This leads to less seed crystals and to longer crystals because of the constant hemihydrate amount so the expansion during hydration is higher. At more than about 90 °C the reaction stops because the degree of saturation obtained by dissolution of hemihydrate is too low for the formation of seed crystals. It was also investigated that the amount of branches on the dihydrate crystals decreases at higher temperatures.

QUANTITATIVE PHASE DEVELOPMENT AND HEAT-FLOW CALCULATION OF CAC HYDRATION WITH CALCIUM SULFATES

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ABSTRACT

The early age hydration (24 h) of CAC (calcium aluminate cement) alone or in combination with two different calcium sulfate sources (anhydrite or hemi hydrate) was investigated. The performed experiments include heat flow calorimetry and in situ X-ray diffraction of the hydrating slurry performed at a constant temperature of 23°C with a w/s ratio of 0.40 and a ratio CAC/calcium sulfate of 70/30.

The quantitative phase development during the first 24 h of hydration obtained by in situ XRD was evaluated by using an external standard approach ("G-factor" method [1,2]). Dissolution of CA and ferrite phase in the cement pastes were used for the calculation of heat flow from thermodynamic data. An interpretation of the obtained results from heat flow calorimetry could be performed by comparing and interpreting with the curves from heat flow calculations.

In situ hydration of CAC alone is visualized by the Rietveld scale factor evolution. The hydration shows formation of C₂AH₈, C₂AH_{7.5}, CAH₁₀ and AH₃. An addition of calcium sulfate leads to a change in hydration products with formation of ettringite, monosulfoaluminate-14H, alumina hydrate and in some case of transient gypsum. For a given composition kinetics and phase assemblage depend on the type of calcium sulfate.

[1] B.H. O'Connor, M.D. Raven, Powder Diffraction 3 (1988), 2-6.

[2] D. Jansen, C. Stabler, F. Goetz-Neunhoeffler, S. Dittrich, J. Neubauer, Powder Diffraction 26 (2011), 31-38.

INFORMATION ABOUT CONCRETE FROM A PETROGRAPHIC STUDY OF THE CEMENT MATRIX

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ABSTRACT

The cement matrix in hardened concrete and related materials contains within it specific information about the composition, quality, post placement history and possible deterioration of the concrete. A detailed petrographic investigation of this matrix using a polarising microscope, SEM/EDS systems and other specialist techniques can provide a wealth of information about the concrete which is unobtainable by other means. The individual mineral species in a cement matrix are typically very small, typically ranging from about 30µm down to sub-micron sizes. The components that can be identified by petrographic means include the fine rock dusts from aggregates, mineral additions, constituents of anhydrous cement grains, calcium hydroxide, amorphous and crystalline cement mineral hydrates, sulphate minerals, carbonation and the products of any deterioration. Chemical admixtures such as plasticisers and air entraining agents usually require special methods for their direct detection, though their presence may often be deduced from alterations to the matrix fabric, the morphology of particular components such as calcium hydroxide, or to the proportions of the various constituents present. Illustrative examples show how a petrographic study of the cement matrix and its components can provide information concerning original mix design and water/cement ratio. They also demonstrate that petrographic study of the cement matrix provides unique information concerning the composition, quality and history of the concrete itself.

PETROGRAPHIC EVALUATION OF THE ALKALI-REACTIVITY POTENTIAL OF AGGREGATES FOR CONCRETE

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ABSTRACT

A risk of long-term damage to concrete from alkali-aggregate reaction (AAR) is now recognised world-wide, but the highly variable combination of causal factors complicates its reliable prediction. In particular, a wide diversity of aggregate types, their combinations and of the potentially reactive constituents or features that might be present within their component particles, present a challenge to the assessment of the reactivity potential for a given proposed concrete mixture. Petrographic examination has long been applied to the assessment of aggregates for this purpose, increasingly alongside complementary analytical techniques and various objective tests. However, although the practice of petrography is sensibly universal, the principles of its application for evaluating concrete aggregates for AAR potential have varied greatly between different regions or countries.

A sequence of RILEM international technical committees, commencing in 1988 and currently represented by TC 219-ACS, was established to prepare AAR recommendations, including both test procedures and interpretation guidance, that could be applied similarly in all regions of the world, irrespective of local materials, conditions and construction practices. Accordingly, draft methods have been published, including a first practice for the petrographic examination of aggregates (in 2003, designated as AAR-1). Now, as TC 219-ACS reaches the end of its tenure, a full set of recommendations will be published in 2014, including a thoroughly revised and updated edition of AAR-1 (which will be designated AAR-1.1). This present paper will summarise the progress made by TC 219-ACS to date and will outline the principles of forthcoming AAR-1.1, which also benefited from a practical research programme, known by the acronym PARTNER, carried out in Europe.

However, any petrographic examination is more than just a systematic procedure, which can be formalised in recipe style relatively easily. It is crucially also dependent on the competence and experience of the petrographer, with the latter being traditionally acquired over time, working with and being mentored by those with more experience, and also by exposure to an increasing range of materials and occurrences. Proving and precision trials have shown that differences in operator experience are a major cause of unacceptable variation in determinative petrography. Consequently, TC 219-ACS has developed a pictorial petrographic atlas (to be designated AAR-1.2), to assist operators with recognising and interpreting potentially reactive constituents and features within a wide range of aggregate types from around the world. This atlas (also to be published in 2014 to complement AAR-1.1), including material and background notes kindly supplied by AAR specialists around the world, is described in this present paper, together with some example entries.

POPCORN CALCITE DEPOSITION: ROLE OF FLY ASH, FLY ASH COMPOSITION AND WATER-TO-CEMENTING MATERIALS RATIO

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ABSTRACT

The term “popcorn calcite deposition (PCD)” has been used to describe the unusual appearance of certain concretes after carbonation where the resulting calcium carbonate forms as discrete crystals of calcite dispersed within a matrix of hydrated silica and alumina gel, rather than the more commonly-seen continuous matrix of calcite in which the silica and alumina are dispersed. An example of “popcorn carbonation” detected in field concrete with high w/cm is illustrated in Figure 1. The presence of fly ash in

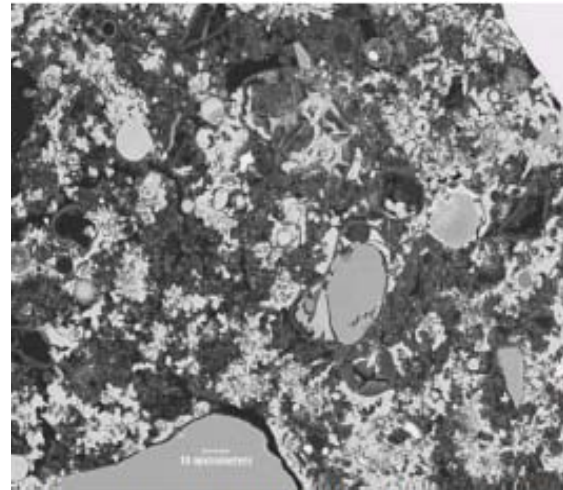


Figure 1 PCD in High W/CM Concrete Containing Fly Ash

this concrete led to a hypothesis that the fly ash may have rendered the concrete more prone to this form of carbonation, due to the reduction in the amount of portlandite prior to carbonation. Subsequent laboratory tests were conducted to test this hypothesis. Cement pastes, mortars and concretes with and without fly ashes of varying composition and with varying water-to-cementing-materials ratios (W/CM) were exposed to different environments. The microstructure of the carbonated zone was examined by scanning electron microscopy and image analysis techniques to determine the “degree of connectivity” of the calciumbearing phases. Furthermore, the impact of the carbonation of the physical and mechanical properties of the pastes, mortars and concretes was determined. The results show that the incorporation of fly ash in high-W/CM pastes and mortars increased the tendency for popcorn carbonation to occur, especially with fly ash high in alkali-sulfate. However, evidence of PCD was not found in pastes at lower W/CM (< 0.70).

AIR-VOID CHARACTERIZATION OF LIGHTWEIGHT CONCRETE USING X-RAY CT

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ABSTRACT

Due to its lightweight and desirable property of thermal insulation, lightweight concrete has been widely used in roof top construction, floor topping, precast sections fabrication as well as some industrial processes for mere thermal insulation purpose. To achieve the desirable property, the control of air void, in both chosen aggregates and paste, proves critical in the design process. Therefore, a quick and reliable method in place to characterize the air void system will enhance the design process significantly.

However, the similar density and color between paste and aggregate common in lightweight concrete as well as their unique nature of air void system pose considerable challenge to quantitatively analyze the air void system efficiently. In this study, through the demonstration on a random type of lightweight concrete, a simple method of characterizing air void system based on the processing of x-ray CT images is proposed. The emphasis of presentation will be put on the determination of threshold value among different phases as well as the process of reliable segmentation of air void in paste and aggregate. Finally, the air void parameter in the form of density of air voids of varying size range is calculated and their errors estimated. The processing involved in this proposed method is carried through computer programming based on Matlab[®] platform.

Keywords: Lightweight concrete, x-ray CT, air void

FROM ALITE TO C-S-H

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ABSTRACT

Alite is the main phase in Ordinary Portland Cement (OPC) and responsible for early strength development of OPC based mortars and concretes. The hydration kinetics of OPC shows similarities with that of pure alite. A stronger initial reaction is followed by a induction period of several hours until the main reaction starts after 2-6 hours. That behavior is well known, but still poorly understood. New fields of cement application like Ultra High Performance Concretes (UHPC) and complex building chemistry formulations show the need for OPC tuned up for the challenging applications. Organic additives guarantee the outstanding performance of such products. For further development of tailor-made additives the mechanism of alite hydration has to be completely understood.

The hydration of synthesized pure alite was followed by isothermal calorimetry and by in-situ XRD at different temperatures (Jansen et al. 2011). In-situ XRD-data were evaluated by Rietveld refinement followed by G-factor evaluation. Direct quantitative determination of alite, portlandite and C-S-H was enabled by the use of a combined G-factor/Ponck's approach (Bergold et al. 2012). With the use of the enthalpies of formation the reaction enthalpies were calculated for dissolution of alite and synchronous precipitation of portlandite and C-S-H. The absolute time dependent phase content of alite and C-S-H was used to calculate the released heat of hydration, which could be compared to the measured heat flow from calorimetry.

Our results show clearly that the heat flow calculated from alite dissolution fits the heat flow measured by calorimetry quite perfect. The heat flow which is calculated from C-S-H precipitation shows a different behavior. Combining both calculations we can conclude that an intermediate C-S-H phase is formed which cannot be detected by XRD. Later on this intermediate C-S-H is transformed to dimeric C-S-H which can be observed by XRD. Up to 24 hours the intermediate C-S-H is consumed completely and only dimeric C-S-H is present. There is no maturation of that dimeric C-S-H during the first 48 h of hydration with respect to the determined coherent scattering domain sizes.

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STUDY ON THE CLINKER MINERAL MATCHING OF NUCLEAR ENGINEERING CEMENT (NEC)

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ABSTRACT

Nowadays and in a long future, there will be more and more nuclear engineering programs in China, lacking of theoretical basis and national standard leads to the insistent demands of the development of a new cement type with unified standards to ensure the cement quality. This study is to develop a preparative technique of nuclear engineering cement(NEC) with high strength, moderate heat and low dry shrinkage. And then to provide theoretical foundation to the production of nuclear engineering cement and the formulation of the national standard. This study is supported by the National Science-technology Support Plan Projects“ The preparation of nuclear engineering cement with high strength and moderate heat”(No.2011BAE27B02). The NEC with different mineral match were experimentally burnt. With chemical analysis, petro-graphic analysis, physical properties tests, scanning electronic microscope (SEM), energy dispersive spectrometer(EDS), X-ray diffraction (XRD), thermo analysis (TA), Differential Scanning Calorimeter(DSC), optimized mineral match, clinker's properties and microstructure were studied. The burnabilities and mineral constituent of nuclear engineering cement with different KH,SM,IM were studied, and the matching relationship was discussed. The results show that the suitable range of KH is less than 0.92, SM 2.2~2.8, IM 0.7~0.9. In this range, the burnability is well, The liquid phase decreases when SM is more than 2.8, crystal misdistribution. The clinker burned at normal firing temperature, the crystal has uniform distribution, edge sharpness, the particle size is between 20~40μm, well crystallization. Furthermore, some test techniques i.e. XRD, SEM and TG-DSC were applied to research the setting process of specimens, hydration products and structure of setting pastes, to prove that all the cement physical properties satisfy the requirements of nuclear power engineering.

**IDENTIFICATION OF AAR IN SOUTH ISLAND BRIDGES
IN NEW ZEALAND**

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ABSTRACT

Aggregate sources in the South Island of New Zealand are generally regarded as non-reactive, and no case of alkali-aggregate reaction (AAR) has previously been reported from this area. In recent investigations of cracking in some piles of two major bridges in the South Island, AAR was found to be the probable cause of cracking, possibly exacerbated by delayed ettringite formation (DEF). This paper presents details of the identification and discusses the main causes of damage to the piles, which sometimes involved a combination of factors.

**RELICTS OF UNHYDRATED CEMENT CLINKER IN A HISTORIC CONCRETE
FROM THE 19TH CENTURY – MICROSCOPY WITH EDS ANALYSIS**

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ABSTRACT

Petrographic examination was made of the oldest concrete used in the early 1890s in Japan. Among these were pillow-like concrete blocks, solidified in jute bags and placed as revetment of a training dyke rising from underwater to the tidal zone at the mouth of Katabira River at Yokohama Port. To reveal the properties of cement manufactured in the Meiji era, polished thin sections of concretes (thickness 15 μm) were subjected to detailed polarizing/reflecting microscopy, SEM observation and quantitative EDS analysis of the clinker phases and hydration products.

These concrete retained unhydrated cement particles, remarkably coarse and inhomogeneous compared with those of modern Portland cement, and included large coalesced alite, pale to dark brownish belite with occasional cross-lamellae, plus extremely coarse interstitial aluminate and ferrite. These suggest slow heating, highly extended burning and annealing, all characteristic of the clinker from the batch-process kiln without a cooling zone (e.g. bottle kiln). Friedel's salt was identified in some reference concretes, reflecting access to sea water. This petrographic approach is useful in reconstructing historical trends of cement production and concreting works in early times, from the view point of civil engineering heritage.

“MICROSCOPY ANALYSIS OF CEMENTITIOUS TILE ADHESIVES”

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ABSTRACT

Cementitious tile adhesives, also called thin sets, are usually applied at a thickness ranging between 3 and 10 mm. Rheology modifiers, water retention agents and polymeric components are added onto the mortar to impart to it a series of desirable properties: a lower specific weight for workability reasons, the capability of retaining water in order not to dry out on water absorbing substrates, improved adhesion properties on impervious substrates and non absorbing and vitreous tiles. In the most common real world applications, the thin layer of adhesive is sandwiched between very different materials. The substrate can be a concrete floor or a water proof membrane, while tiles might have highly differing surface properties, they can be highly or poorly water absorbing or they can be surface modified by a resin or by a net. This variety of conditions can significantly alter the distribution of the formulation components within the thin layer, but also influence the hydration of the cementitious binder thereby affecting the adhesion properties of the product. In this paper, performance characteristics of model formulations evaluated in terms of adhesion pull-out will be correlated with a microscopical analysis of the mortar. In particular, the behavior of the thin set on a concrete vs. a plastic water proof membrane, and its adhesion absorbing vs. non-absorbing vitreous tile will be compared.

INVESTIGATIONS ON COMMERCIAL AND SYNTHETIC CALCIUMSULFOALUMINATE CEMENTS

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ABSTRACT

Calciumsulfoaluminate cements have special advantageous properties in comparison with Portland cements (OPC) or OPC - blended cements like recognizable lower CO_2 – production rapid hardening, high strength development, slight expansions and low alkalinity.

For the production of calciumsulfoaluminate cements different types of pure and impure bauxites, limestones and different sulfate sources are used. Depending on the raw materials those cements are composed predominately of yeelimite C_4AS_3 - the crystal structure is build of corner sharing AlO_4 - tetrahedra and Ca^{2+} and SO_4^{2-} occupy the cavities. Furthermore, additional main phases like belite or ferrites coexist in certain ratios with yeelimite, thus these cements can be summarized as

Sulfoaluminate/Belite cements or Sulfoaluminate/Ferrite/Belite cements.

Our investigations cover experiments on a laboratory scale where sulfoaluminate cements with phase assemblages of yeelimite - belite - ferrite were produced. The raw materials were composed of lime + anhydrite + granulated blast furnace slags. Other types of secondary cementitious materials also were investigated. The sinter products yielded cements with a high ability to react with water. In comparison with the laboratory clinker, the properties of a technical clinker from China was checked against.

The hydration behaviour was studied using calorimetry and time-dependant X-ray diffraction. Besides hydration compounds like ettringite and kuzelite also strätlingite was formed in some hydrated CSBA-cements. The hydration of Belite in the clinkers was accelerated forming different amounts of CSH-phases in the course of hydration. The chemical compositions of the main oxides were obtained by ICP/OES. For chemical analysis of polished sections a LEO 1525 GEMINI field emission SEM equipped with EDX was used. Quantitative phase analyses were done by the Rietveld method using the software package Highscore Plus 3. Heat flow calorimetric analysis was performed using different calorimeters according Kuzel and Pöllmann et al. (1991).

The microstructure of cement clinkers were studied using different microscopic techniques. A typical detail of a clinker is shown in figure 1.

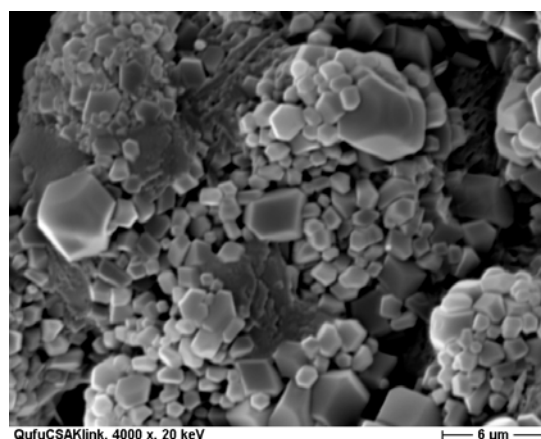


Fig. 1 : Yeelimite crystals in a typical CSA-clinker from China

**TECHNICAL ASPECT OF ADOBE STONE RESTORATION OF
THE HISTORIC MANILA CATHEDRAL (EST. 1581), PHILIPPINES**

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ABSTRACT

The Metropolitan Cathedral of Manila is a historical landmark located within Intramuros, Manila. Fire and hurricane destroyed the first structure while earthquakes have caused the second up to the sixth structures to collapse. The seventh building was constructed in 1879 and was heavily damaged during the Second World War. The eighth building was reconstructed between 1954 and 1958 using adobe blocks from the ruined convent of Nuestra Señora de Gracia in Guadalupe, Makati. Presence of sodium dioxide in the walls was one of the factors that caused powdering and spalling of the original 1879 adobe blocks and 1950s cladding.

This paper will present the restoration of the Cathedral's 55-meter high concrete belfry and northwest (front) façade by Tertex International Philippines. Inc. Comparative analyses using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), X-Ray Fluorescence Analysis (XRF) and compressive test have indicated minimal difference of elemental, material and physical composition among original 1879 adobe blocks, 1954-1958 and 2013 reconstituted adobe thus proving the compatibility of the modern cement to the existing building composition.

Treatment included consolidation of loose concrete/masonry, adobe reconstitution for the disintegrated adobe cladding, and retrofitting of the belfry. Vent holes were also introduced in equal distance on areas to prevent moisture and humidity from being trapped on the interface of masonry and plaster or cladding as well as to arrest rising damp phenomenon. Chromatic alterations were addressed by mechanical cleaning while incompatible cement mortars were replaced with tested reconstituted adobe.

**NANO-DISPERSIONS OF SILICATE HYDRATE FOR THE
SOLIDIFICATION/STABILIZATION OF WASTE**

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ABSTRACT

Stabilization/solidification (S/S) technology aims at decreasing the mobility and toxicity of inorganic contaminants by encapsulating waste materials into a solid with structural integrity. The most popular binder for such technology is portland cement. One of the main problem facing quite often in S/S technology is the interaction many contaminants show towards cement hydration, with the consequence of a reduction in the potential of their immobilization. Nano-dispersion of a new silicate hydrate have been used to improve the binding potential of portland cement in the solidification/stabilization of fly ash from the combustion of petcoke. The addition of the nano-dispersion of the new silicate hydrate to the fresh mixture promotes cement hydration and improves the microstructure of the hydrated phase, producing a more dense structure, as confirmed by mechanical tests and electron microscope investigation. As a result, the leaching of contaminants is reduced and the environmental compatibility of the solidified/stabilized material is consequently improved. The mechanism of nano-dispersion of the new silicate hydrate is discussed in terms of nucleation and growth of calcium silicate hydrate from the pore solution of the hydrating mixture

COMPARISON OF PORE STRUCTURE OF HARDENED MORTARS BASED ON ORDINARY PORTLAND CEMENT AND CALCIUM ALUMINATE CEMENT

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ABSTRACT

Hardened mortars are porous materials their pore structure being developed during hydration as a function of water binder ratio, the binder's chemical reactions, time, temperature and pressure. Different binder systems and as a consequence different chemical reactions will influence the pore structure. For two different cementitious binders, Portland cement (PC) and Calcium Aluminate Cement (CAC), the Calcium Silicate Hydrate (CSH) formation and Calcium Aluminate Hydrate (CAH) formation, respectively, are investigated with respect to the developing pore structure. The water binder ration is kept constant while the temperature-pressure conditions during hydration are varied. The pores structure and porosity is investigated by different method such as sorption methods, mercury intrusion porosimetry (MIP) small angle x-ray scattering (SAXS) and secondary electron microscopy (SEM).

The presented results show differences in microstructure based on the individual hydrates. This becomes first of all obvious by SEM micrographs where the hydrates from CAC show easily to identify plate like crystals, while the CSH phases are much smaller and are not as easily identified by SEM. Results from SAXS, water vapor sorption and MIP are in line with electron optical observations and show the overall pore size distribution or median pore sizes. The results are compared with the underlying, respective chemical reactions using Powers approach to calculate capillary porosity.

THE ROLE OF MICROSTRUCTURE ON THE THERMAL DECOMPOSITION AND BURNABILITY OF LIMESTONES USED IN INDUSTRIAL CEMENT CLINKER

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ABSTRACT

Portland cement is usually produced by heating a mixture of limestone and clay minerals at ~1450° C. At present, the thermal decomposition of limestone is not well studied despite its considerable practical interest (constructions, steel manufacture, chemical process, etc.). In particular, the role of limestone properties (*i.e.* the types and quantities of impurities, degree of calcite crystallinity, microstructure) on the dissociation reaction is not well understood.

In such a light, a study on the thermal decomposition of three cement-grade run-on-mine limestones has been performed by means of isothermal analysis. In particular, the research aim is to evaluate the influence of limestone petrography (*i.e.* texture, micrite/sparite ratio, grain composition and crystal size) on the carbonate decomposition in terms of mechanism and kinetics of dissociation. In particular a preliminary characterisation of the limestone samples was performed by X-Ray Powder Diffraction (XRPD) and Optical Microscopy (OM). Then, isothermal treatments for following the calcite decomposition was performed by means of *in situ* High Temperature X-Ray Powder Diffraction (HT-XRPD) analyses and Scanning Electron Microscopy (SEM). Besides, to investigate the influence of the limestone features on the reactivity of the cement raw mix and agglomeration process in a rotary kiln, a burnability test was performed.

The kinetics results attest that limestone texture coupled with the micrite/sparite ratio become interdependent and interrelated factors hardly affecting the limestone *T* of decomposition as well as its kinetics, the latter in terms of Apparent Activation Energy values and the rate of dissociation.

**DURABILITY OF MASONRY MORTAR IN HISTORICAL BUILDINGS:
COMPARISON AMONG HYDRAULIC BINDERS COMMONLY USED IN
COMMERCIAL PRODUCTS**

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ABSTRACT

Masonry walls of historical buildings could be rich in alkaline sulphates. Reaction between sulphate ions and hydraulic binder in restoration mortars could produce expansion, weakening and cracking phenomena. High open porosity and good chemical inertia to aggressive ionic solution are the main properties of this type of product.

Some commercial mortars used for wall rendering are presently being compared. They are produced with different hydraulic binders ranging from Portland cement to hydrated lime. For this purpose the exposition effects to alkaline sulphate solution (5% Na₂SO₄) on mechanical properties and on dimensional stability of the finished product are studied. The physical data are supported by morphological investigation with Electron Scanning Microscopy (SEM) and mineralogical analysis by X ray diffraction (XRD).

The collected data highlight not only that hydration products depend on the hydraulic system used, but also that the same aging process generates different reaction products according to the binder used. These differences influence the dimensional change rate and furthermore the other product performance properties such as open porosity and water vapor permeability.

INVESTIGATION OF A GEOPOLYMER CONCRETE USED IN RETAINING WALLS OF A BRIDGE

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ABSTRACT

Geopolymer concrete is a new generation of concrete which is free of Portland cement, and utilises alkali-activated alumino-silicate materials, such as fly ash and blast furnace slag, amongst other materials, as the binder. Major advantages of geopolymer concrete relate to environmental benefits (i.e., mitigation of CO₂ emission generated from the manufacture of cement, utilisation of industrial by-products and preservation of natural resources) and superior performance in several applications. However, the performance of the new binders needs to be validated before they are used in major structures. For these reasons a geopolymer concrete mix has been utilised in non-structural, reinforced concrete components of a bridge in order to establish its properties and performance under field conditions. This paper presents the results of an investigation, including microstructural studies, to determine the properties the reinforced geopolymer concrete, and discusses its performance.

IN-SITU X-RAY DIFFRACTION ANALYSIS OF EARLY HYDRATION OF CEMENTITIOUS SYSTEMS AND MICROSTRUCTURAL INVESTIGATION WITH SEM

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ABSTRACT

Investigation into the early hydration of a cementitious system was performed by in-situ X-ray diffraction (XRD) in combination with the Rietveld method. Mixtures of Portland Cement, Calcium Aluminate Cement, Hemihydrates, limestone powder and quartz sand was used for the experimental work. All diffraction patterns of the in-situ measurements which were recorded up to 24 hours of hydration were analyzed by Rietveld refinement. Measurements were performed in reflection and transmission mode. The goal of the study was the comparison of the two modes as to their reliability and variability. The identified phases were gypsum, ettringite, quartz, calcite and calcium aluminate oxide (CA). Differences in quantitative analysis were noted between reflection and transmission results. Experiments pointed out that transmission mode provides better information about the sample due to its geometry. A field emission SEM (FE-SEM) was used to obtain images of microstructure evolution of the hydration products.

Key words: *X-ray diffraction, hydration, Rietveld method, reflection mode, transmission mode, SEM*

MICROSTRUCTURE AND MICROCHEMISTRY OF MECHANICALLY MANIPULATED WELLBORE CEMENT SHEATH

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ABSTRACT

Wellbore integrity is dependent on cement completion, formation damage near the wellbore, the bond between the casing and cement as well as the bond between cement and the rock. The fractures within the cement sheath typically result from the impact of pressure on the cement during hydraulic fracturing operations, and degradation of cement resulting in creation of gas migration pathways. The potential pathways may occur in annulus between cement and formation and fractures within the cement sheath during the long-term production period. The gas migrates to the surface leading to pollution of the environment and contamination of underground water aquifers.

In this research, the expandable casing technology was used to mechanically manipulate the metal pipe and compress the cement sheath behind it in order to prevent the gas migration through the cement-metal interface. The manipulation of the cement sheath during the casing altered the microstructure of the cement. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to investigate the microstructure of the hydrated cement paste before and after the pipe expansion. The hydration product of calcium silicate hydrate (C-S-H) clusters of 200 nm in length and 10 to 50 nm in width was observed in both pre- and post-expanded samples. After casing expansion at 8% expansion ratio, compared to the control sample, TEM images show that expanded cement has more density of the hydration products, higher toughness and lower permeability. SEM images also indicated the decrease of pore size in the cement matrix of the expanded sample.

Key words: Wellbore Cements, SEM, TEM, Microstructure, Casing Expansion.

EXAMINATION OF RAW MIX COMBINATIONS TO DETERMINE THE IMPACT ON BURNABILITY FACTORS

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ABSTRACT

Various raw mix combinations from normal, sulphate-resistant or oil-well production were examined using XRF, microscope and chemical dissolution techniques.

Raw meal samples from Plant#1 (dry line) and Plant#2 (wet line) were analyzed to determine the proportion of coarse limestone (+125 μ m) and coarse quartz (+45 μ m) which have a significant impact on burnability or combinability in the clinkering process as identified by Fundal¹. For both Plants, samples were collected from ‘normal’ OPC production as well as a ‘coarser’ production period (for special clinker production). The results show significant differences in the “theoretical Free lime” according to the formula of Theisen².

The manufacture of various types of clinker require differences in the constitution of the raw meal, not only chemical (e.g. for low C₃A cement), but also different fineness to enhance the crystal phase morphology (larger alite size). In production trials, these differences are clearly identified by the higher heat requirement as shown in previous publications (du Toit and Feiner³).

**MINERALOGICAL AND MICROSCOPICAL STUDY OF TWO CALCSCHIST
ROCKS TO ASSESS SUITABILITY OF AGGREGATES FOR CONCRETE
FABRICATION**

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ABSTRACT

The mineralogies of two calcschist rock core samples are determined to assess the suitability of calcschist aggregates for concrete fabrication. Mineralogies are assessed using complimentary techniques - traditional petrographic examination by polarizing optical microscopy; Scanning electron microscopy and elemental analysis EDS with polished sections; X-Ray diffraction and Rietveld quantification.

The SEM and XRD results show that both calcschist rock samples contain relatively significant amounts of fine quartz crystals within a carbonate/silicate based groundmass matrix. The traditional petrographic study using 30µm thick thin sections does not allow identification and characterisation of quartz and silicate minerals within the rock due to several factors: the small micron size of the quartz crystals intimately intermixed with other rock minerals, the limiting resolution of the optical microscope and the thickness of the thin section.

To assess the suitability of the calcschist rock samples for concrete fabrication, the alkali-silica potential reactivities of crushed calcschist aggregates are determined using the aggressive French Standard accelerated mortar bar test XP P 18-594 for alkali reactivity. Although both calcschist samples contain significant quantities of micron-sized quartz grains, only one calcschist sample shows an expansion that defines it as ASR potentially reactive. Examination by SEM/ EDS of polished sections of the mortar bar samples after the alkali reactive expansion test confirms the formation of ASR gel in the sample defined as potentially reactive; also that the ASR gel formation is associated with the small micro-cryptocrystalline quartz grains in the numerous fine veined silicate matrix regions of this calcschist rock. The non-reactive calcschist sample also contains small micron-sized quartz crystals but no expansion or ASR gel is detected. Different ASR classifications of these calcschists are probably linked to several factors, principally the amount of quartz, the degree of schistosity & alteration and the different proportions of quartz/calcite.

In conclusion, micro-cryptocrystalline quartz crystals within these calcschist rock samples studied cannot be detected/identified by traditional optical microscopy techniques and requires examination in an SEM/EDS. Furthermore, the ASR potential reactivity of the micro-cryptocrystalline quartz in carbonate based calcschist rocks as determined by the aggressive French accelerated mortar bar test XP P 18-594 is confirmed by SEM/ EDS examination of polished sections.

Keywords: Mineralogy & microscopy, calcschists, micro-cryptocrystalline quartz, ASR potential reactivity & mortar bar expansion test

MICRO-CHEMICAL AND MICRO-MINERALOGICAL CHARACTERIZATION OF CLINKER RELICTS FROM AGED CEMENT COMPOSITES

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ABSTRACT

Despite the general tendency to consider portland cement virtually fully hydrated within few years from preparation, the occurrence of non-reacted clinker phases in cementitious materials even several decades old is rather common. Here the results of the characterization of clinker relicts from different types of aged cement composites are reported. The integration of microstructural analysis by scanning electron microscopy and quantitative micro-chemical and micro-mineralogical characterization techniques such as electron probe microanalysis and electron backscatter diffraction (EBSD), allowed the evaluation of the crystal-chemical properties of partially hydrated cement residuals within aged concretes. The results relative to several relicts showed that calcium silicates are always highly reacted, while calcium aluminate and ferrite are often persistent in the anhydrous state (Figure 1). They can be safely characterized by chemical maps, peculiar microtextural features, and by direct identification through EBSD. These observations open interesting questions relative to the long-term hydration kinetics, durability, and the reactivity of old cementitious materials in real systems.

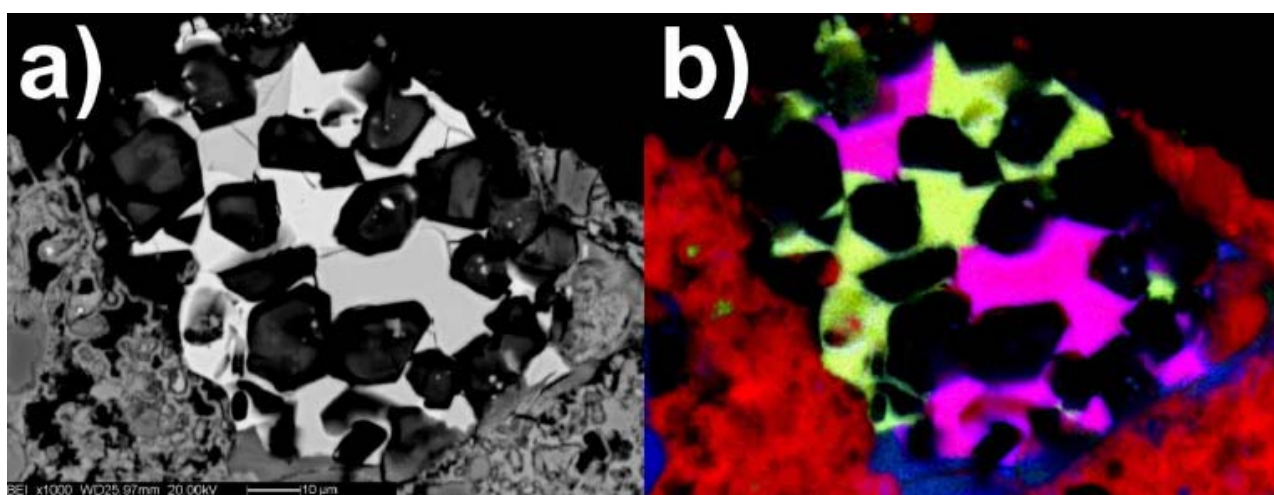


Figure 1. Backscattered electron image of a clinker relict within a concrete sample (a) and combination of EDS chemical maps of the same relict (b), obtained by RGB merging of calcium, iron and aluminum elemental maps in the R, G and B bands, respectively.