2012100410 - Hydration studies of yeelemite at early ages for understanding eco-cement performances
Standard Proposal

Research area: Chemistry
Keywords: eco-cements, yeelimite, ettringite, hydration

Beamline: MSPD (Material Science and Powder Diffraction)
End Station: Powder Diffraction

Proposer: DE LA TORRE, ANGELES G, 0034952131877, mgd@uma.es, (UMA - Dept Química Inorgánica, Cristalografía y Mineralogía - Química Inorgánica - Málaga)

Co-proposer 1: Santacruz, Maria Isabel (UMA - Dept Química Inorgánica, Cristalografía y Mineralogía - Química Inorgánica - Málaga)
Co-proposer 2: Cuesta García, Ana María (UMA - Dept Química Inorgánica, Cristalografía y Mineralogía - Química Inorgánica - Málaga)
Co-proposer 3: Aranda, Miguel A.G. (UMA - Dept Química Inorgánica, Cristalografía y Mineralogía - Química Inorgánica - Málaga)

Photon energy range: 20 keV
Spot size: 1000x2000 Micrometers x Micrometers (FWHM) Horizontal x Vertical
Number of shifts required: 9
Comments about the number of visits:

Unacceptable Dates: any
Preferred Dates: any

EXPERIMENT CONTEXT

Why is SR needed to solve the proposed scientific case? This type of experiments cannot be carried out in laboratory diffractometers as very intense, high energy "penetrating" X-rays, are needed. Furthermore, the fast-recording feature of MYTHEN detector, combinined with good-resolution data, is ideally suited for this type of experiments.

Have you already performed synchrotron radiation experiments? Yes
If yes, specify where: ALBA, ESRF, Diamond, Daresbury, Max-lab, APS

Have you already used synchrotron radiation for this project? No

Have you already submitted this proposal to another synchrotron radiation facility? No

PROPOSAL FRAMEWORK

Is the proposal supported by any grant? No

Is the proposal in collaboration with an industrial group? No

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Is the proposal a significant part of PhD thesis? Yes
If yes, give a reference title: "Hydration studies of pure phases related to sulfobelite cements"

Do you intend to request or have you requested European support (TNA program)? No

Are all co-proposers and main proposer in this proposal early career researchers, i.e., less than ten years after ph.D. thesis? No

List of most relevant publications or patent references of all co-proposers. 1. Rietveld quantitative phase analysis of Yeelimite-containing cements. G. Álvarez-Pinazo, A. Cuesta, M. García-Maté, I. Santacruz, E.R. Losilla, A.G. De la Torre, L. León-Reina, M.A.G. Aranda. Cement and Concrete Research, 2012, 42, 960-971.
2. Rietveld Quantitative Phase Analysis of OPC clinkers, cements and hydration products. Miguel A. G. Aranda, Ángeles G. De la Torre, Laura León.Reviews in Mineralogy and Geochemistry, 2012, 74, 169-209.
3. Reactive belite stabilization mechanisms by boron-bearing dopants
A. Cuesta, E. R. Losilla, M. A. G. Aranda, J. Sanz, Á. G. De la Torre. Cement and Concrete Research, 2012, 42, 598-606.
4. Rheological and hydration characterization of calcium sulfoaluminate cement pastes. M. García-Maté, I. Santacruz, A. G. De la Torre, L. León-Reina and M. A. G. Aranda. Cement and Concrete Composites, 2012, 34, 684-691.
5. In situ powder diffraction study of belite sulfoaluminate clinkering. A.G. De la Torre, A.J. M. Cuberos, G.Álvarez-Pinazo, A.Cuesta and M.A. G. Aranda. J. Synchrotron radiation, 2011, 18, 506–514.
6. Active iron-rich belite sulfoaluminate cements: Clinkering and Hydration. A.J.M. Cuberos, A. G. De la Torre, G. Álvarez-Pinazo, M. C. Martín-Sedeño K. Schollbach, H. Pöllmann, M.A.G. Aranda. Environmental Science and Technology, 2010, 44, 6855-6862.
7. Aluminum-rich belite sulfoaluminate cements: clinkering and early age hydration. M. C. Martín-Sedeño, A.J.M. Cuberos, A. G. De la Torre, G. Álvarez-Pinazo, L.-M. Ordonez, M. Gateshki, M.A.G. Aranda. Cement and Concrete Research, 2010, 40, 359–369.
8. Colloidal processing of macroporous TiO2 filters for photocatalytic water treatment. A. Natoli, A. Cabeza, A. G. De la Torre, M. A. G. Aranda, I. Santacruz. J. American Ceramic Society, 2011, 95, 502-508.
9. Quantitative Phase Analysis of Laboratory Active Belite Clinkers by Synchrotron Powder Diffraction. K. Morsli, A. G. De la Torre, S.Stöber, A.J. M. Cuberos, M. Zahir, M.A. G. Aranda. Journal of the American ceramic society, 2007, 90(10), 3205-3212.
10. Preparation of photocatalytic TiO2 coatings by gel-dipping with polysaccharides. I. Santacruz, A. Cabeza, P. Ibeh, E.R. Losilla, A.G. De la Torre, M.A.G. Aranda. Ceramics International, 2012, 38, 6531–6540.

Abstract: The main phase of calcium sulfoaluminate cements (CSA), a new type of eco-cement, is yeelimite. Yeelimite, $Ca_4Al_6O_{12}SO_4$, is very reactive and most of the hydration heat it released during the first eight hours. Here, we propose to study the hydration reaction(s) of yeelimite at early ages (the first 48 hours) to understand eco-cement performances. Stoichiometric yeelimite crystallizes in an orthorhombic sodalite-type structure while doped yeelimite presents a pseudo-cubic structure. Influence of polymorphism on hydration (kinetic, hydration products, etc…) will also be studied. Pastes will be prepared with different water/cement ratios and using various sulfate sources. The main outcome of the experiment will be the determination of the yeelimite hydration

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mechanism(s) which needs synchrotron radiation as the kinetics is too fast and complex for laboratory powder X-ray diffraction.

Description: See attached pdf file

Description PDF (available at the end of this document): 2012_10_08_ALBA_Yeelimite.pdf

PROCESSES (SAMPLE OPERATIONS) PERFORMED BY USERS DURING THE EXPERIMENT AT ALBA

1. Brief description: Polycrystalline powders are mixed with water and loaded in borosicates capillaries by using a syringe. A balance is needed to weight the powder and the water
2. Main characteristics:
3. Where are the processes going to be performed (Laboratory name, Experimental Hall area, ...): Beamline and chemistry laboratory.
4. Safety aspects: any
5. Preventive actions to avoid any accident: any
6. Personal protection equipment: any
7. What to do in case of an accident:

EQUIPMENT AND PRODUCTS PROVIDED BY ALBA DURING THE EXPERIMENT

Sample environment: Any

ALBA laboratory support required for sample preparation: Deionized water, a balance, 0.7mm capillaries and 0.8mm pinhole methal sample holders.

EQUIPMENT BROUGHT BY THE USERS DURING THE EXPERIMENT AT ALBA

List of equipment brought by the users: any

Equipment description: any

CHEMICAL PRODUCTS BROUGHT BY THE USERS DURING THE EXPERIMENT AT ALBA

List of chemical products brought by the users: only samples detailed above

Chemical products description:

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NON-BIOLOGICAL SAMPLE 1

Substance formula: Ca4Al6O12SO4, CaSO4(H2O)2, CaSO4(H2O)0.5, CaSO4 and H2O

Brief sample description: polycrystalline powders and polycrystalline phastes within borosilicate capillaries

Number of samples: 5

Sample state: Powder

Comment:

Quantity:

Holder, container and solution for transportation:

Sample environment at ALBA:

Radio-active sample: Not applicable

Further safety information related to the sample itself or any preparation process that will be done at ALBA:

Additional information for technical evaluation:

Q-range or 2 Theta range: 2theta range for 0.6 amstrongs: 1-35 º

Detectors to be used: Mythen

Other information that may be relevant for the evaluation procedure:

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Description of the experiment proposed

'Hydration studies of yeelemite at early ages for understanding eco-cement performances'

Abstract:

The main phase of calcium sulfoaluminate cements (CSA), a new type of eco-cement, is yeelimite. Yeelimite, $Ca_4Al_6O_{12}SO_4$, is very reactive and most of the hydration heat it released during the first eight hours. Here, we propose to study the hydration reaction(s) of yeelimite at early ages (the first 48 hours) to understand eco-cement performances. Stoichiometric yeelimite crystallizes in an orthorhombic sodalite-type structure while doped yeelimite presents a pseudo-cubic structure. Influence of polymorphism on hydration (kinetic, hydration products, etc…) will also be studied. Pastes will be prepared with different water/cement ratios and using various sulfate sources. The main outcome of the experiment will be the determination of the yeelimite hydration mechanism(s) which needs synchrotron radiation as the kinetics is too fast and complex for laboratory powder X-ray diffraction.

Scientific background:

The reduction of cement industry environmental impact is a challenge for researchers. On average, for every tone of ordinary Portland cement (OPC) produced, 0.97 tons of CO_2 are released into the atmosphere. So, cement industry contributes around 6% of all CO_2 anthropogenic emissions and consequently approximately 4% of the global warming of the planet. Calcium sulfoaluminate cements (CSA) are very promising environmentally friendly materials as during their production, CO_2 emissions are diminished, when compared to OPC. These new binders contain a slightly different chemistry composition and they are objective of intense research as a reduction of 30-35% of carbon dioxide emissions may be attained.

CSA cements[1] may have variable compositions, but all of them contain yeelimite, also called Klein's salt or tetracalcium trialuminate sulfate ($Ca_4Al_6O_{12}SO_4$). Commercial cements with large amounts of yeelimite have special applications such as high strength developments at early-ages. This phase is also included, ~25 wt%, in sulfobelite cements[2]. Yeelimite reacts at a high pace with water and calcium sulfate sources, according to reaction 1 (given for gypsum but they are analogous for anhydrite and bassanite). This reaction yields ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$, and quasi-amorphous gibbsite, $Al(OH)_3$, and these phases are responsible of the high compressive strength at early ages. If sulfate source is depleted, reaction 2 may take place, forming laminar phases, for instance $Ca_4Al_2(SO_4)(OH)_{12}{\cdot}4H_2O$, also called AFm type phases, which modify the setting, rheological properties and strength development of the resulting mortars and concretes.

$$Ca_4Al_6O_{12}SO_4 + 2CaSO_4{\cdot}2H_2O + 34H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O + 4Al(OH)_3 \quad [1]$$

$$Ca_4Al_6O_{12}SO_4 + 16H_2O \rightarrow Ca_4Al_2(SO_4)(OH)_{12}{\cdot}4H_2O + 4Al(OH)_3 \quad [2]$$

Stoichiometric yeelimite presents an orthorhombic sodalite type structure[3] [a=13.0357(7) Å, a=13.0350(7) Å and c=9.1677(2) Å] while Fe-doped yeelimite crystallizes in a pseudo-cubic unit cell [a=9.2047(2) Å], see Figure 1. The reactivity of these pseudo-polymorphs has to be studied. The early ages of these processes are of great importance to understand the performances of pastes: plasticity/workability, water segregation, fluidity, etc.

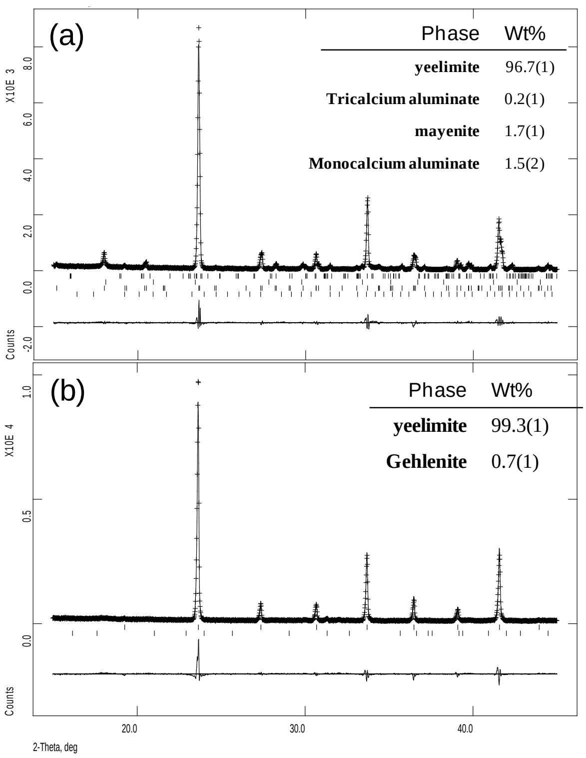

Figure 1. *Rietveld refinement plots of (a) stoichiometric yeelimite and (b) Fe-doped yeelimite.*

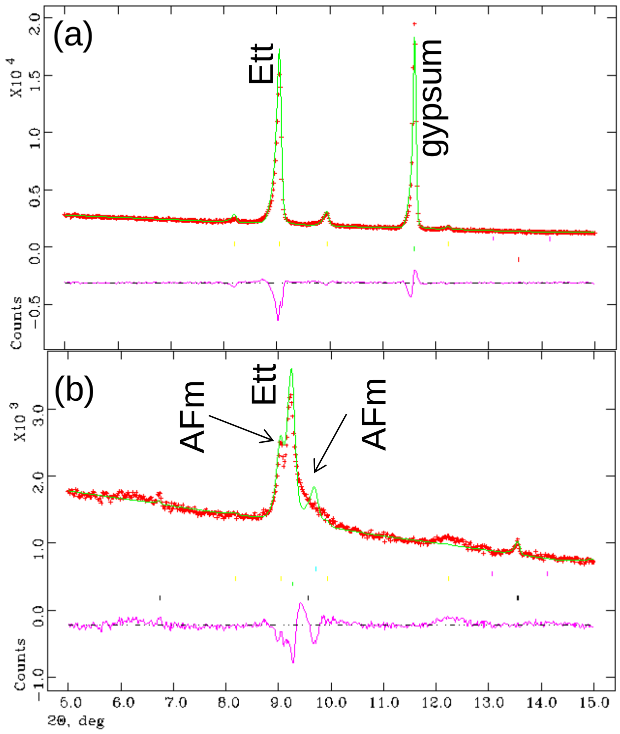

Figure 2. *Low-angle region of LXRPD ex-situ hydrated Klein salt Rietveld plots at 2 d of hydration (a) with gypsum and water, (b) only with water.*

Objectives:

The aim of the proposed work is to study the hydration behavior of yeelemite, both stoichiometric and Fe-doped polymorphs, at early ages in order to understand “eco-cement” performances. Chiefly, we want to determine the hydration kinetic of the yeelimite phase with different water/cement ratio and with different calcium sulfate sources. The final goal is to study the hydration in the early ages in order to understand the dissolution/crystallization processes that take place. We have already experience with the use of synchrotron radiation for analyzing the hydration of cements[4], and it is worth to underline that this type of experiments cannot be carried out in laboratory diffractometers as a very intense, high-energy penetrating X-rays, are needed.

Experimental technique(s), required set-up(s), measurement strategy, sample details:

Stoichiometric yeelimite $Ca_4Al_6O_{12}(SO_4)$ and a Fe-doped one, have been prepared in our laboratory in order to obtain both polymorphs as part of the Mrs. Cuesta PhD Thesis. The samples were characterized by laboratory X-Ray powder diffraction, LXRPD. Figure 1 shows Rietveld plots for both samples.

The hydration behavior of these samples have been studied using an X`PERT diffractometer (PANalytical), by using an ex-situ hydration methodology. Figure 2 shows the low angle region of the Rietveld plots of yeelimite hydrated in the presence of gypsum (Figure 2a) and only with water (Figure 2b). The presence of free water is a complex characteristic of cement hydration as the kinetics of dissolution and crystallization processes may (are) different. Thus, performing a two days hydration study, the information obtained is only partial, as the process of dissolution and crystallization of new phases takes place at very early ages.

Experimental technique: *in-situ* powder diffraction.

Required set-up: the standard powder diffractometer with the MYTHEN detector for fast data acquisition. Short wavelength, λ~0.7 Å, is required to pass capillaries width enough to yield accurate phase assemblage. High resolution crystal-analyzer detector system is an asset which will benefit the study (for collecting a high-resolution data at a later age when reaction(s) is/are not developing fast) but it is not a requirement.

Sample details: Two different yeelimite samples, stoichiometric and doped, have been already synthesized and studied at Malaga University. These samples will be mixed with stoichiometric gypsum/bassanite/anhydrite at Malaga University. Pastes of these cements will be prepared *in-situ* (at ALBA), with different water/cement ratios and loaded in borosilicate glass capillaries of 0.7 and/or 0.5 mm of diameter. The pastes will be injected into the capillaries with a syringe, and then sealed with wax or grease.

Measurement strategy: We plan to collect patterns with time using the MYTHEN detector every 15 minutes up 15 hours in order to follow the hydration in the first hours. Capillaries will be kept allocated in the sample holder to perform single patterns after several hours, i.e. 24 h and 48 h. In order to accelerate hydration process high water/solid ratios will be used.

Expected results and their significance in the respective field of research:

We should have good quality patterns in order to follow quantitatively the dissolution and crystallization process during first hours of yeelimite hydration. This will allow understanding the kinetic of reactivity of this phase depending on polymorphism, water to cement ratio and type and amount of sulfate source. The hydration of eco-cements is a hot topic as OPC largely contributes to the Earth green-house effect.

Beamline and beam time requested with justification:

MSPD beamline. As described above, synchrotron data are needed as LXRPD can not provide accurate data for reaction with fast kinetics. Furthermore, we were allocated (2nd to 5th October 2012) beamtime in this BL to perform a related experiment on hydration of eco-cements, which was successful, see Figure 3. “2012010118, In-situ hydration study of sulfobelite eco-cements: Role of sulfate content and solubility”. Unfortunately, there is not space in the proposal to explain the results obtained but the experiment report will be available in due time. We highlight that the know-how to carry out this experiment is available and the associate risk is minimum. We ask for 9 shifts, 3 days, to carry out this *in-situ* experiment.

References

[1] M. García-Maté, et al. (**2012**) “Rheological and hydration characterization of calcium sulfoaluminate cement”, *Cement and Concrete Composite* 34 684–691.

[2] G. Álvarez-Pinazo, et al. (**2012**), “Rietveld quantitative phase analysis of Yeelimite-containing cements”, *Cement and Concrete Research*, 42, 960-971.

[3] N.J. Calos, et al. **(1995),** “Structure of calcium aluminate sulphate $Ca_4Al_6O_{16}S$”, *J. Solid State Chem.* 119, 1-7.

[4] A.J.M. Cuberos, et al. (**2010**), “Active Iron-Rich Belite Sulfoaluminate Cements: Clinkering and Hydration”, *Environmental Science & Technology*, 44, 6855-6862.

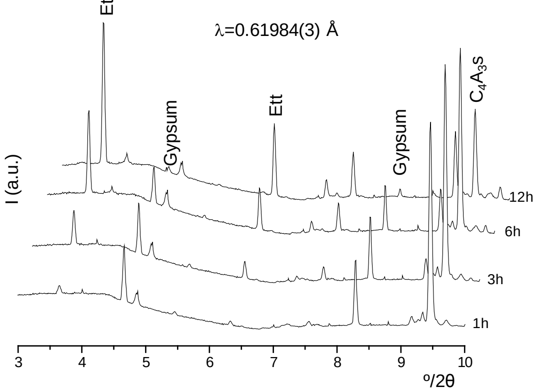

Figure 3. *Raw pattern evolution for eco-cement hydration, experiment 2012010118 @ MSPD*