

The Development and Utility of In-Situ Synchrotron Diffraction for Studying Oil Well Cement Hydration at Elevated Temperatures and Pressures

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1. Introduction

Cements are used in the oil and gas industry primarily for zonal isolation in forming a seal between the bore wall and an inner metal casing. They can be subject to a very wide range of temperatures and pressures, depending up the depth of the well, and this can lead to major changes in the hydration process as compared to that seen under surface conditions. *In-situ* powder diffraction is, potentially, a very valuable tool for examining the effect of both temperature and pressure on the hydration chemistry. However, special sample environments are needed for these studies. There have been prior diffraction studies of how temperature effects cement hydration behavior using *in-situ* x-ray diffraction [1-3], but there is no published diffraction work examining how the combination of pressure and temperature changes the hydration process, although pressures of ~ 100 bar can significantly affect the hydration of C₃S (Ca₃SiO₅) [4]. The current paper presents an overview of the sample environments that we have developed for *in-situ* diffraction studies of cement hydration along with selected results to illustrate the utility of the equipment.

Our work has made extensive use of relatively high energy (30 - 90 keV, $\lambda \sim 0.41 - 0.14 \text{ \AA}$) synchrotron radiation as it is both more penetrating and far more intense than laboratory x-ray sources. This enables good quality x-ray data to be collected quite rapidly (a data set every 4-5 minutes) in transmission mode, even when the x-rays have to pass through a substantial sample cell.

We have employed two distinct types of sample environment; small autoclaves for autogenous pressure (equilibrium steam pressure) studies, and externally pressurized sapphire or stainless steel sample tubes for high temperature and pressure experiments. At the time of submission, pressures up to ~ 50 MPa (7500 psi) have been used. Our early autogenous pressure measurements employed titanium autoclaves as reported elsewhere [3], but recently we have employed a re-usable polybenzimidazole (PBI or Celazole™) autoclave which is usable at least

to 200°C. For both kinds of sample environment monochromatic synchrotron radiation was used in combination with image plate detectors. The 2D detector measures the intensity of the entire Debye-Scherrer ring for each x-ray reflection, rather than just a small segment as is the case with conventional point detectors. This enables rapid data acquisition and, importantly, dramatically improves powder averaging when compared to a static sample with a point detector.

As synchrotron beam time is a very valuable commodity, our work has focused on early hydration, *i.e.* the first 0–12 hours after mixing. This time period is difficult to study reliably by quenching samples and measuring them using *ex-situ* methods. At elevated temperatures, or in the presence of CaCl_2 as an accelerator, this is sufficient time for C_3S to hydrate to a substantial extent, which shows up in the x-ray data as depletion of this phase along with the precipitation of CH. The formation of amorphous C-S-H gel is unfortunately not directly measurable by diffraction methods. However, x-ray diffraction is very sensitive to reactions between the alumina-bearing clinker phases and gypsum.

Our experiments have included studies of: 1) retarders in the 90–180°C temperature range, under autogenous pressure, and at both 7 MPa (1,000 psi) and 50 MPa (7,500 psi), with Class H cement, 2) 0–4%, by weight of cement (bwoc) CaCl_2 addition with Class H and Class A cements at 25 and 50°C, 3) zeolite, silica flour and amorphous silica with Class H cement at 180°C under autogenous pressure, and at both 7 MPa (1,000 psi) and 50 MPa (7,500 psi).

2. Experimental

All diffraction data were collected at the Advanced Photon Source (APS), Argonne National Laboratory. The cement slurries were prepared in a Waring blender largely in accordance with API Spec. 10 for testing of oil-well cements [5], except that the weight of cement for each sample was reduced to 200 g.

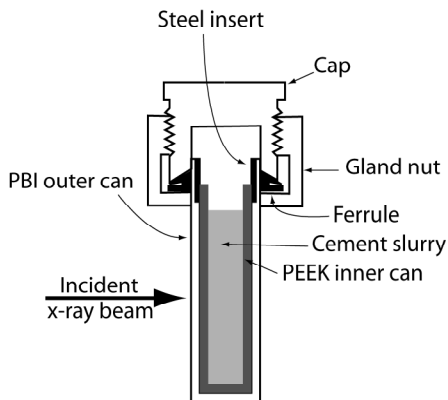


Figure 1. The all polymer autoclave design used for autogenous pressure diffraction measurements at up to 200 °C.

For experiments where only autogenous pressure was required, cement slurry samples were contained in PBI cans with disposable PEEK (polyether ether ketone) liners; the properties of PEEK at up to 200°C are adequate, and the much more costly PBI outer container is readily reusable. The containers were sealed with compression-fittings; a steel tube insert in the top of the PBI shell enable the steel ferrules to be swaged satisfactorily (Fig. 1). The sample thickness along the x-ray beam direction was ~1.6 mm (0.0625"), and the PBI and PEEK walls were 0.8 mm (0.0312") and 1.6 mm (0.0625") thick respectively. With a typically cement slurry, 30% transmission of 40 keV x-rays ($\lambda \sim 0.31 \text{ \AA}$) is expected. These sample containers were heated in a custom built fan oven fitted with Kapton windows through which the incident and diffracted x-rays could enter and leave. Temperature could be regulated $\pm 0.2^\circ\text{C}$.

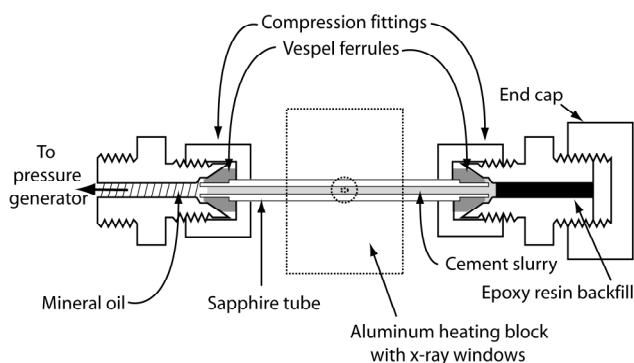


Figure 2. Schematic of sample environment for high pressure studies of cement hydration.

A different apparatus (see Fig. 2) was used when comparisons between hydrations under autogenous and externally applied pressure were required. Slurries were injected into sapphire tubes with ~1.7 mm (0.068") internal diameter and ~0.85 mm (0.034") wall thickness. Pressure was applied using a hand-operated screw-plunger pump, with white mineral oil as the pressure medium. The oil interfaced directly with the slurry in the sapphire tube. This arrangement worked well provided that head space at the capped end of the tube was minimized; without this, the slurry would move too much as pressure was applied, resulting in break up of the oil-slurry interface, and ingress of oil into the section of the tube where the x-ray beam passed through. The sample is heated by a two piece aluminum heating block, which fastened around the tube. The block contains two miniature 15 W cartridge heaters, and temperature control to about $\pm 0.5^\circ\text{C}$ is possible. Details of this apparatus for high pressure diffraction studies have been recently published elsewhere [6].

2D diffraction images were recorded using a Mar 345 image plate detector. An x-ray beam size of 0.5×0.5 mm and 180 s exposures were typical. The detector readout time was ~ 80 s, so one diffraction pattern

could be recorded every ~260 s. This time scale is well matched to cement hydration under oil well conditions.

For each experimental run, the sample-to-detector distance was calibrated using a NIST Al₂O₃ powder diffraction standard, assuming the wavelength to be 0.309963 Å. The image files were integrated to give I/2θ text format data using FIT2D [7].

Crystalline phases in the samples were identified using the diffraction peak listings in the ICDD database. Relative amounts for each phase were estimated from the integrated intensities of a single selected peak, as determined by Gaussian peak shape fitting. The following peaks were used: C₃S (201) ($d=5.93$ Å), CH (020) ($d=4.90$ Å), C₄AF (020) ($d\approx 7.25$ Å), gypsum (020) ($d=7.60$ Å), ettringite (100) ($d=9.72$ Å), “14-water” monosulfate (003) ($d=9.55$ Å), hydrogarnet (211) ($d\approx 5.13$ Å), tobermorite (002) ($d\approx 11.4$ Å) and jaffeite (100) ($d=8.60$ Å). Approximate d spacing values have been given for phases which are subject to unit cell dimension changes due to composition variation.

3. Results and discussion

3.1 General utility of in-situ diffraction studies

Real time powder diffraction provides a very detailed picture of the crystalline phases involved in cement hydration. In Fig. 3a, we present a 2D contour plot showing how diffracted intensity versus 2θ evolves with time for a Class H slurry hydrating at 97 °C under autogeneous pressure in the presence of an AMPS (acrylamido-methyl-propane sulfonate) copolymer retarder. These data can be processed to determine how the amounts of all the crystalline phases present in the slurry changes with time as shown in Fig. 3b.

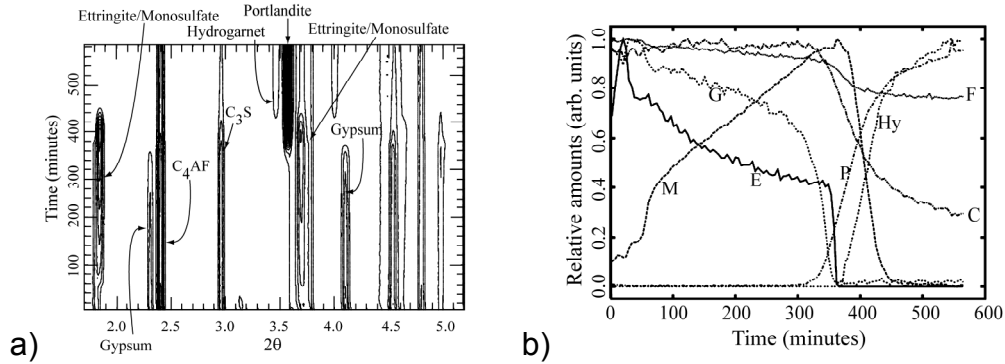


Figure 3. a) Contour plot representation of the diffraction data for a hydrating Class H cement slurry, b) relative amounts of the crystalline phases in the slurry versus time. M - monosulfate, E - ettringite, G - gypsum, P - portlandite, Hy - hydrogarnet, C - C_3S , F - C_4AF .

The results provide insight into a variety of phenomena, such as how the induction period varies with temperature or additive type, and correlations between the exhaustion of gypsum and the formation of other sulfate bearing phases.

3.2 Class H cement with retarders at elevated temperature

Some of our earlier work in this area using titanium autoclaves has already been reported [3]. Here we present data recorded using PBI autoclaves. Class H cement slurries were prepared with a water-to-cement ratio of 0.394. The retarders AMPS copolymer, tartaric acid or lignosulfonate were dry blended with the cement prior to mixing with water in a Waring blender at high speed (~12,000 rpm) for 35 s. The concentration of all retarders was 0.3% bwoc. Retarded slurries as well as unretarded controls were hydrated at 97, 108, 119 and 130°C under autogenous pressure. In each case, the oven temperature was ramped from approximately 30°C to the target temperature in 35 minutes.

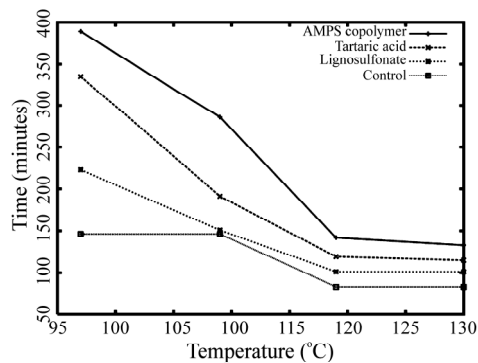


Figure 4. Time for the hydration of 1/3 of the C_3S in a Class H slurry as a function of temperature for different retarders.

The strong temperature dependence of the initial hydration behavior in this temperature range is apparent in Fig. 4, which shows estimated times for one-third depletion of C_3S . All the retarders are much less effective at 119°C than at 97°C, but increasing the temperature to 130°C makes little further difference. The initial rates of gypsum consumption and the times for the onset of portlandite precipitation correlate well with these results, which are, however, more difficult to link directly to the time evolutions observed for ettringite and monosulfate. Although, it is evident that the behaviors of these phases are influenced by retarder type. The time profiles for ettringite content at 97°C for all four mixes are compared in Fig. 5. Of particular interest is the delayed, but then very rapid, formation of ettringite in the presence of tartaric acid. Hydroxycarboxylic acids are known to form soluble complexes with Al^{3+} [8], which could account for the initial retardation. The subsequent acceleration followed by a sudden plateau might be due to some form of self catalysis, whereby ettringite precipitation is favored once a sufficient number of nuclei are present; the plateau might correspond to the near exhaustion of Al^{3+} in solution.

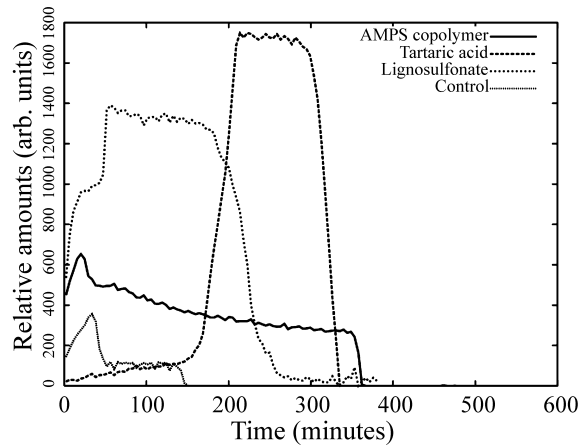


Figure 5. Ettringite content versus time for Class H slurries hydrating at 97°C in the presence of different retarders.

3.3 Class H and Class A cement with 0–4% bwoc $CaCl_2$

$CaCl_2$ is a well-known accelerator of portland cement hydration, but although there is an extensive literature on the effects of $CaCl_2$ on the hydration of synthetic cement phases, relatively little detailed work on cement hydration with $CaCl_2$ seems to have been published. We have performed *in situ* x-ray diffraction measurements on Class A and Class H cement slurries with 0, 1, 2 and 4% bwoc $CaCl_2$, at 25 and 50°C. The water ratios were 0.460 for the Class A and 0.394 for the Class H slurries; the difference reflects the lower water demand of the less finely ground Class H cement. For these experiments the oven temperature was not ramped, but heated to the required temperature before the autoclave was loaded.

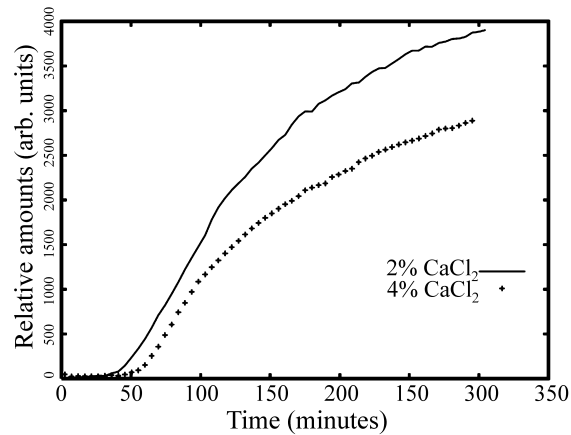


Figure 6. Portlandite precipitation versus time for Class H slurries at 50°C. 4% bwoc CaCl₂ leads to retardation relative to 2%.

In Class A samples, increasing concentration of CaCl₂ leads to a shortening of the induction period followed by suppression of portlandite precipitation, at both 25°C and 50°C. In Class H samples, a distinctly different trend is observed. At 4% bwoc, CaCl₂ actually retards relative to 2% addition (see Fig. 6). This type of effect has been observed in C₃S hydration with CaCl₂. A complete report on our CaCl₂ work has been submitted for publication [9].

3.4 Retarded Class H cement at high pressure and temperature

Class H cement slurries with 0.3% of AMPS copolymer, tartaric acid and lignosulfonate were hydrated in sapphire tubes at temperatures up to 180°C, at 'low' (7 MPa / 1,000 psi) and 'high' (50 MPa / 7,500 psi) pressure. At least 7 MPa was always applied, to ensure that the water vapor pressure was balanced. The water-to-cement ratio was again 0.394. Once a sample was loaded, pressure was applied and the sample ramped to the required final temperature in 35 minutes.

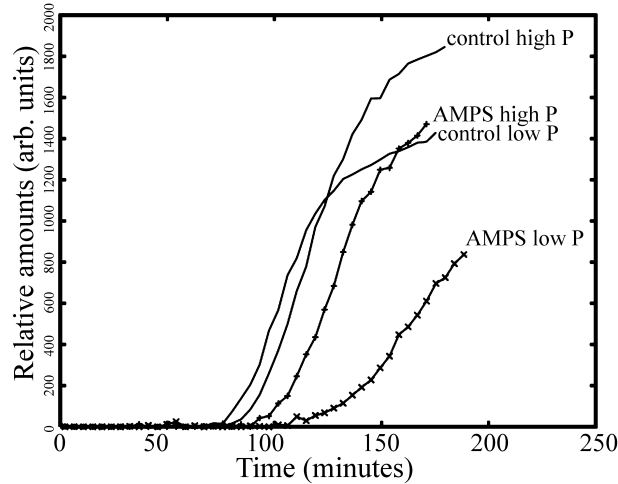


Figure 7. Jaffeite formation at different pressures for control and AMPS copolymer containing Class H slurries at 180 °C.

These experiments indicate that the effect of pressure on cement hydration is strongly dependent on temperature. In general, although the induction period is not significantly shortened at high pressure, the precipitation of portlandite which ensues from it may be considerably faster. In some samples at 180°C the effect of pressure is most clearly manifest in the formation of α -C₂SH and jaffeite [Ca₄(Si₃O₇)(OH)₆], particularly the latter (see Fig. 7). A complete account of our extensive studies of retarded cement hydration at different pressures will be published elsewhere [10].

3.5 Class H cement with silica containing additives at high temperature and pressure

For these experiments, Class H cement was dry blended with substantial quantities of mineral admixtures (typically 35% bwoc), and made into a slurry with much higher than normal water content (typically 135% bwoc). In some cases a small amount (up to 1% bwoc) of soluble cellulose derivative was added to keep the solids in suspension during early hydration. The silica containing additives were silica flour, amorphous silica, and a natural zeolite mixture. The main crystalline hydration product in these samples was tobermorite [Ca₅Si₆O₁₆(OH)₂·4H₂O] when silica flour and/or zeolite was used. The effect of pressure on the hydration process was found to be strongly dependent on the silica source that was used. It is interesting to note that in the samples containing mixed silica flour and zeolite, the *d* spacing for the 002 reflection was 11.5 Å compared with 11.38 Å when only silica flour or zeolite was present. This suggests significantly increased Al substitution in the silica+zeolite case [11]. It is known that cement-formed tobermorite typically contains some Al³⁺; it has been shown that it substitutes for Si⁴⁺, probably with OH⁻ substituting for

O²⁻ to maintain charge balance [11, 12] Details of our added silica experiments will be published elsewhere [13].

4. Summary

Powder diffraction can be used to study, in real time, the hydration of oil well cement slurries under a wide range of pressures and temperatures. The time scale for these measurements, when using synchrotron radiation from an appropriate source, is very well matched to the chemistry that is occurring. The data is information rich, even though the formation of C-S-H gel can not be studied directly using Bragg scattering. It seems reasonable to envision building sample environment to go to the limits of temperature/pressure that are of relevance to the oil industry, and to consider combining diffraction with other measurement types such as ultrasound for sensitivity to mechanical property development or small angle x-ray scattering for sensitivity to sample nanostructure.

5. Acknowledgements

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6. References

- [1] P. Barnes, S. Colston, B. Craster, C. Hall, A. Jupe, S. Jacques, J. Cockcroft, S. Morgan, M. Johnston, D. O'Connor and M. Belloto, "Time- and Space-resolved dynamic studies of ceramic and cementitious materials," *J. Synchrotron Rad.* **7**, 167-177 (2000).
- [2] P. Barnes, S. L. Colston, A. C. Jupe, S. D. M. Jacques, M. Attfield, R. Pisula, S. Morgan, C. Hall, P. Livesey and S. Lunt, "The use of synchrotron sources in the study of cement materials"; pp.477-499 in, *Structure and performance of cements*. Ed. Bensted, J.; Barnes, P. SPON press, London, 2002.
- [3] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "Class H Oilwell Cement Hydration at Elevated Temperatures in the Presence of Retarding Agents: An in-situ High Energy X-ray Diffraction Study," *Ind. Eng. Chem. Res.* **44**, 5579-5584 (2005).
- [4] B. Bresson, F. Meducin and H. Zanni, "Hydration of Tricalcium Silicate at High Temperature and High Pressure," *J. Mat. Sci.* **37**, 5355-5365 (2002).
- [5] "Well simulation thickening time tests"; pp.18-21 in, *Recommended Practice for Testing Well Cements, API Recommended Practice 10B*, American Petroleum Institute, 1997.
- [6] A. C. Jupe and A. P. Wilkinson, "Sample cell for powder X-ray diffraction at up to 500 bar and 200°C," *Rev. Sci. Inst.* **77**, 113901 1-4 (2006).
- [7] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hausermann, "Two-dimensional detector software: From real detector to idealised image or two-theta scan," *High Pressure Research* **14**, 235-248 (1996).
- [8] S. Rai, S. Chaturvedi and N. B. Singh, "Examination of Portland cement paste hydrated in the presence of malic acid," *Cem. Concr. Res.* **34**, 455-462 (2004).
- [9] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "Slurry Consistency and In-situ Synchrotron X-ray Diffraction during the Early Hydration of Portland Cements with Calcium Chloride," *J. Am. Ceram. Soc.*, (submitted for publication).
- [10] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "The effect of pressure on Class H cement hydration at high temperature," *J. Am. Ceram. Soc.*, (in preparation).
- [11] G. L. Kalousek, "Crystal chemistry of hydrous calcium silicates : I, Substitution of aluminum in lattice of tobermorite," *J. Am. Ceram. Soc* **40**, 74-80 (1957).
- [12] P. Faucon, J. C. Petit, T. Charpentier, J. F. Jacquinet and F. Adenot, "Silicon substitution for aluminum in calcium silicate hydrates," *J. Am. Ceram. Soc* **82**, 1307-1312 (1999).

[13] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "Class H cement hydration at 180 °C and high pressure in the presence of added silica," *Cem. Concr. Res.*, (submitted for publication).