Effect of Admixture on Cement Hydration Kinetics by Synchrotron XRD and Isothermal Calorimetry

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Abstract
The effect of an accelerating and a retarding chemical admixture on the hydration of an industrial Portland cement was investigated at room temperature by means of synchrotron XRD and isothermal calorimetry. While the calorimetry results offer general information on the kinetics of cement hydration, the synchrotron XRD data provides insights into the degree of hydration of individual cement phases as well as semi-quantitative information on crystalline hydrates formed. The results indicate that at high dosage, both admixtures increase the ettringite formation within the few first hours of hydration, yet exhibit different kinetics afterwards. The acceleration effect of calcium nitrite can be attributed to an accelerated hydration of both aluminate (with corresponding accelerated ettringite formation) and alite. However, the synchrotron data indicated that acceleration of ettringite formation preceded any acceleration of the alite hydration. As for sodium gluconate, the results indicated a retardation of the initial heat evolution by calorimetry during the first minutes of hydration accompanied by a retardation of the alite hydration peak, while little if any effect was seen on the rate of ettringite formation as detected by the synchrotron data. The precipitation of additional ettringite then stops until the end of the dormant period, coinciding with the onset of increased alite hydration.

1. Introduction

Chemical admixtures are commonly used in concrete to adjust for weather conditions or meet construction requirements. Their mechanism of interaction with cement and cement hydrates include adsorption, dispersion, chelation and solubilization that may affect cement hydration kinetics, phase composition, and hydrates morphology. The study of the effect of admixtures on cement hydration therefore requires the combination of a variety of techniques such as isothermal conduction calorimetry, X-Ray diffraction, TGA, DSC, SEM, etc.

Isothermal calorimetry is a well-established technique for studying the overall kinetics of cement hydration [1]. However, while the heat evolution over time can be studied with great accuracy, isothermal calorimetry does not offer any direct insight into the details of the underlying cement

hydration. Synchrotron XRD was therefore applied in parallel tests with the objective to measure the depletion of the unhydrated cement phases as well as the formation of crystalline phases detectable by synchrotron XRD. While the calorimetry method captures essentially all heat released by hydration activity including adsorption, dissolution and formation of crystalline as well as non crystalline hydration products, XRD would only capture the reduction of crystalline anhydrous phases and formation of hydration products crystalline enough to be detectable by XRD. This paper presents results on the depletion of alite and gypsum and formation of ettringite in hydrating cement paste. Depletion of aluminate and ferrite is not considered here because of excess peak overlaps with other phases.

1.1 Hydration of portland cement

A detailed description of the hydration of portland cement is available in [2,3]. The following somewhat simplified information extracted from [2,3] and [4] is important for the study presented in this paper:

Portland cement releases a strong heat exotherm upon initial hydration, originating from the dissolution of alkali salts, some aluminate phase and formation of amorphous hydration products on the cement surface. The aluminate phase is generally the most reactive cement phase and rapidly precipitates ettringite-like phases on the cement surface in presence of excess calcium and sulfate in solution. The ettringite-like phases are thought to be initially amorphous with increasing degree of crystallinity over time, however still at least partially detectable by XRD after a few minutes of hydration [4]. The ettringite together with amorphous hydrates containing calcium, alumina, sulfate and some silica rapidly precipitates on the surface of the cement grains and prevents flash set by providing a coating that restricts water from accessing the unhydrated cement surface. It also allows enough time to place the mix while it is still fluid. The so-called "dormant period" lasts until water percolates through the coating and initiates rapid alite hydration because of the improved water access to the unhydrated cement surface. The detailed mechanisms leading to the onset of the main alite hydration is not well understood.

1.2 Analytical methods used in this study

Synchrotron XRD
While conventional XRD suffers from limited penetration depth in dense cement paste samples, synchrotron XRD with greater penetration depths offers the possibility to perform in situ hydration studies to reduce surface effects and obtain information on bulk properties while eliminating preferred orientation effects.

Isothermal calorimetry
Isothermal calorimetry has been used to study the hydration kinetics of cement for many years. A classic paper by Lerch [1] described its

significance and demonstrated how isothermal calorimetry can be used to optimize the sulfate content of Portland cement based on its reactivity [1]. More recently, isothermal calorimetry has been widely used to monitor the kinetic effect of admixture on cement hydration [5]. The isothermal calorimeter used offers the possibility to perform test at constant temperature within 5-60 C.
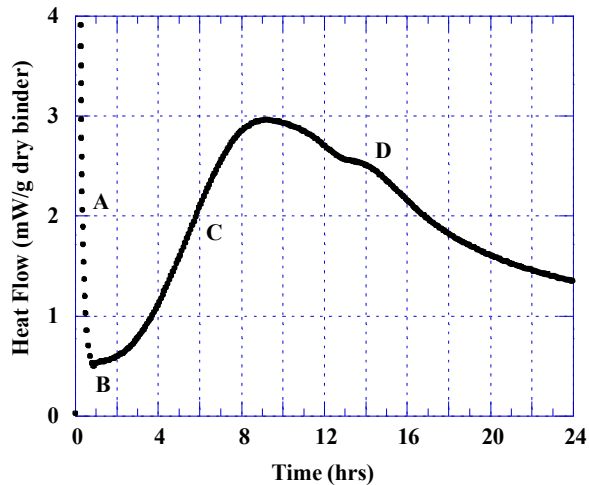

Fig. 1: Example of normal hydration of an ASTM Type II portland cement, water-to-cement ratio of 0.45.

Fig. 1 shows an example of hydrating Portland cement in the absence of admixture, a water-to-cement ratio of 0.45, monitored at 20 ^{o}C by an isothermal conduction calorimeter. Portland cement mixed with water initially displays a strong exotherm (A) caused by rapid dissolution and initial hydration of mainly the aluminate phase. If sufficient calcium sulfate is available in solution, the hydration rate rapidly decreases (B) as aluminate reacts with calcium and sulfate to form ettringite like phases. After some time the strength generating alite hydration takes off, which results in a broad exotherm (C). Set usually occurs at the initial part of the alite exotherm. The alite and aluminate hydration continue in parallel until the mixture runs out of soluble sulfate, indicated by the "sulfate depletion" peak (D) as introduced by Lerch [1]. The "sulfate depletion" peak should for a well-balanced mixture according to Lerch occur well after the maximum of the alite exotherm.

2. Experimental

2.1 Chemical admixtures
Many chemical admixtures impact the rate and the sequence of hydration of the different portland cement phases. Many set retarders for example accelerate the aluminate hydration while retarding the alite hydration. Calcium nitrite, a set and early strength accelerator, and sodium gluconate, a set retarder and low range water reducer, were selected for this study.

Calcium nitrite

Calcium nitrite was initially developed as a corrosion inhibitor by W.R. Grace, but has since earned reputation as a powerful accelerator of set and early strength development. Calcium nitrite is typically used at dosages higher than 0.5% s/s. The detailed mechanism of acceleration is unclear although it is known that calcium nitrite provides soluble calcium that is thought to accelerate the formation of calcium hydrates.

Sodium Gluconate

Sodium gluconate is commonly used both as a stand-alone set retarder and formulated with other admixtures to provide set retardation and some water reduction. As a sugar acid, sodium gluconate is thought to complex with calcium and thereby impact both the dissolution rate of anhydrous compounds and the rate of formation and morphology of hydrates. Sodium gluconate is typically used at dosages lower than 1000 ppm as it may cause excessive retardation at higher dosages.

2.2 Portland cement and mixtures

A Portland cement conforming to ASTM Type I and II (designated cement "A"), Table 1, was used at w/c 0.50. Calcium nitrite at 1.2% s/s and 2.0% s/s, and sodium gluconate at 0.10% s/s and 0.15% s/s were dosed with the mix water. A reference paste without admixture was made at the same w/c ratio. All mixes contained 5.0% 30µm quartz powder by weight of cement as an internal standard for XRD analysis.

Table 1. Characteristics of portland cement A

Analyte	Weight %	Analyte	Weight %	
SiO_2	20.86	Alkalies as Na_2O	0.60	
Al_2O_3	4.00	*Water-soluble Alkali*		
Fe_2O_3	3.33	Na_2O	0.06	
CaO	64.61	K_2O	0.40	
MgO	1.09	Calculated Compounds per ASTM C 150-00		
SO_3	2.88	C3S	65	
Na_2O	0.18	C2S	11	
K_2O	0.64	C3A	5	
TiO_2	0.17	C4AF	10	
L.O.I. (950^oC)	1.80	Blaine Surface Area (m^2/kg)		360.9
Total	99.69			

2.3 Isothermal calorimetry

Cement pastes for calorimetry were prepared by 15 seconds in situ mixing using a hand-operated impeller. All materials were pre-conditioned to 23 C equal to the temperature maintained in the isothermal calorimeter. 1.00 g of portland cement was used for each test. A TAM AIR 8-cell isothermal calorimeter supplied by Thermometric was used for all calorimetry tests.

2.4 Synchrotron XRD

Cement paste samples for synchrotron XRD were prepared using a conventional planetary mixer for 60 seconds. Each paste sample was transferred into 0.7 mm diameter glass capillary immediately after mixing. Both ends of each capillary were sealed using high vacuum grease. Paste sample preparation and alignment of sample capillaries prevented any synchrotron XRD data collection during the initial 10 minutes hydration. Experiments were carried out at the Brookhaven National Laboratory synchrotron X-Ray source, on beam line X7A. The beam line was equipped with a custom-made position sensitive detector and provided a 0.703792 Å beam. The experimental set-up permitted following the cement early-age hydration through 5-minute acquisitions performed in transmission with a d-spacing resolution of 10-3. The synchrotron acquisitions covered a 2θ range of 3.5° to 25.5°. This corresponds to a 7.7° to 57.8° 2θ range using Cu Kα radiation. The ettringite, gypsum, alite and quartz peaks were measured at 4.17°, 5.34°, 22.98° and 12.08° 2θ. (These values correspond to 9.14°, 11.70°, 51.70° and 26.65° 2θ using Cu Kα radiation.)
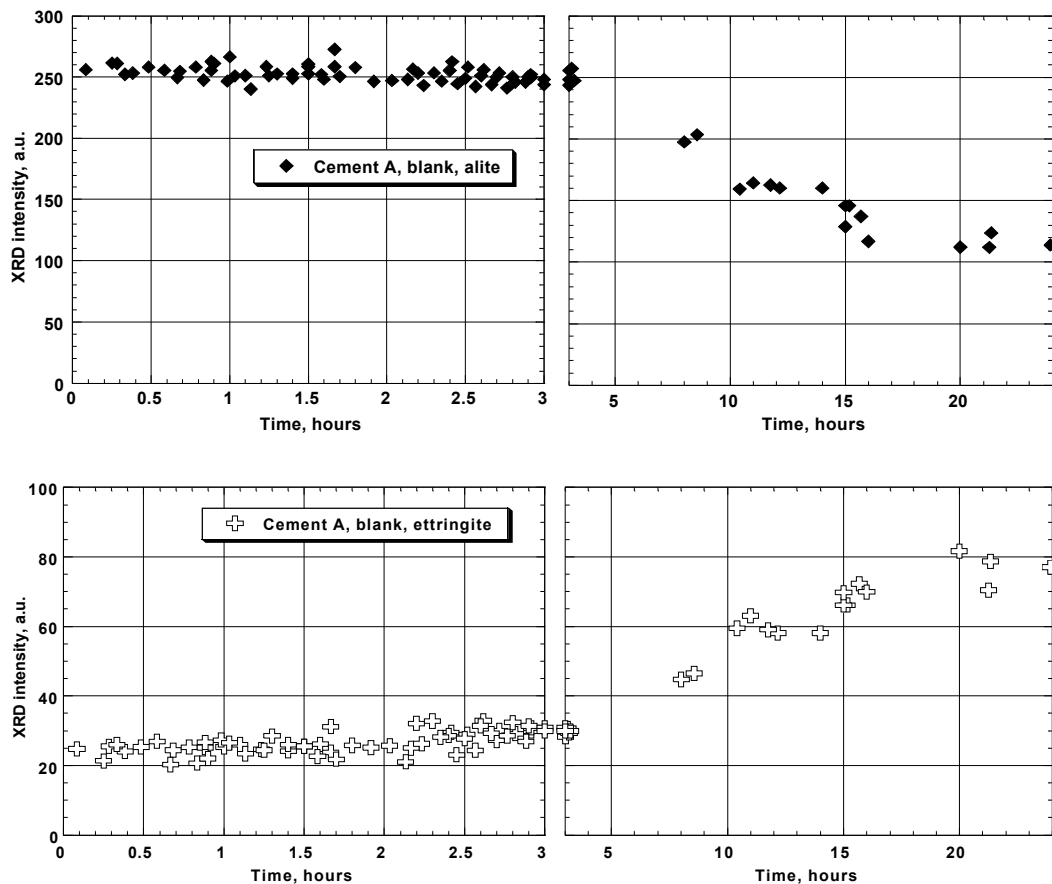
Fig. 2. Repeatability of the calculated amounts of alite and ettringite obtained by 4 repeated test series of portland cement A hydrated in absence of admixture. Left: 0-3 hrs hydration. Right: 3-24 hrs hydration.

Fig. 2 indicates the repeatability of the calculated amounts of alite and ettringite obtained by 4 repeated test series of cement A hydrated in absence of admixture.

The synchrotron XRD patterns obtained were analyzed qualitatively and semi quantitatively by conventional peak integrated intensity analysis by means of normalizing peak integrated intensities relative to the integrated intensity measured for the internal standard, 5% 30µm quartz powder. The ettringite peak at 0.967 nm, the alite peak at 0.1768 nm, the gypsum peak at 0.756 nm and the quartz peak at 0.3342 nm were selected for their limited overlapping with peaks of other phases.

3. Results and discussion

The results from the calorimetric test and the corresponding ettringite formation as well as the consumption of gypsum and alite as measured by Synchrotron XRD was plotted as a function of cement hydration time.

3.1 Initial heat evolution in mixes without cementitious material

Mixes with both portland cements and with cement replaced with quartz powder were prepared and tested by isothermal calorimetry at 20 ^{o}C in a similar way as cement paste, Fig. 3. The results indicated that the heat induced by wetting and mixing of the inert powders was significantly smaller than the heat generated by initial cement wetting, dissolution and hydration. As indicated, the rate of heat dissipation in the calorimeter was such that it took approx 30 minutes after mixing to reach a stable baseline in the absence of cementitious material.
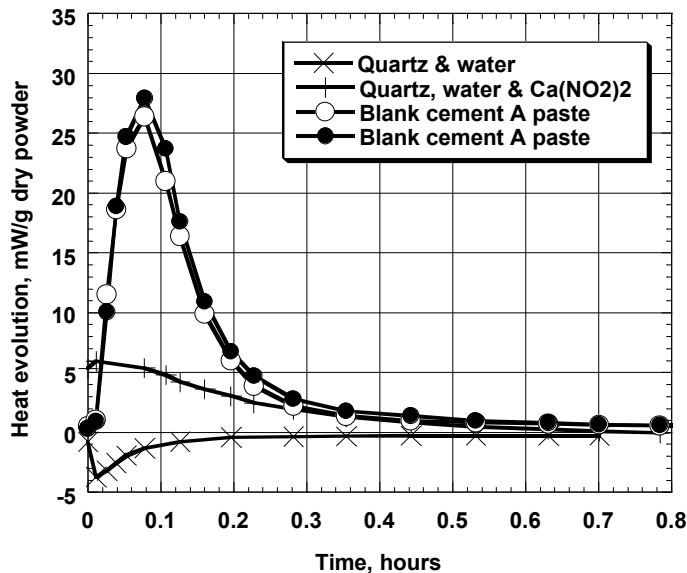

Fig. 3. Initial heat evolution from mixes with inert powder and portland cement prepared with identical water content at 20 ^{o}C.

3.2 Initial hydration kinetics by isothermal calorimetry

Fig. 4 shows the initial heat evolution at 20 ^{o}C for portland cement A in presence of calcium nitrite and sodium gluconate, respectively.
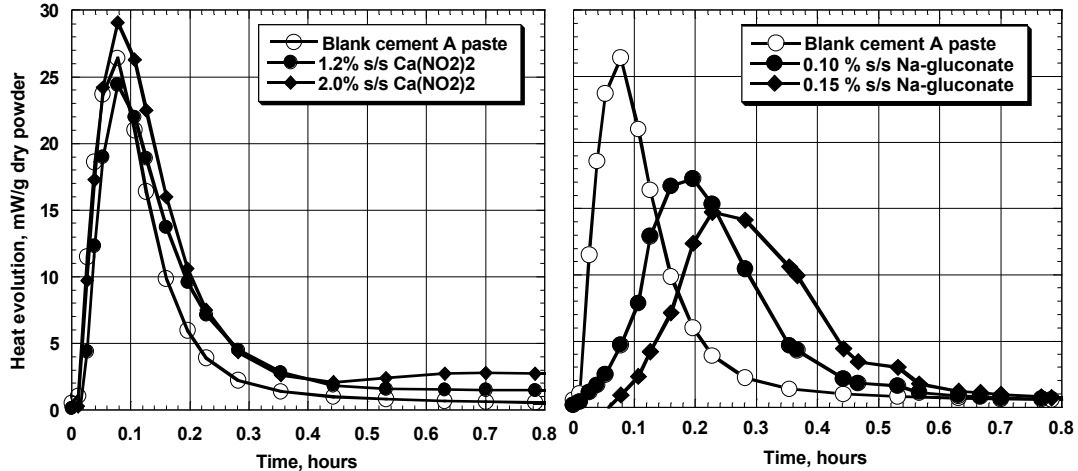

Fig. 4. Initial heat evolution at 20 ^{o}C for portland cement A in presence of calcium nitrite and sodium gluconate, respectively.

Discussion of the effect of admixture on the initial cement hydration
Gluconate seemed to retard the very first cement hydration, possibly we speculate by poisoning the initial precipitation of ettringite.

3.3 Hydration of portland cement A in absence of admixture

Fig. 5 shows the heat evolution at 20 ^{o}C, gypsum depletion and ettringite formation for portland cement A without admixture. Fig. 6 shows the corresponding depletion of alite.
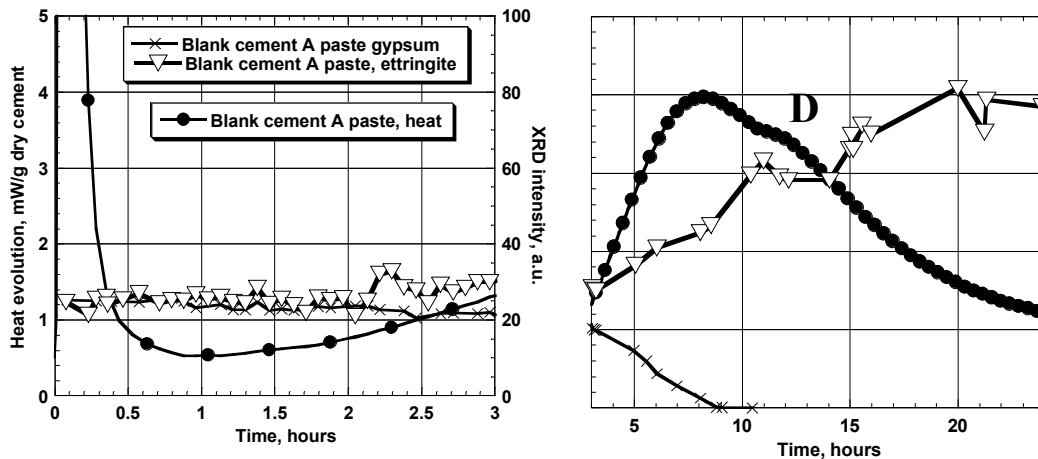
Fig. 5. Heat evolution at 20 ^{o}C, gypsum depletion and ettringite formation by Synchrotron XRD for portland cement A.
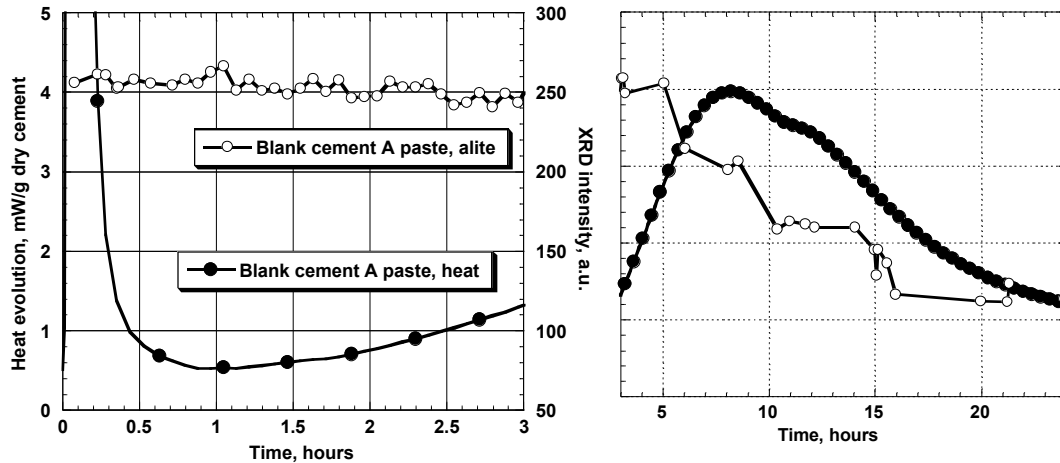
Fig. 6. Heat evolution at 20 °C and alite depletion by Synchrotron XRD for portland cement A.

Discussion of results obtained without admixture:
The timing of the so-called sulfate depletion peak ("D" in Fig. 5) coincided with the depletion of gypsum detectable by the synchrotron XRD. It is well known that the timing of the sulfate depletion peak can be readily controlled by addition of soluble calcium sulfate [1,5]. However, no clear change in detectable ettringite could be seen at the time of "sulfate depletion". The continued growth of ettringite after depletion of gypsum may indicate that significant sulfate remains available for ettringite formation even after the depletion of gypsum.

3.4 Hydration of portland cement A in presence of calcium nitrite

Fig. 7 shows the heat evolution at 20 °C and ettringite formation for Cement A with calcium nitrite. Figs. 8-9 show the corresponding depletion of gypsum and alite, respectively.
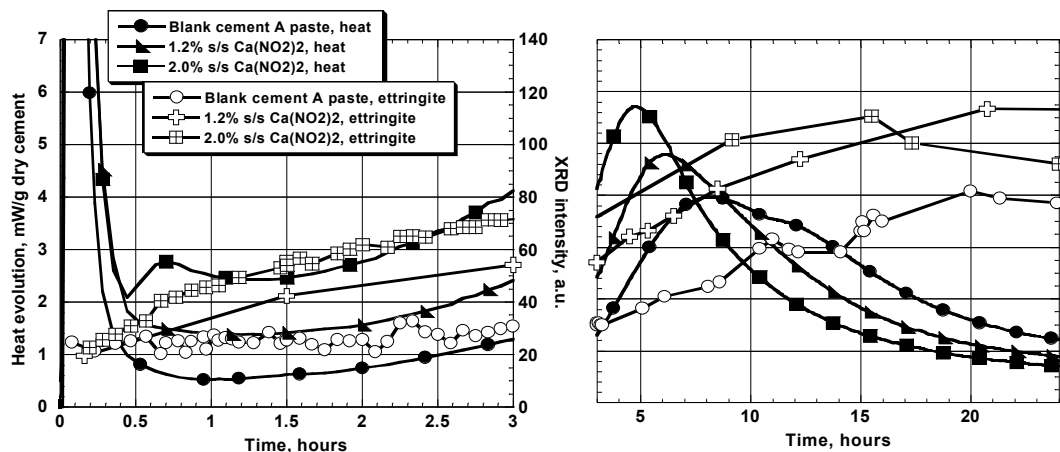

Fig. 7. Heat evolution at 20 °C and ettringite formation by Synchrotron XRD for portland cement A in presence of calcium nitrite.
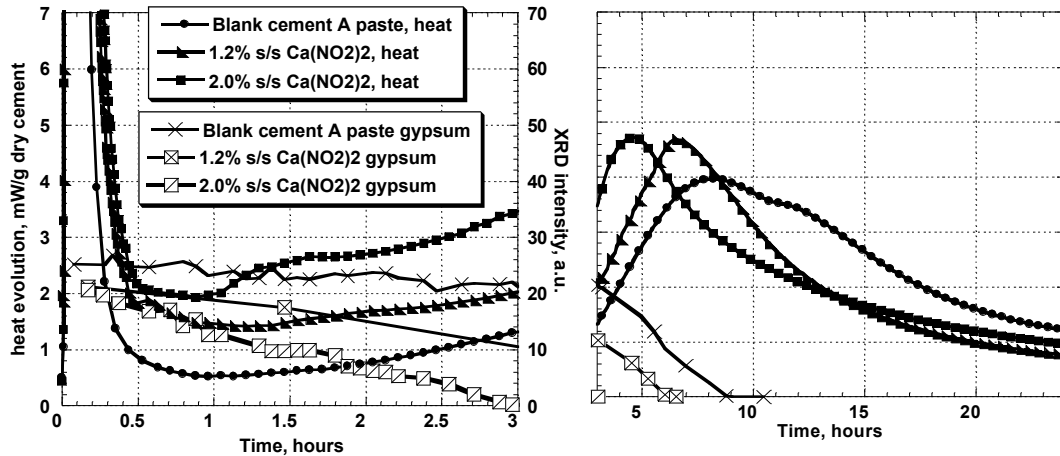
Fig. 8. Heat evolution at 20 °C and gypsum depletion by Synchrotron XRD for portland cement A in presence of calcium nitrite.
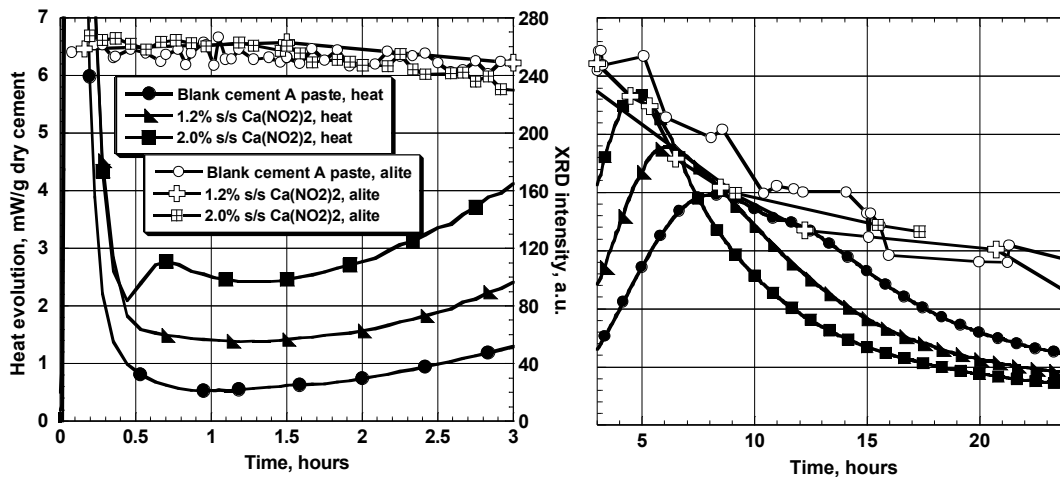

Fig. 9. Heat evolution at 20 °C and alite depletion by Synchrotron XRD for portland cement A in presence of calcium nitrite.

Discussion of results using calcium nitrite:

The high dosage of calcium nitrite (2.0% s/s) significantly increased the rate and amount of ettringite formation, correlating with an increased heat output. Furthermore, it appeared that the high dosage of calcium nitrite also induced some moderate acceleration of the alite hydration. Calcium nitrite is a known accelerator of set and early strength development. It appears from these results that calcium nitrite accelerates primarily the ettringite formation.

3.5 Hydration performance of cement A in presence of sodium gluconate

Figure 10 shows the heat evolution at 20 °C and ettringite formation for portland cement A with sodium gluconate. Figs. 11-12 show the corresponding depletion of gypsum and alite, respectively.
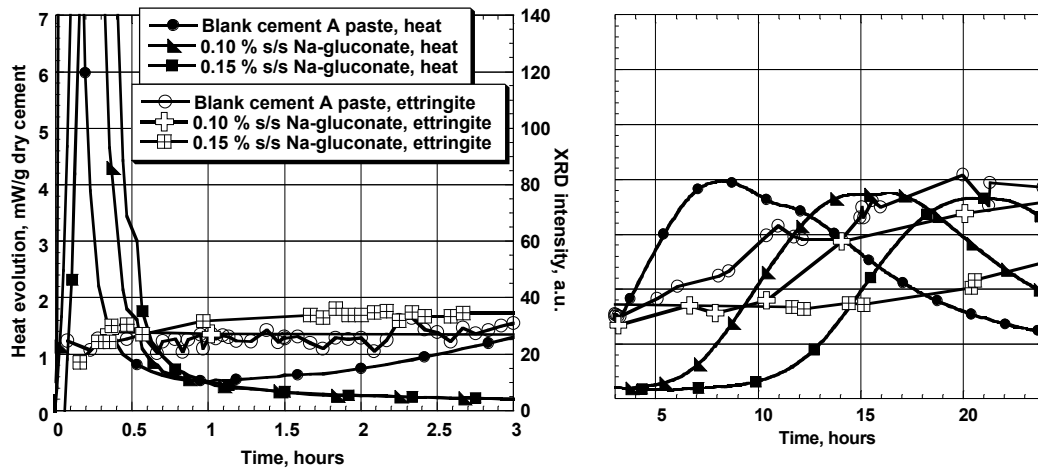
Fig. 10. Heat evolution at 20 °C and ettringite formation by Synchrotron XRD for portland cement A in presence of sodium gluconate.
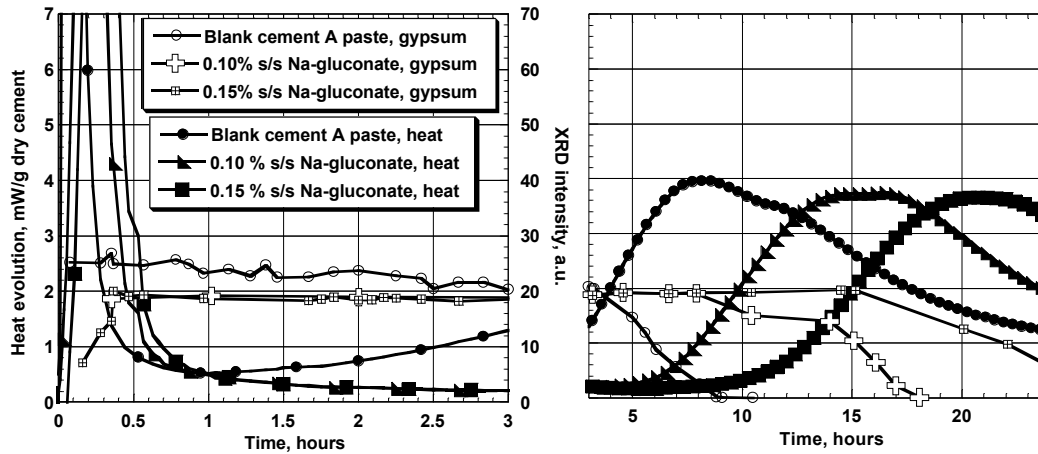

Fig. 11. Heat evolution at 20 °C and gypsum depletion by Synchrotron XRD for portland cement A in presence of sodium gluconate.
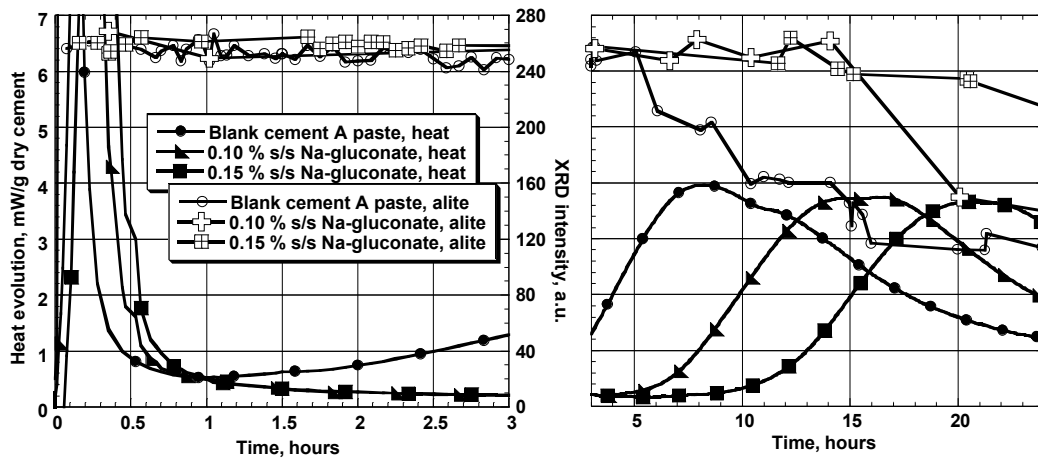

Fig. 12. Heat evolution at 20 °C and alite depletion by Synchrotron XRD for portland cement A in presence of sodium gluconate.

Discussion of results using sodium gluconate:
Sodium gluconate at the high dosage (0.15% s/s) appeared to initially accelerate the formation of ettringite detectable by synchrotron XRD. We speculate that this accelerating effect is related to the ability of gluconate to solubilize iron. By increasing the solubilization of C4AF, the surface of other cement phases is more accessible to water for hydration according to a mechanism similar to that of triisopropanolamine which thereby accelerates hydration and increases compressive strength [6,7]. However, the ettringite content after initial acceleration in presence of gluconate seemed to level off after about one hour, with an extended dormant period typical of many retarders. The high dosage of gluconate significantly retarded the onset of the alite hydration, with remaining alite detected by synchrotron XRD correlating well with heat output. It was interesting to note that for gluconate the initial acceleration of ettringite did not seem to accelerate the alite hydration, as was the case for calcium nitrite. It seems evident that other factors than the rate and amount of ettringite formation impacts the alite hydration. Studies of pore solution composition and morphology of hydrates, especially those coating the cement grains after the initial hydration, may give further insights into the mechanisms of acceleration and retardation by calcium nitrite and sodium gluconate, respectively.

4. Conclusion
A good correlation was found between the rate of heat evolution by isothermal calorimetry and the rate or ettringite formation detectable by synchrotron XRD. The onset of the main alite heat evolution peak did not correlate well with measured reduction in alite content by synchrotron XRD, indicating that alite and aluminate hydration occurrs in parallel. We found a correlation between the so-called sulfate depletion calorimetry peak and the depletion of gypsum, although there was no evident effect on the rate of ettringite formation. However the noise level in the data was high and further work is encouraged to explain the mechanism controlling the peak.

References

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