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Tricalcium silicate (C_3S) hydration under high pressure at ambient and high temperature (200 °C)

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Abstract

The hydration of a tricalcium silicate paste at ambient temperature and at 200 °C under high pressure (up to 1000 bar) has been studied. Two high pressure cells have been used, one allows in-situ electrical conductivity measurements during hydration under high pressure. The hydration products were characterized by thermal analysis, X-ray diffraction and ^{29}Si NMR measurements. The pressure has a large kinetic effect on the hydration of a C_3S paste at room temperature. The pressure was seen to affect drastically the hydration of a C_3S paste at 200 °C and this study evidences the competition between the different high temperature phases during the hydration.

Keywords: Hydration; Temperature; Oil well cement; C_3S; Pressure

1. Introduction

The hydration of a cement paste at high temperature and high pressure is of great importance in determining the durability of oil wells. Many studies have been carried out in hydrothermal conditions or have been carried out on model systems at high temperature [1–7] without additional hydrostatic pressure. And the studies under high pressure concern mainly thermodynamic equilibrium between high temperature and high pressure phases in the ternary H_2O–CaO–SiO_2 system [8,9]. However, those results cannot be easily transposed to the hydration of a cement paste at high temperature under high pressure for two reasons. The first is that the behavior of a hydrating cement paste under high pressure and high temperature is very far from the behavior of a system in equilibrium and the second is that the combined effect of the pressure and the temperature produces dramatic changes in the hydration of the paste. This combined effect can be missing in hydrothermal conditions. This paper focuses on the modification induced by high pressure at room and at high temperature (200 °C) on a tricalcium silicate paste hydration (C_3S in cement chemist's notation: C=CaO, S=SiO_2, H=H_2O). The C_3S is the main component of Portland cement of which oil well cement is composed. The high pressure cells have been specially designed for this study: an original result has been obtained thanks to a high pressure cell which allows in-situ electrical conductivity measurement under high pressure. Under normal conditions of temperature and pressure, C_3S paste hydration yields to the poorly crystallized and non-stoichiometric C–S–H and Portlandite [10]. At higher temperatures, it has been observed that C–S–H is no longer stable and is replaced by more stable crystallized products [1], the composition and proportions of which depend on the initial conditions (Ca/Si ratio, water/solid ratio). The effect of the high pressure at room temperature has been studied through the measurement of electrical conductivity, an appropriate tool to investigate kinetic

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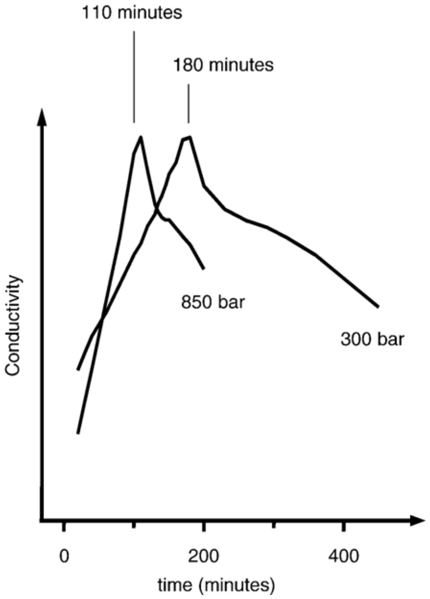

Fig. 1. Comparison of the electrical conductivity obtained during the hydration of a C_3S paste at room temperature under 300 bar and 850 bar. Both signals are normalized against the maximum conductivity peak.

processes in these conditions. For the high temperature measurements, single pulse ^{29}Si NMR experiments, thermal analysis and X-ray diffraction will allow to show the drastic effect of the pressure on the hydration of a C_3S paste at high temperature.

2. Experimental

2.1. Materials and synthesis

Anhydrous C_3S was obtained from Ciments Français-Italcementi. Samples for the hydration studies were prepared by mixing C_3S with deionized and boiled water with a water to solid weight ratio of 0.44. The paste was transferred to a Teflon® container, and placed in the high temperature and high pressure cell. The samples were hydrated for a period extending typically from a few hours to a few days under pressure (Argon gas). Once removed from the cell, further hydration was inhibited by acetone–ether drying before the samples were studied by thermal analysis, X-ray diffraction and ^{29}Si NMR.

2.2. High temperature and high pressure cell description

Two cells were specially designed for high pressure and high temperature hydration. The first cell allowed the in-situ measurement of electrical conductivity during the hydration of the cement at temperatures from ambient to 160 °C and under pressure of 1 to 1000 bar. The body of the cell consisted of a steel cylinder of diameter 65 mm and length 130 mm in which a Teflon® pot containing the hydrating cement paste (typically a few cm^3) could be located. A Bridgeman cap-screw-seal system provided a hermetical seal. Two isolated wires (electrodes) were passed through the cap and embedded in the paste during hydration to allow measurement of the electrical conductivity. Similarly, a thermocouple was also introduced through the cell cap so that the temperature of the paste could also be determined. The cell was connected to a gas compressor providing the required static argon pressure for the hydration experiment. Sample heating was achieved by the addition of a heating collar around the cell connected to a temperature regulator. Conductivity measurement could then be performed with a conductimeter operating with a 16 kHz sampling rate.

A second cell was especially designed to permit longer duration hydration experiments (up to a few days) at high pressure (1000 bar) and high temperature (200 °C). Electrodes were excluded from this design to minimize heat loss and irregularities in the sample environment although a thermocouple was again introduced for temperature control. The system used for pressure and temperature generation was the same as that used with the first cell.

In the operation of both cells, the desired sample conditions were achieved in a three-step process. First the cell was pressurized to half that required. The cell was then heated to the required temperature. Finally, the pressure was raised to the desired value. The time required to reach the target temperature and pressure up to 200 °C and 1000 bar was typically half an hour.

2.3. Characterization techniques

Thermal analyses were performed, with a thermobalance TAG24 SETARAM. Samples were submitted to temperatures ranging from 20 °C to 1050 °C with a 10 °C/min ramp rate under ambient pressure during which, the weight loss was recorded. XRD experiments were performed with powdered samples on a Philips PW 1820 device using the Cu Kα radiation. The diffraction patterns were performed in the range $2\theta = 10$ to $80°$ with a step of 0.03° and 4 s per step. ^{29}Si NMR experiments were

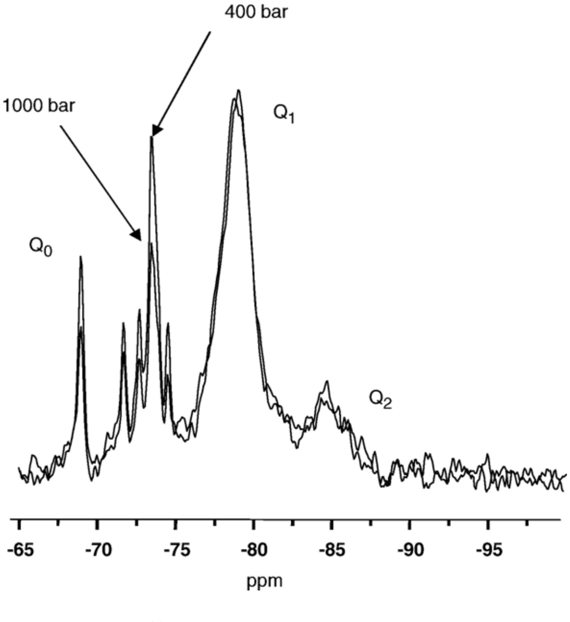

Fig. 2. Comparison of ^{29}Si NMR single pulse spectra of C_3S hydrated under 1000 bar and under 400 bar at room temperature for 1 day. Spectra are normalized against the Q_1 intensity.

Table 1
Weight proportion (%) of the C_3S hydrated samples at 200 °C under 600 bar for 2, 4 and 6 days and at 200 °C under 400 bar for 4 and 16 days

Temperature (°C)	Pressure (bar)	Duration (days)	Portlandite	α-C_2SH	Jaffeite	Hillebrandite
200	600	2	18	68	13	1
200	600	4	12	45	40	3
200	600	6	11	35	46	8
200	400	4	15	4	36	45
200	400	16	12	0	39	49

carried out on a Bruker ASX 500 MHz spectrometer operating at 12 T. The spectra were single pulse experiments, with a recycle delay of 60 s. The sample was spun at 5 kHz in a Bruker 7 mm Bruker Magic Angle Spinning probe. The pulse duration was 4 µs.

3. Results and discussion

3.1. Effect of high pressure at room temperature

Fig. 1 shows the conductivity signal of a hydrating C_3S paste obtained at room temperature under two isostatic pressures (300 bar and 850 bar). The measured conductivity was observed to be dependent upon the conductivity of the solution inside the porous C–S–H and on the texture of this porous material [11,12]. It is known that the conductivity of the interstitial solution is proportional to the Ca^{2+} concentration resulting from the dissolution of C_3S. Thus, the conductivity versus hydration time curve of a hydrating C_3S paste (in normal conditions of temperature and pressure) can be roughly divided in two steps. The first step, observed as an increase in the conductivity, corresponds to C_3S dissolution. The maximum of conductivity is reached just before the precipitation of Portlandite CH when the solution is over-saturated in Ca^{2+} ions with respect to this phase. Portlandite precipitation yields to a decrease of conductivity of the hydrating paste, the time constant of this process being very short (~several minutes). The second step corresponds to the slow decrease of conductivity, the time constant of this process being several hours. The growth of C–S–H leads to the progressive disconnection of pores. In this second step by comparison to the first one, Ca^{2+} concentration in the pores is fixed and equal to an equilibrium concentration between CH and CSH. It is clearly apparent from Fig. 1 that a higher isostatic pressure increases the rate of dissolution of C_3S. For comparison, the maximum conductivity under the ambient conditions is attained after more than 4 h. The precipitation of CH occurs earlier under high pressure and the porous network closes rapidly. The pressure effect at room temperature is a kinetic effect. This is confirmed by NMR spectroscopy for longer hydration times. ^{29}Si NMR allows characterisation of poorly crystallized phases C–S–H with a structure based on SiO_4 chains with variable length. ^{29}Si single pulse NMR spectra were analyzed using the Q_n classification [13], where Q stands for SiO_4 tetrahedron and *n* refers to the number of tetrahedra linked by oxygen bonds to the previous tetrahedron. In Fig. 2, it can be seen that the hydration of C_3S under high pressure and room temperature shows that anhydrous C_3S (Q_0 species between −65 ppm and −75 ppm) disappears more rapidly under higher pressure. Q_2 is a middle chain site (linked to two tetrahedra), Q_1 is an end-chain site and Q_0 is a monomeric site. The peaks located around −80 ppm and −85 ppm correspond to Q_1 and Q_2 entities characteristic of C–S–H [14]. This figure also shows that the same hydrates are formed under pressure as those formed in normal conditions: average short chains composed by three silica tetrahedra (deduced from Q_2/Q_1 ratio). The presence of C–S–H is also evidenced by the loss of water found below 150 °C during thermal analysis [10] and the presence of a shoulder in the background of the X-ray diffraction pattern at around $2\theta = 35°$ (Kα, Cu).

3.2. Combined effect of high pressure and high temperature

It is known that the C–S–H phase ceases to be stable above 120 °C and is replaced by crystallized phases [1,7,15]. The hydration of the C_3S paste has been studied at 200 °C under two pressures over times between 2 days and 16 days. The weight proportion (%) of each phase for different hydration times and for two pressures is displayed in Table 1 (2, 4 and 6 days at 600 bar, and 4 and 16 days at 400 bar). The following phases were identified [16]: Jaffeite $Ca_6(Si_2O_7)(OH)_6$ (tricalcium silicate hydrate), Hillebrandite $Ca_2(SiO_3)(OH)_2$ (β-dicalcium silicate hydrate), α-C_2SH $Ca_2(SiO_3)(OH)_2$ (α-dicalcium silicate hydrate) and Portlandite $Ca(OH)_2$(CH) according to the literature in the same conditions of temperature. All the phases observed in these experiments were crystallized phases. The combination of thermal analysis and X-ray diffraction allowed quantification of the phases. These results were compared with ^{29}Si single pulse NMR experiments in the case of the hydration of C_3S at 600 bar (Fig. 3). The ^{29}Si NMR experiments performed on these samples are semi-quantitative. Indeed, the α-C_2SH-Q_0 species seemed to be underestimated by NMR. This could be due to the relaxation time T_1 which can be too low. It is known that the ^{29}Si relaxation time T_1 of some calcium silicates can be very long (several hundreds of seconds) so that a quantitative ^{29}Si NMR would require at the same time a large number of scans necessary to give a good signal to noise ratio and a very long delay between two consecutive scans. In our case, the NMR was not used to quantify the phases because the

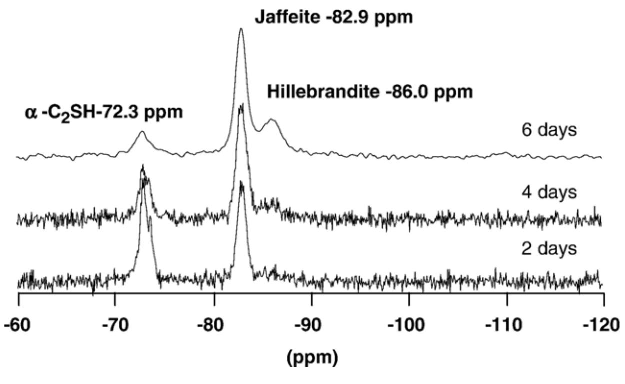

Fig. 3. Comparison of the ^{29}Si NMR single pulse spectra of a C_3S paste hydrated at 200 °C under 600 bar for 2, 4 and 6 days.

quantification is ensured by other methods. However, the NMR results confirm the relative evolution of each phase. The peaks at −82.9 (Q_1) and −86.0 ppm (Q_2) are related to Jaffeite and Hillebrandite respectively. The thermal analysis shows the absence of the loss of water before 150 °C confirming the absence of the C–S–H. The role of pressure on the evolution of phases during hydration can be readily observed from the comparison of samples hydrated at 200 °C under 400 bar and 600 bar. After 2 days, the hydration is complete (C_3S has completely disappeared) but the sample is still evolving through dissolution–precipitation mechanisms. The competition between the three high temperature phases is clearly shown on Fig. 3 and in Table 1. The first observation is that Hillebrandite and Jaffeite amounts always increase with time of hydration. The second observation is that the α-C_2SH is mainly formed at the beginning of hydration and is favoured by high pressure.

4. Discussion

The phases appearing at 200 °C and their evolution are greatly modified by the pressure. After a first step of the hydration (in our case at least after 2 days), the C_3S is fully hydrated but the sample continues to evolve because the free water (limiting factor of these reactions) is still available to allow the dissolution–precipitation mechanism. It has to be noticed that even if it is not observed in this study, the formation of C–S–H can occur before the formation of the crystallized phases, this preliminary step has been reported in the literature in hydrothermal conditions even at high temperature [1]. In our case, under high pressure, this step occurs too rapidly to be observed in the time scale of these experiments. The amount of Jaffeite is always increasing with hydration time whatever the pressure. It is explained by the fact that it is a stable phase at this temperature and it has the same C/S ratio as in the solution (C/S equal to 3) and as the initial product (C_3S). This result matches those obtained at a lower temperature [15] (160 °C and 120 °C) where it was found that under hydrothermal conditions, Jaffeite was always readily formed for an initial C/S ratio equal to 3. The Hillebrandite also appears along with the Jaffeite and its amount also always increases with hydration time. This is supported by the literature dealing with equilibria at high temperature [5,8] showing that Hillebrandite is in equilibrium with Jaffeite. It is also known that another metastable phase can appear [1,6,7] when a C_3S paste is hydrated between 130 °C and 200 °C known as α-C_2SH. It has been clearly demonstrated [7] that the α-C_2SH phase appears and develops after 200 min in a hydrating cement paste at 130 °C. Other studies [15] showed that the α-C_2SH phase is present even at 120 °C in a C_3S hydrating paste with silica flour under high pressure (400 bar). At 160 °C, the pressure highly favours this phase [15]. In our case, the results illustrate the competition between the two stable phases (Hillebrandite and Jaffeite) and the metastable phase. It is clearly shown that at the first stage of the hydration, the α-C_2SH phase is favoured by high pressure. It is progressively replaced by more stable phases with time in accordance with the literature [5]. Indeed, the α-C_2SH phase dissolves to form a more stable hydrate (Hillebrandite) with the same C/S ratio (equal to 2) or a more stable hydrate as Jaffeite with a higher C/S ratio and with consumption of the Portlandite. It has to be noticed that in this temperature range, the pressure effect is critical in the sense that small changes of the conditions of pressure and temperature can induce great changes in the phase composition of the product after a few days. The unstable system hydrates with a competition between the two stable phases and the metastable phase favoured by the pressure. The results are clearly different from those obtained under hydrothermal conditions.

5. Conclusion

This study focused on the influence of high pressure on a hydrating tricalcium silicate (C_3S) paste at room temperature and at 200 °C. At room temperature, the electrical conductivity results (for a short hydration time) as well as the ^{29}Si NMR results (for a longer hydration time) showed that the effect of the pressure is a kinetic effect. The hydrates formed under high pressure at room temperature are the same as under atmospheric pressure. On the contrary, at high temperature (200 °C), the pressure greatly affects the formation of the crystallized phases. The evolution occurs even after the full hydration of the C_3S phase. First, it has been shown that the α-C_2SH is formed at the first stage of hydration. This phase progressively disappears during hydration. It is replaced by a more stable phase with the same C/S ratio equal to 2 or by a more stable phase with a higher C/S ratio (Jaffeite C/S ratio is equal to 3), this reaction being possible with Portlandite consumption. Secondly, the α-C_2SH phase is favoured by the hydrostatic pressure which can induce drastic changes during the hydration of an instable system at high temperature. These results obtained at 200 °C confirm precedent results obtained at lower temperature (160 °C).

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