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DELAYED ETTRINGITE FORMATION: THE EFFECT OF TEMPERATURE AND BASICITY ON THE INTERACTION OF SULPHATE AND C-S-H PHASE

L. Divet[1] and R. Randriambololona
Laboratoire Central des Ponts et Chaussées, Service Physico-chimie des Matériaux,
75732 Paris Cedex 15, France

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ABSTRACT

The aim of this work was to learn more about the role of C-S-H phase in delayed ettringite formation. Some authors assume that, when the temperature of a concrete rises during setting, sulphates are trapped by physical adsorption on C-S-H. The sulphates are then likely to lead, in the long term, to the formation of ettringite. Our work clearly shows that the adsorption capacity of sulphate ions is high and is directly related to the basicity of the pore solution of the concrete and to the temperature of the heat treatment: a higher pH and temperature favour adsorption. The adsorption isotherm can be described by a Langmuir model. Finally, the reversibility of the adsorption has also been confirmed. *© 1998 Elsevier Science Ltd*

Introduction

Sulphate activity following heating of concrete at an early age is well known in several countries under the name delayed ettringite formation. The mechanisms of this reaction are not perfectly known and are the object of many researches. On this subject, Glasser's work (1) shows that a higher concentration of SO_4^{2-} in the pore solution of concretes directly correlates both with a higher alkali content of the cement and a higher heat treatment hold temperature. This last phenomenon results mainly from the thermal stability of ettringite. Under these conditions, free sulphates can remain in solution and give rise, in the long term, to the recrystallization of potentially expansive ettringite. Furthermore, when the temperature of the concrete rises during setting, the sulphates released by the cement do not react completely with the C_3A. Moreover, the primary ettringite (AFt) that may form during the first hours decomposes above 60–70°C. It is hydrated calcium monosulphoaluminate (AFm) that is observed upon cooling. In consequence, the cement matrix still contains free sulphates likely to react in the long term to re-form ettringite. Kalousek (2), Odler (3), and Fu et al. (4) suppose that the sulphates are trapped by physical adsorption on the surfaces of the calcium silicate hydrate (C-S-H). There would then be a competition between two reactions involving the consumption of sulphate ions in the early stages of hydration: 1) the reaction between the

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[1] To whom correspondence should be addressed.

sulphate ions and the C_3A to form primary ettringite; and 2) the fixing of the sulphates by the C-S-H phase to form phase X as it has been defined by Lerch (5,6).

The work presented in this article is aimed at a better understanding of the interactions between the C-S-H phase and SO_4^{2-} ions, and in particular at determining the adsorption isotherm. We analyze the parameters that influence the adsorption process, such as the basicity of the medium and the temperature. To eliminate more complex phenomena due to the hydration of the cement particles, we did this work on the C-S-H samples synthesized in the laboratory. In addition, because of the complexity resulting from the number and type of phases present, this study is difficult to perform on cement pastes. In a first stage, it is therefore preferable to consider only the solid (C-S-H) phase and the pore solution of the concrete likely to act in the adsorption mechanisms.

Experimental

Synthesis and Characterization of the C-S-H Samples

The C-S-H samples are produced by a reaction, at ambient temperature, between a solution of sodium metasilicate and a solution of calcium hydroxide. After centrifuging, the precipitate is washed and dried. The product is then identified by x-ray diffraction. The reticular distances of the main peaks were observed at 12.31 Å (very wide spike), 3.04 Å, 2.79 Å, and 1.93 Å, and confirm that C-S-H samples were obtained. The C/S ratio was 1.57 and was determined by inductively coupled plasma (ICP). The H/S ratio was 1.26 and was calculated using the water content determined by thermogravimetric analysis. The specific surface area (S) was measured by the BET method (nitrogen adsorption, $S = 350\ m^2/g$) and by thermoporometry ($S = 320\ m^2/g$) (7).

Measurement of Sulphates Adsorption

The protocol consists of putting 3.4 g of C-S-H into 250 mL of a sodium hydroxide solution in the presence of various sodium sulphate concentrations contained in a 400-mL centrifuging tube. The suspension is mechanically agitated by a magnetic bar. The speed of rotation is adjusted to 700 r.p.m. to ensure that the suspension is permanently homogeneous. The quantity adsorbed is calculated from the difference between the quantity introduced and the quantity in the solution, which is evaluated by ICP using the emission peaks of sulphur (8). The repeatability of the measurement of adsorbed sulphate ions has been verified. For a mean value of 0.68 mmol of sulphates adsorbed per gram of C-S-H, determined on a sample of 11 individuals, the standard deviation was 0.04 and the bilataral confidence interval to the 0.95 probability threshold was 0.07 mmol/g of C-S-H. A prior study showed that adsorption is complete and reproducible after 1 h of mechanical agitation of the suspension. After adsorption of the sulphates, the C-S-H preparations were subjected to analysis by x-ray diffraction, which did not find any formation of mineral phases containing sulphates

Influence of Liquid Phase Composition and of Temperature on Adsorption

To demonstrate the role played by the pH, we measured the adsorption of the sulphate ions in the presence of various sodium hydroxide solutions simulating the basicity of the pore

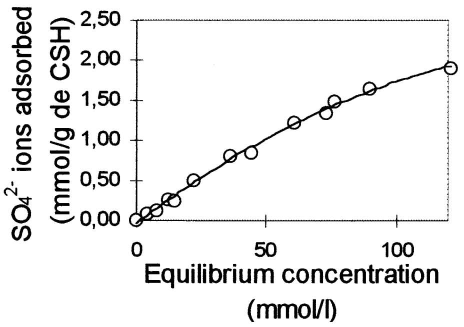

FIG. 1.
Adsorption isotherm of SO_4^{2-} ions on C-S-H in 0.5 mol/L NaOH at T = 25°C.

solutions of concretes (0.05, 0.1, 0.2, and 0.5 mol/L). The influence of the ionic strength was investigated at a pH of 13.3 using sodium chloride solutions at 0.5 mol/L and 2 mol/L. Otherwise, all of the tests were performed at ambient temperature (25°C). Only a few experiments were performed at 50°C and 80°C, to analyze the influence of temperature on adsorption.

In all cases, the C-S-H suspensions in the media concerned were prepared and the temperature adjusted 1 h before the addition of the sulphates, so that the chemical equilibrium of the suspensions would be established.

Results and Discussion

Adsorption Isotherm

Plotting the quantity of SO_4^{2-} ions adsorbed on C-S-H vs. the sulphate concentration at equilibrium in the solution is the most common way of representing the results of an adsorption study. The shape of the isotherm obtained can provide clues to the mechanism of adsorption and to the intensity of the substrate/adsorbates interactions (Fig. 1). It can be seen in particular that the adsorption capacity of the SO_4^{2-} ions is relatively high.

A classification of adsorption isotherms has been established by Giles et al. (9) in solid/liquid systems for dilute solutions. Four categories have been defined in this way: S, L, H, and C. Type L is the most common; it corresponds to the isotherm shown in Figure 1. In effect, the initial branch of the type L isotherm is linear over a rather large range of concentrations. Moreover, the maximum quantity adsorbed is reflected by a plateau on the adsorption isotherm.

The type L isotherm recalls those described by Langmuir in solid/gas systems. Under well-defined conditions (in particular when adsorption is limited to a single layer, without side interactions, and the surface is homogeneous in terms of energy), the true Langmuir isotherm is obtained; it is governed by the relation:

$$1/C_b = 1/kC_{bm} \quad 1/C + 1/C_{bm}$$

with k the affinity constant; C the concentration at equilibrium; C_b the quantity adsorbed; and C_{bm} the quantity adsorbed when the surface is saturated.

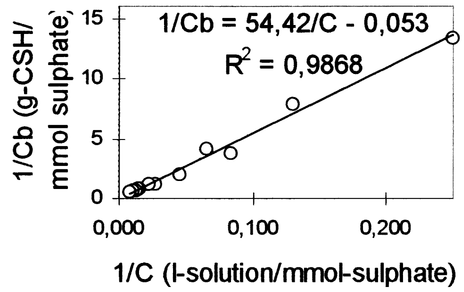

FIG. 2.
Langmuir isotherm of SO_4^{2-} ions on C-S-H in 0.5 mol/L NaOH at T = 25°C.

Figure 2 shows the adsorption isotherm in Langmuir's coordinates. It can be seen that the experimental points are correctly aligned. The equation of the isotherm, calculated by a linear regression method, and its correlation factor are also given in Figure 2. These results show that the adsorption isotherm of SO_4^{2-} ions on C-S-H samples is in fact governed by a Langmuir law.

Influence of pH

The isotherms obtained at different NaOH concentrations (pH between 12.7 and 13.7) are grouped in Figure 3. The pH has a marked influence both on the maximum quantity adsorbed and on the slope of the first part of the curve. This last point reflects a variation of the affinity of the sulphates for the surface. Qualitatively, it is found that the maximum quantity adsorbed (start of the isotherm plateau) and the affinity of the sulphates for the surface increase as the pH increases.

To explain this phenomenon, one can analyze the electrostatic contribution of the interaction between the sulphates and the surface. C-S-H in all likelihood has a surface charge that becomes more and more negative as the pH increases. Because of this, the Coulomb contribution to the sulphate/C-S-H interaction is a repulsion. The increase of the Coulomb repulsions with pH cannot explain the greater affinity of sulphates for the substrate (C-S-H).

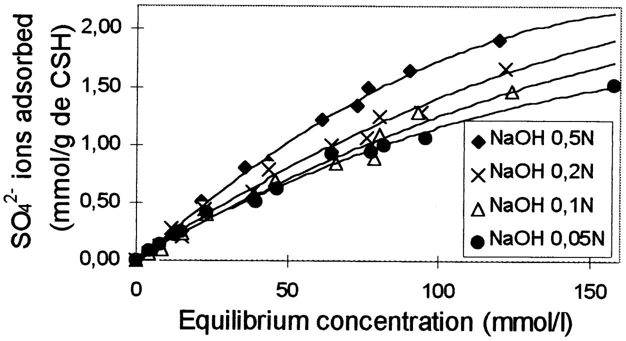

FIG. 3.
Influence of NaOH concentration on adsorption isotherm.

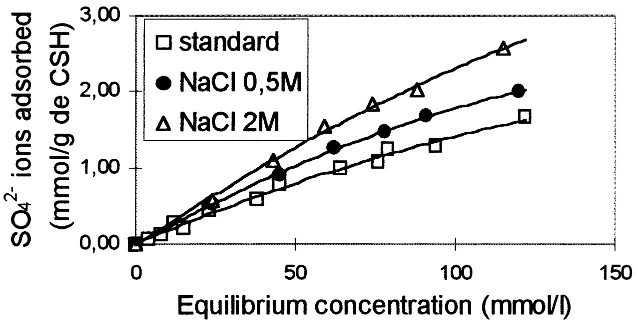

FIG. 4.
Influence of NaCl concentration on adsorption isotherms in 0.2 M NaOH.

It may, then, be assumed that the adsorption is explained by various elementary interface forces, mainly Van der Waals forces.

The ions on the periphery of the C-S-H particles are organized into shallow layers according to the triple ionic layer model (Stern and Grahamme), which takes the adsorption of the solvated ions into account. Adsorption can occur when the particles are at a distance corresponding to one of the interaction potential minima. These minima correspond to situations where the Van der Waals forces prevail over the Coulomb forces. In basic media such as cement paste, it is primarily the thickness of the diffuse layer (in which the charges of the underlying layers are compensated by a different statistical distribution of the anions and cations), that determines the adsorption of SO_4^{2-} ions. This thickness varies inversely with $C^{1/2}$, where C is the concentration of the ions in the pore solution of the concrete. We are going to check this phenomenon by investigating the influence of the ionic strength by the controlled addition of sodium chloride solutions at constant pH.

Influence of Ionic Strength

Figure 4 summarizes the effect of the ionic force on the adsorption of sulphates. At pH 13.3, adding sodium chloride increases the adsorption. One can then hypothesize a compression of the diffuse layer by the ionic strength such that the Van der Waals forces prevail over the electrostatic repulsion. This phenomenon also occurs in the pore solution of the concrete, Because the ionic strength depends essentially on the basicity of the aqueous phase of the concrete, which is directly related to the alkaline oxides content of the cement.

Influence of Temperature

Figure 5 shows the isotherms obtained at different temperatures. It appears, strangely, that increasing the temperature leads to more adsorption of the SO_4^{2-} ions. Recall that the variation of free enthalpy associated with the adsorption (ΔG_{ads}) is governed by the following relation: $\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$. Given the small temperature range studied, the enthalpy ΔH_{ads} and the entropy ΔS_{ads} can be regarded as relatively constant in the domain in question. This being the case, ΔG_{ads} depends basically on the temperature, so an increase of the latter must normally result in a decrease of the affinity of the sulphates for the surface. The reverse

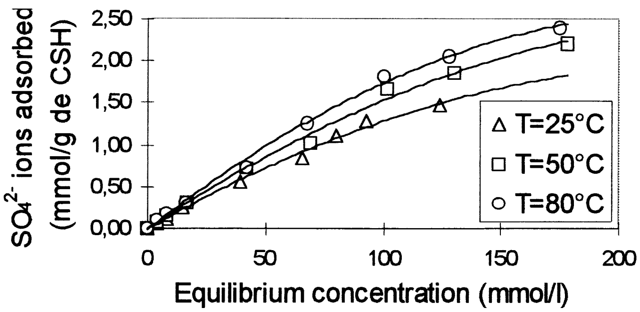

FIG. 5.
Influence of temperature on adsorption isotherms in 0.1 mol/L NaOH.

is observed, and is hard to explain. However, the temperature increase of the C-S-H suspensions before the addition of the SO_4^{2-} ions could result in a partial desorption of the OH^- ions located in the plane of the counter-ions of the surface of the C-S-H. New positive sites likely to fix more SO_4^{2-} ions would then form.

The effect of temperature on sulphate adsorption could be also explained by structural changes of C-S-H gel. Heating of C-S-H removes both interlayers' water molecules and OH^- groups, resulting in a more polymerized and disordered structure with a smaller basal-spacing (10,11).

Study of the Reversibility of the Adsorption

The desorption isotherm is obtained by successive dilutions of a suspension of C-S-H previously put into equilibrium with a solution containing SO_4^{2-} ions in 0.05 mmol/L NaOH (Fig. 6).

It is then clear that the adsorption of the SO_4^{2-} ions onto the C-S-H is a totally reversible phenomenon. In effect, the adsorption and desorption isotherms have no hysteresis loop, and the two curves are perfectly superposed down to the origin. On the other hand, the rate of return to equilibrium is slower for desorption. Equilibrium is reached only after 2 h of mechanical agitation of the suspension of C-S-H, against one hour for adsorption. In consequence, in concretes that have undergone a heat treatment, sulphates can be trapped on

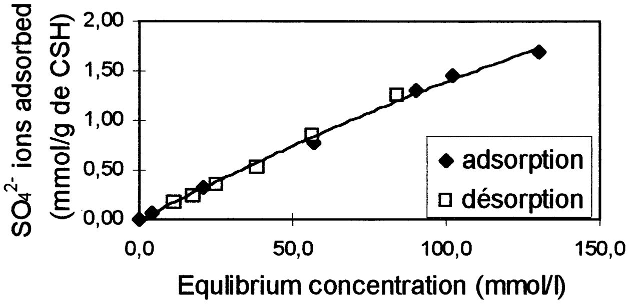

FIG. 6.
Adsorption and desorption isotherms in 0.05 mol/L NaOH.

the walls of the C-S-H and released in the more or less long term into the pore solution of the concrete. They are then available to form ettringite crystals.

Conclusions

1. The capacity of adsorption of SO_4^{2-} ions on C-S-H is high, and depends both on the basicity of the pore solution of the concrete and on the temperature to which the concrete structure is subjected. A higher pH and temperature favour adsorption.
2. The relation between free sulphates and bound sulphates can be described by an adsorption isotherm in Langmuir coordinates.
3. The adsorption of SO_4^{2-} ions on C-S-H is reversible.
4. The Glasser's work (1) has shown that, in the presence of a large quantity of alkalis and with high temperatures, the domain of thermal stability of ettringite is considerably reduced. There results an increase of the alkali and sulphates contents in the pore solution of the concrete. This phenomenon combines with the one observed in our experiments, namely physical adsorption of the sulphates onto the C-S-H samples. In consequence, there is a synergy between these two phenomena that favours delayed ettringite formation.
5. Questions remain for an understanding of the adsorption reactions, in particular concerning the type of bond between the SO_4^{2-} ions and the surface and the mechanism by which this bond is established.

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