PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Microanalytical Studies (X-ray Photoelectron Spectrometry) of Surface Hydration Reactions of Cement Compounds [and Discussion]

Micheline Regourd, C. Defosse, S. A. Jefferis and J. Bensted

Phil. Trans. R. Soc. Lond. A 1983 **310**, 85-92
doi: 10.1098/rsta.1983.0068

Phil. Trans. R. Soc. Lond. A **310**, 85–92 (1983) [85]
Printed in Great Britain

Microanalytical studies (X-ray photoelectron spectrometry) of surface hydration reactions of cement compounds

By Micheline Regourd
Microstructures Department, C.E.R.I.L.H., Paris, France

X-ray photoelectron spectrometry (X.p.s.) measures the kinetic energy of electrons photoejected from a solid surface by soft X-rays. The kinetic energy of the photoelectrons can be related to the binding energy that these electrons had originally in the solid. X.p.s. is a rather new technique for studying cements. It has been used recently in the surface analysis of C_3S, C_2S, C_3A and blast-furnace slag grains during their hydration. Changes in chemical composition have been found as soon as the surface comes into contact with water, shown by a change in the shape, position and intensity of characteristic peaks like Ca_{2p}, Si_{2p}, O_{1s} and a reduction of characteristic ratios Ca/Si or Al/Si. A tentative interpretation of X.p.s. kinetic curves as a function of hydration time is presented.

1. INTRODUCTION

The initial hydration of cement compounds has not yet been completely clarified because of the complexity of the physico-chemical changes up to the end of the dormant period. Among the microanalytical techniques, the photoelectron spectrometry X.p.s. is a rather new one in the cement field but it has already been used for the study of the early hydration of cement compounds. X.p.s. measures the kinetic energy E_K of electrons photoejected from a solid surface. The kinetic energy is related to the binding energy E_B that these electrons had originally in the solid. X.p.s. is a surface analysis method as the depth of investigation is between 5 and 10 nm, and a quantitative method as it can be standardized on materials of known composition. This paper reports the modification of the chemical composition at the surface of cement compound grains that occurs as soon as they come into contact with water.

2. STUDY OF THE EARLY HYDRATION OF TRICALCIUM SILICATE

(i) *X.p.s. data*

A typical X.p.s. spectrum of C_3S shows the peaks Ca_{2p} ($E_B = 346.9$ eV), Si_{2p} ($E_B = 101.2$ eV), O_{1s} ($E_B = 530.9$ eV). The variation of Ca_{2p}/Si_{2p} X.p.s. ratios against time of hydration (figure 1) of C_3S pastes (w/s = 0.5) proves the importance of the perturbations on the surface at very early ages (Thomassin *et al.* 1979). The atomic Ca/Si ratio related to the X.p.s. Ca_{2p}/Si_{2p} ratio relative to a standard curve is, at any time of hydration, lower than in anhydrous C_3S. The binding energy and the shape of the Si_{2p} peak change within a very short period (table 1) (Regourd *et al.* 1980*a*). The increase of the O_{1s} binding energy from 532.9 eV, at $t = 0$, to 533.5 ± 0.2 eV, at $t = 10$ min, and simultaneously a broadening of the X.p.s. peak from 2.7 to 3.5 eV have also been observed (Ménétrier *et al.* 1979).

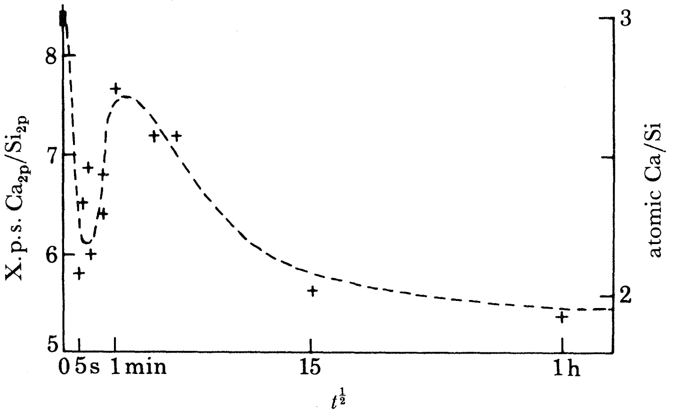

FIGURE 1. C_3S: variation of characteristic X.p.s. Ca_{2p}/Si_{2p} ratio and atomic Ca/Si ratio against (time of hydration)$^{\frac{1}{2}}$ (Thomassin *et al.* 1979).

TABLE 1. C_3S: DIFFERENCE BETWEEN BINDING ENERGIES OF X.P.S. PEAKS AND WIDTH OF THE Si_{2p} PEAK (REGOURD *et al.* 1980*a*)

time of hydration	$\delta(Ca_{2p}-Si_{2p})$/eV ($\pm$0.2 eV)	$\delta(Si_{2p}-O_{1s})$/eV ($\pm$0.2 eV)	(width of Si_{2p} peak)/eV ($\pm$0.1 eV)
0	247.7	429.7	2.5
5 s, 10 s, 15 s, 30 s, 1 min, 3 min, 5 min, 15 min, 1 h, 2 h	245.1	429.3	2.8
4 h	245.1	429.1	2.4

(ii) *Interpretation of X.p.s. data*

It is admitted that the beginning of the hydration is an instantaneous dissolution. A congruent dissolution could be assumed (Fuji *et al.* 1975; Barret *et al.* 1977), although an incongruent dissolution was also stated (Skalny *et al.* 1980).

The second stage, detectable in the first few seconds, corresponds to a drop of the Ca/Si ratio from 3 to 2.1 (figure 3). The cloud of points shows that the surface between 5 s and 1 min is a site of continuous exchange and is not in a state of equilibrium. The broadening of Si_{2p} and O_{1s} peaks indicates changes in the environment of electrons in the superficial layer. The higher binding energy of O_{1s} has been related to the existence of O—H bonds (Ménétrier *et al.* 1979).

A tentative quantitative interpretation of the X.p.s. data has been done according to the formula $I = \int_0^\infty \mathrm{d}I$, where I is the area of the photoelectron peak corresponding to a given energy and $\mathrm{d}I$ the contribution of a thickness $\mathrm{d}x$ to the depth x (Regourd *et al.* 1980*a*),

$$\mathrm{d}I = \sigma FSC\,\mathrm{e}^{-x/\lambda}\mathrm{d}x \qquad (1)$$

with σ the cross section of the sublayer irradiated by the X-ray beams, F the X-ray flux, C the concentration within the solid, and λ the mean free path of electrons, S a function of the apparatus. Considering a model of two layers, i.e. anhydrous C_3S and hydrated C_3S with an average Ca/Si close to 1 (Stein *et al.* 1977; Dent-Glasser *et al.* 1978) and assuming the thickness of the hydrated layer to be uniform and the mean free path of electrons Ca_{2p} and Si_{2p} to be the same in both layers, we obtain for the integration of (1)

$$\left.\begin{aligned} I_{\mathrm{Ca}} &= \sigma_{\mathrm{Ca}}\,FS_{\mathrm{Ca}}\left(\int_0^{d_1} C^1_{\mathrm{Ca}}\,\mathrm{e}^{-x/\lambda}\mathrm{d}x + \int_{d_1}^{\infty} C^2_{\mathrm{Ca}}\,\mathrm{e}^{-x/\lambda}\mathrm{d}x\right)\\ I_{\mathrm{Si}} &= \sigma_{\mathrm{Si}}\,FS_{\mathrm{Si}}\left(\int_0^{d_1} C^1_{\mathrm{Si}}\,\mathrm{e}^{-x/\lambda}\mathrm{d}x + \int_{d_1}^{\infty} C^2_{\mathrm{Si}}\,\mathrm{e}^{-x/\lambda}\mathrm{d}x\right)\end{aligned}\right\} \text{(1, hydrate; 2, } C_3S\text{).}$$

From the standard curve, for a value of $I_{Ca}/I_{Si} = 2.25$ at $t = 10$ s, the computed thickness d_1 of the hydrated layer is 0.8 nm.

The third stage manifests itself by an increase of the I_{Ca}/I_{Si} ratio in which the maximum is attained at the end of 1 min of hydration (figure 3). This could be explained by a chemisorption of Ca^{2+} ions on a surface enriched in silicon (Tadros *et al.* 1976). However, the Ca/Si of the hydrated layer would be lower than the observed maximum value of 2.7 because it includes a contribution from underlying C_3S. The calculation of I_{Ca}/I_{Si}, for Ca/Si close to 2, in the hydrated layer at $t = 1$ min gives a thickness of 0.8 nm, which strongly suggests that during the first stages of hydration the fixation of Ca^{2+} occurs from the solution only. The value of 0.8 nm is comparable to the thickness of the layer of C_3S dissolved after 1 min in the experiments of Fuji & Kondo (1975). The value of Ca/Si = 2 in the hydrate growing on C_3S seems to be confirmed by the same value obtained when the hydrated layer is thicker than 6 nm at $t > 15$ min. The Ca^{2+} ions can originate from two places, the solution and the inner part of the grain. These latter ions are released by the solid during the advancement of the interface hydrate, C_3S. The hydrated layer would develop and persist through the dormant period, up to the supersaturation of the solution.

After 4 h, important reorganizations take place in the hydrated layer, as evidenced by the change in the Si_{2p} peak. As already known, the end of the dormant period manifests itself by the nucleation of C—S—H with dimeric silicate ions $Si_2O_7^{6-}$ (Tamas *et al.* 1976) and $Ca(OH)_2$.

(iii) *Role of retarders*

The kinetic curve of C_3S hydrated with a solution containing NaF 10 g l^{-1} shows the instantaneous drop in Ca/Si ratio and a plateau at Ca/Si = 2 (figure 2), which is reached at 3 min (Regourd *et al.* 1980*b*). The variations of the binding energy and the shape of the Si_{2p} peak are the same as for C_3S hydration in distilled water.

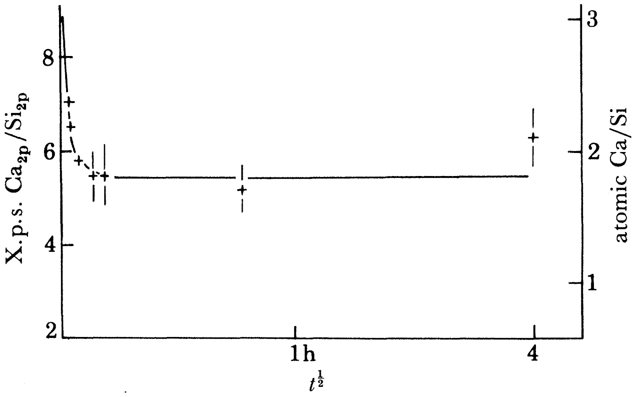

FIGURE 2. $C_3S + 1\%$ NaF: variation of characteristic X.p.s. Ca_{2p}/Si_{2p} ratio and atomic Ca/Si ratio against (time of hydration)$^{\frac{1}{2}}$ (Regourd *et al.* 1980).

The interpretation of the X.p.s. kinetic curve is not univocal. The lack of increase in the I_{Ca}/I_{Si} ratio could be related to the simultaneous formation of a hydrated layer, with Ca/Si $\ll 3$, and CaF_2 (Young *et al.* 1977), as the peak of the fluoride element is more intense than in NaF. Kinetic curves of C_3S hydrated in solutions containing amounts of NaF increasing from 0.001 % to 1 % show that the chemisorption of the Ca^{2+} ions on the surface enriched in silica is slowing down proportionally to the amount of NaF and disappears at 1 % NaF (Regourd *et al.* 1982). The dormant period is extended.

The same shape of kinetic curve as that of C_3S with NaF has been done for C_3S hydrated at 4 °C (Ménétrier *et al.* 1979). Low temperatures are well known to delay the setting of the cement pastes, but X.p.s. shows that if the first stage, the drop of Ca/Si ratio, remains unchanged, the superficial chemisorption of Ca^{2+} ions is missing, presumably in relation to the higher solubility of $Ca(OH)_2$ at 4 °C than at 20 °C.

3. STUDY OF THE DICALCIUM SILICATE HYDRATION

The same characteristic X.p.s. peaks (Regourd *et al.* 1980*c*) and the same shape of kinetic curve (Thomassin *et al.* 1980; Jawed *et al.* 1980) as those of C_3S have been obtained for C_2S (figure 3), although the changes in surface composition were less pronounced and occurred later. The variations in the binding energies and the width of Si_{2p} peak have also been measured (table 2).

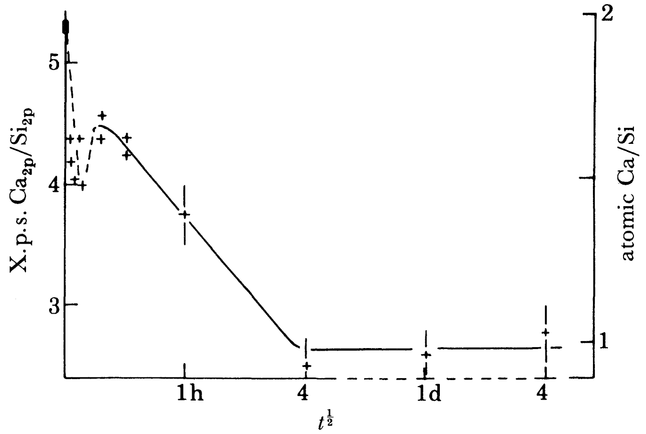

FIGURE 3. βC_2S: variation of characteristic X.p.s. Ca_{2p}/Si_{2p} ratio and atomic Ca/Si ratio against time of hydration (Thomassin *et al.* 1979).

TABLE 2. C_2S: DIFFERENCE BETWEEN BINDING ENERGIES OF Ca_{2p} AND Si_{2p} PEAKS AND WIDTH OF THE Si_{2p} PEAK (Thomassin *et al.* 1980)

time of hydration	$\delta(Ca_{2p}-Si_{2p})$/eV ($\pm$0.2 eV)	(width of Si_{2p} peak)/eV ($\pm$0.2 eV)
0	245.4	2.7
10 s, 15 s, 30 s, 5 min, 15 min	245·2	3.0
1 h	245.0	3.2
4 h, 24 h	244.6	3.4
4 d	244.9	3.4

The Ca/Si ratio at first drops by up to 1.5 at 1 min and the plateau at Ca/Si = 1 is reached at 4 h, remaining unchanged for up to 4 days in our study. Considering the same mechanism of hydration as for C_3S, i.e. a hydrated layer depleted in calcium and then a chemisorption of Ca^{2+} leading to Ca/Si = 1 during the dormant period, the calculated thickness is 0.8 nm at 5 min, 2 nm at 1 h and 6 nm at 4 h (Thomassin *et al.* 1980). Somewhat different results were obtained by Jawed *et al.* (1980) who, estimating the depth of their X.p.s. probing to be only 2 nm, used an indirect measurement of the hydrated layer by sputtering the surface of their pellets and then measuring the X.p.s. Ca/Si ratio. This evaluated depth was 5 nm after 15 s and 10 nm after 6 h.

4. Study of the early tricalcium aluminate hydration

The kinetic curve of C_3A hydration (figure 4) shows that the Ca/Al atomic ratio rises to about 2.0 at 2 sec, then decreases to about 1.7 at 1 min and stays there for up to 3 h (Jawed *et al.* 1982). The X.p.s. results do not prove the existence of an Al-rich superficial layer. The Ca/Al ratio close to 2.0 would suggest the formation of hexagonal C_4AH_x and the decrease to 1.7 would correspond to the formation of cubic C_3AH_x.

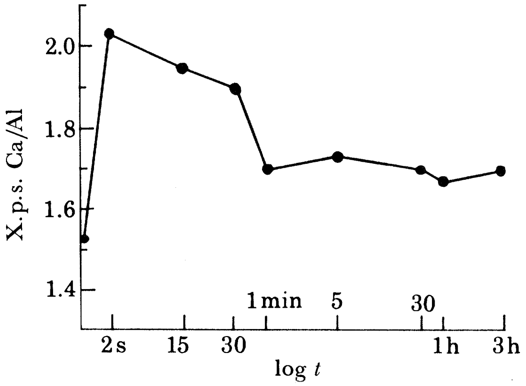

FIGURE 4. C_3A: variation of atomic Ca/Al ratio on surface as a function of hydration time (Jawed *et al.* 1982).

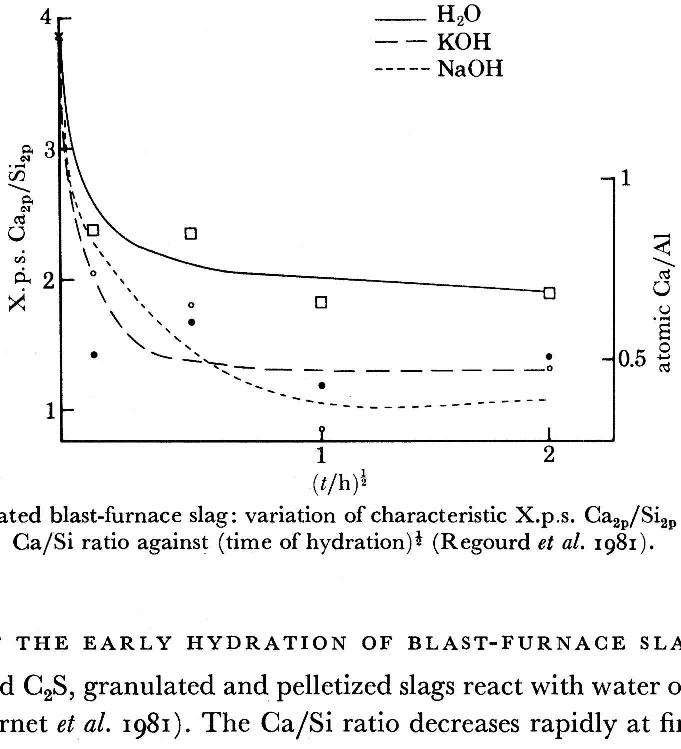

FIGURE 5. Granulated blast-furnace slag: variation of characteristic X.p.s. Ca_{2p}/Si_{2p} ratio and atomic Ca/Si ratio against (time of hydration)$^{\frac{1}{2}}$ (Regourd *et al.* 1981).

5. Study of the early hydration of blast-furnace slag by X.p.s.

Just as for C_3S and C_2S, granulated and pelletized slags react with water or alkaline solutions within minutes (Vernet *et al.* 1981). The Ca/Si ratio decreases rapidly at first, but after 1 min gradually reaches an essentially constant value (figure 5) (Regourd *et al.* 1981). After 15 min the different hydraulic slags tested, granulated or pelletized, gave the same Ca/Si ratio despite their different initial value. So, only the very first step of hydration, the incongruent dissolution (Dron *et al.* 1980), is related to the particular reactivity of the slag specimen. Sodium Na_{2s} (E_B = 64.5 eV) and potassium K_{2p} (E_B = 292 eV) are detected at the surface of slags hydrated in alkaline solutions, incorporated into the hydrated layer. The value of the Ca/Si ratio at the plateau is 0.8 in water and 0.5–0.6 in alkaline solutions. The trapping of alkalis has been confirmed later by the electron probe microanalysis. A very slight change was found to occur in the variation of Al_{2s}/Si_{2p} ratio (E_B = 120 eV for Al_{2s}) (figure 6). We could assume after the binding energies that Al and Si were still in tetrahedral coordination after having gone through the solution.

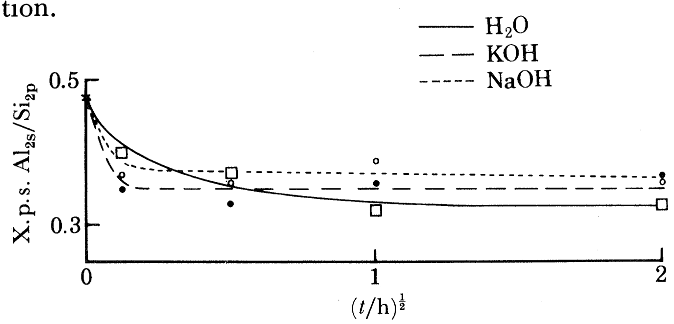

FIGURE 6. Granulated blast-furnace slag: variation of characteristic X.p.s. Al_{2s}/Si_{2p} ratio against (time of hydration)$^{\frac{1}{2}}$ (Regourd *et al.* 1981).

6. CONCLUSION

X.p.s. appears to be a very sensitive method in the study of early hydration in cement compounds. Surface transformations of C_3S, C_2S, C_3A and blast-furnace slag grains are observed from the first few seconds of their contact with water. These modifications are related to a change of the environment of Si and O atoms and a variation of the characteristic ratios, i.e. a decrease for Ca/Si and Al/Si in C_3S, C_2S and slags, an increase for Ca/Al in C_3A. So, the first drop in Ca/Si ratio in C_3S pastes does not indicate the formation of a first hydrate with Ca/Si = 3 and there is no Al-rich superficial layer in the C_3A early hydration.

The interpretation of the variation of X.p.s. characteristic ratios with time is not always easy and univocal, as the depth of investigations is of the order of only 6 nm. Results reported here have assumed a double layer model with a uniform hydrated layer on an anhydrous substratum. The computed thickness has required an average composition of the different hydrates (Ca/Si $\approx$ 1 then Ca/Si $\approx$ 2 for C_3S). More research is needed to explain the action of retarders like NaF in the early hydration of C_3S. Lastly, microanalytical X.p.s. results of surface analysis need to be compared to data from other electron optical techniques and s.t.e.m. in particular.

REFERENCES

Barret, P., Ménétrier, D. & Bertrandie, D. 1977 *Rev. Int. Hautes Temp. & Réfrac.* **14**, 127.
Dent-Glasser, L. S., Lachowski, E. E., Mohan, K. & Taylor, H. F. W. 1978 *Cem. Concr. Res.* **8**, 733.
Dron, R. & Brivot, F. 1980 *7th Int. Congress on the chemistry of Cements, Paris*, vol. II, III – 134.
Fuji, K. & Kondo, W. 1975 *J. Ceram. Ass. Japan* **83**, 214.
Jawed, I., Ménétrier, D. & Skalny, J. 1980 *7th Int. Congress on the chemistry of Cements, Paris*, vol. II, III – 182.
Jawed, I. & Skalny, J. 1982 *Int. Sem. on Calcium Aluminates, Torino*, vol. II, 3.
Ménétrier, D., Jawed, I., Sun, T. S. & Skalny, J. 1979 *Cem. Concr. Res.* **9**, 473.
Regourd, M., Thomassin, J. H., Baillif, P. & Touray, J. C. 1980*a* *Cem. Concr. Res.* **10**, 223.
Regourd, M., Thomassin, J. H., Baillif, P. & Touray, J. C. 1980*b* In *7th Int. Congress on the chemistry of Cements, Paris*, vol. II, II – 123.
Regourd, M., Thomassin, J. H., Baillif, P. & Touray, J. C. 1980*c* In *9th Int. Symp. on the Reactivity of Solids, Cracow, Poland*, VI – 39, 769.

Regourd, M., Thomassin, J. H., Baillif, P. & Touray, J. C. 1981 83rd Am. Ceram. Soc. meeting, Washington. To be published.

Regourd, M., Thomassin, J. H., Baillif, P. & Touray, J. C. 1982 84th Am. Ceram. Soc. meeting, Cincinnati. *Cem. Concr. Res.* **13**, 549, 1983.

Skalny, J. & Young, F. Y. 1980 In *7th Int. Congress on the chemistry of Cements, Paris*, vol. I, II – 1/3. Paris: Éditions Septima.

Stein, H. N. 1977 *Ind. Cemento*, **74**, 3.

Tadros, M., Skalny, J. & Kalyoncu, R. 1976 *J. Am. ceram. Soc.* **59**, 344.

Tamàs, F. D., Sarkar, A. K. & Roy, D. M. 1976 In *Hydraulic cement pastes: their structure and their properties*, p. 55. Slough: Cement and Concrete Research Association.

Thomassin, J. H., Regourd, M., Baillif, P. & Touray, J. C. 1979 *C. r. hebd. Séanc. Acad. Sci., Paris*, C **288**, 93.

Thomassin, J. H., Regourd, M., Baillif, P. & Touray, J. C. 1980 *C. r. hebd. Séanc. Acad. Sci., Paris*, C **290**, 1.

Vernet, C., Demoulirn, E., Gourdin, P. & Hawthorn, F. 1980 In *7th Int. Congress on the chemistry of Cements, Paris*. vol. II, III – 128. Paris: Éditions Septima.

Young, J. F., Tong, H. & Berger, R. L. 1977 *J. Am. ceram. Soc.* **60**, 193.

Discussion

C. Defossé (*Dowell-Schlumberger Research and Development, Z.I. Molina La Chazotte BP* 90, *F.* 42003 *Saint-Etienne, Cedex*). Concerning drying treatment, can Dr Regourd exclude any possibility of having species in solution precipitating on the surface of the grain at the very moment of the quenching? For instance, fluoride ions or CaF_2 in suspension could precipitate on the surface and account for the F_{1s} peak observed.

M. Regourd. We cannot exclude any possibility of CaF_2 precipitating from the solution on the C_3S surface. We only observed that the intensity of the F_{1s} peak was higher in $C_3S + 1\,\%$ NaF than in NaF, after several minutes of hydration.

S. A. Jefferis (*Civil Engineering Department, King's College London, Strand, London, WC2R* 2*LS, U.K.*). I was interested to see Dr Regourd's data on the changes in surface chemistry that occur during the first seconds and minutes after cement components are wetted and to hear that she feels that this could affect mix rheology.

Such rapid reactions could explain a phenomenon that I have observed when ordinary Portland cement is mixed with water containing a chloride based accelerator. The rheology and subsequent setting times of the particular mixes appeared to depend very much on the level of shear during the first seconds of mixing and to be largely independent of any subsequent shearing. Low shear mixing may not disperse any clusters of anhydrous grains present in the dry cement. If such clusters are very rapidly tied together by surface reactions, subsequent high shear may not be able to disperse them. Whereas cements initially subjected to high shear may be more fully dispersed and thus present more active surface area with its consequent effects on rheology and setting time.

Does Dr Regourd have any data or hypotheses on how surface reactions affect rheology?

M. Regourd. Surface reactions affecting rheology have been shown through Zeta potential measurements. The early hydration reactions leading to the dissolution of ionic species modify the superficial electrical charge on cement grains then disperse the flocculi by mutual repulsion.

Calcium chloride is an accelerator for C_3S, it forms chloro-aluminates with C_3A and leads to a more dispersed calcium hydroxide crystallization. So its action may be effective in the early hydration, i.e. it may play a role in the precipitation of hydrates and the modification of the double electrical layer.

J. Bensted (*Blue Circle Technical Research Division, Greenhithe, U.K.*). Has Dr Regourd looked at the different types of C_3S polymorphs by X.p.s. or e.s.c.a to see whether there are differences in the early reactivity.

M. Regourd. Pure triclinic C_3S was used in this study. We have not yet studied C_3S solid solutions.