

## Fly Ash and Silica Fume Chemistry and Hydration

by D.M. Roy

Synopsis: The hydration of cements containing the supplementary cementing materials fly ash (FA) and silica fume (SF) is discussed and compared with the hydration of ordinary portland cement (OPC). Early stage heats of hydration, changes in the chemistry of the solution (both at early stages, and later pore solution compositions), microstructural development, and pore structure are compared. The hydration rates normally follow the order: SF>OPC>FA. The complex hydration processes may be controlled so that the use of these cements enables development of materials having superior strength and durability.

Keywords: chemical analysis; conductivity; diffusion; electrical properties; fly ash; heat of hydration; hydration; microstructure; porosity; portland cements; silica fume

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## INTRODUCTION

This paper discusses the chemistry and hydration reactions of SF and FA blends in a general sense not specifically making a distinction between whether the materials are blended with Portland cement at the time of the manufacture of the cement, as is done for example with ASTM Type IP cements, or whether they are added during concrete manufacture.

The hydration of cement is relatively complex and becomes additionally so when supplementary cementing materials are added. It is useful, however, to start with the hydration of normal hydraulic (or portland) cement powder, consisting of the four major components: tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ , alite), dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ , belite), tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ), and calcium aluminoferrite solid solution ( $\text{Ca}_2\text{Fe}_x\text{Al}_{2-x}\text{O}_5$ ) [the latter two also called interstitial phase]. Small amounts of sulfates, especially gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and other minor components, such as alkali sulfates, are also present. When mixed with water, cement undergoes an exothermic hydration-hydrolysis reaction. Immediately after the paste is formed, there is a period of time--up to several hours, depending on composition and temperature--before setting.

The reaction rate and consequent rate of heat evolution are a function of the total chemical and mineral composition, the fineness of the powder (1), and the temperature of setting. Setting and hardening are the result of a complex sequence of processes illustrated schematically in Fig. 1 (Roy, 1987) (37a). Hardened cement paste has a finely intergrown microstructure dominated by the major binding component, the very fine high surface area intergrowth of calcium silicate hydrate (C-S-H). These particles grow between and link together larger crystallites and residual anhydrous cement grain cores and their perimeters, leaving a microporous material which, under favorable conditions, has minimal interconnected capillaries.

When fly ash or silica fume are added, the hydration process is affected substantially, reflecting the modified chemical composition, reactivity of the components, their particle size, size distribution, shape, and other factors which affect the final paste structure and its performance as the matrix of concrete. The utilization of fly ash (FA) and silica fume (SF) therefore presents challenges and opportunities; their addition to the concrete mixture affects both the hydration process and the characteristics of the hardened concrete.

### Characteristics of Materials

Figure 2 shows typical compositional ranges of fly ash and silica fume, along with portland and high-alumina cements, projected on a  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  ternary composition diagram (Glasser et al., 1987) (11). The compositions are averages, and fly ash particles also exist as a range of compositions within a single ash sample. Nevertheless, the figure is useful in illustrating the variation in bulk FA compositions and the potential changes in cement system chemistry which may arise as a consequence of adding ash or silica fume.

Fly ash compositions and characteristics depend on combustion conditions, ash collection procedures, and coal source (Gumtz et al., 1986) (16). However, even within one plant, much interparticle variability occurs. The major component is a glassy phase, which differs in amount and type depending on the coal source and burning conditions. Many ashes are dominantly aluminosilicates (in ASTM Class F ashes) while others may contain much calcium (ASTM Class C). The Class F fly ashes are characterized by their relatively high glass content, which also contributes to their reactivity with alkali and calcium hydroxides. Additional crystalline minerals are present, e.g., quartz, mullite, hematite, and Fe-rich spinels or magnetite. These crystalline mineral phases, as well as unburned carbon, are relatively unreactive. The more Ca-rich Class C ashes often contain substantially less glass, of a higher Ca content, and a different suite of minerals, some of which are reactive, such as  $\text{C}_3\text{A}$ ,  $\text{C}_2\text{S}$ ,  $\text{CaO}$ ,  $\text{C}_4\text{AF}$ ,  $\text{C}_4\text{A}_3\text{S}$ , and other sulfates.\*

Fly ash particles occur in a variety of shapes and surface characteristics. Most are solid spheres, but often irregular residual coal fragments (carbon) are present, imperfectly rounded ellipsoids, vesicular solids of irregular shape, and various hollow or partly hollow spheres. The content of 'cenospheres'--thin walled hollow particles without smaller interior particles--tends to be quite small in most fly ashes, but there may be a more appreciable content of 'plerospheres'--hollow spheres with smaller spheres enclosed (McCarthy et al., 1987) (29).

Silica fume of the type used with cement has a relatively high  $\text{SiO}_2$  content, often containing <5% total  $\text{SiO}_2$  material aside from adsorbed volatiles. Silica fume is typically composed of extremely fine spheres, with a mean size of the order of 0.1 to 0.2  $\mu\text{m}$  and BET surface area of about  $20 \text{ m}^2\text{g}^{-1}$  (Aitcin et al., 1984). Some silica fume contains particle clusters which may be difficult or impossible to disperse chemically.

A summary of the characteristics of these materials is given in Table I.

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\*Cement abbreviations used are C =  $\text{CaO}$ , A =  $\text{Al}_2\text{O}_3$ , F =  $\text{Fe}_2\text{O}_3$ , S =  $\text{SiO}_2$ , S =  $\text{SO}_3$ .

### Cement Hydration

As indicated, cement hydration is an exothermic process; hydration reactions begin immediately upon mixing with water. Normally gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , (or some other suitable source of calcium sulphate) is incorporated as a set regulator which is added to the clinker during grinding.

The main effects occur in three stages, as shown in the hydration calorimetric curves of Fig. 3. Stage I includes a very early heat liberation peak due primarily to  $\text{C}_3\text{A}$  hydration. The size is decreased due to reaction with calcium sulfate to form the calcium sulfoaluminate hydrate, ettringite, which forms a partly protective coating, retarding the  $\text{C}_3\text{A}$  hydration. Stage I for  $\text{C}_3\text{S}$  is characterized by a slow heat evolution period immediately after mixing with water, corresponding to the so-called pre-induction and induction periods. The hydrate produced is composed mostly of C-S-H.

Stage II is characterized by rapid heat evolution, developing the second, major peak in the heat evolution curve, corresponding to the acceleration and deceleration periods. The hydrates produced are mainly type I (fibrous) and II (reticulate) varieties of C-S-H, and platy  $\text{Ca}(\text{OH})_2$ . Setting occurs near the inflection point preceding the second peak, reflecting the formation of sufficient C-S-H to develop a network structure with some rapidity. In addition, a third exothermic peak or shoulder is often distinguished due primarily to the conversion of ettringite (tetracalcium-aluminate trisulfate-32 hydrate) to the monosulfate hydrate form. Belite and the ferrite phase also contribute to the formation of C-S-H, and ettringite/monosulfate, respectively, in the Stage I and II reactions. All the principal phases dissolve incongruently, liberating  $\text{Ca}^{2+}$  ions to the solution and leaving an insoluble solid residue enriched in the less-soluble constituents, although in cements the incongruent dissolution is somewhat suppressed. Nevertheless, the initial hydration usually occurs within minutes of mixing, and is characterized by supersaturation with respect to  $\text{Ca}(\text{OH})_2$ ; this supersaturation is eventually relieved by precipitation. Again, in real cement systems the solubility of Ca is depressed by the presence of alkali ( $\text{Na}^+$ ,  $\text{K}^+$ ), which effectively increases the concentration of hydroxyl and the pH. The compositions of the fluids in contact with the early hydrating cement paste system, as well as from pore fluids obtained from cement pastes at advanced stages of hydration, have been monitored in a number of investigations. An important feature is the high pH (commonly above 13) which is an important factor in activating the hydration of silica fume and siliceous fly ash.

Additional insight into the hydration recently has been gained by using AC electrical conductivity and dielectric permittivity measurements such as shown in Fig. 4. Perez-Pena (1986) (31), Tamas et al. (1984) (40), Perez-Pena et al. (1986,1988) (32,33), and McCarter and Curran (1985) (30), have also investigated resistivity and permittivity. As seen in Fig. 4(a) the conductivity decreases as the heat evolution increases. Additions which accelerate the reaction enhance the conductivity also. Chemical reactions which take place in fly ash cement systems in both early and later stages strongly influence the final properties of the

and markedly increase the early dielectric permittivity [Fig 4(b)]. The electrical conductivity of cement pastes increases shortly after mixing,

followed by a later decrease. In some cements a second, sharp transient conductivity increase occurs; the time to this second peak is influenced by the presence of admixtures, temperature, w/c ratio and by grinding fineness to a lesser extent. This second peak has been observed only in cements having a critical gypsum content. (Tamas et. al., 1984, 1987) (40,41).

The earliest hydration results in formation of filmy deposits on some of the surfaces of individual cement grains, which appear to be variable from cement to cement and even from grain to grain, perhaps a consequence of smearing of interground gypsum on some surfaces. The occurrence of amorphous films of calcium aluminate sulfate hydrate compositions resembling that of ettringite have been reported by numerous authors. Gel-like material and the presence of hollow sacs have been observed by Barnes et al. (1980) (2), and by Pratt and Jennings (1985) (34). Deposits of very small crystals of calcium hydroxide, ettringite, and fibrous C-S-H on cement grain surfaces are reported to arise from the initial filmy deposit by Dalgleish et al. (1982) (5).

Subsequently calcium hydroxide continues to deposit, as does C-S-H gel, the latter primarily of the Type III variety. The earlier skeletal deposits and the hydration shells tend to be covered up and, depending on the original water:cement ratio, the original space between grains may be entirely filled. Mature fracture surfaces of hardened pastes tend to show primarily these later stage deposits, although in local areas of higher original water content, the early morphology can still be recognized.

The amount of calcium hydroxide deposition may not be quite proportional to the extent of hydration expected from stoichiometric equations. Late deposition and perhaps a process of redissolution and precipitation in different areas may occur, and sometimes massive  $\text{Ca(OH)}_2$  crystals develop in formerly empty space. Ettringite also tends to deposit as a secondary process in such spaces (Roy, 1987a) (37).

Once initial set is achieved cement hydration processes continue over a period of months or even years.

### FLY ASH REACTIONS

The effects of fly ash on the hydration of cement pastes and concretes are still being explored, and no fully definitive summary can yet be made. It is difficult to generalize about reactions in fly ash bearing systems because of the variations between different fly ashes and between different particles within a fly ash [Roy et al., 1985 (38); Glasser et al., 1987 (11); Roy, 1987b (37b)]. Fly ashes are assemblages of particles of individually varied compositions and crystalline contents, some of which are reactive, others not.

and a uniform duplex coating has been observed on the surface of the fly ash (Diamond et al., 1980) (8). Rod-like ettringite crystals have been reported to grow on the surface of fly ash at the age of one day (Ghose and Pratt, 1981) (9). At three days age, the fly ash surface is thickly coated with the hydrate, some of which breaks off from the fly ash particles; while the structure of hardened paste becomes dense after 14 days.

In the case of high calcium fly ash, the hydration mechanism is generally similar to that of low-calcium ash, and C-S-H grows toward the outside of the glass phase, as explained in more detail by Grutzeck et al. (1982a) (12). Numerous others have confirmed these general hydration trends, as reported in McCarthy et al. [1986 (28), 1987 (29)] and Malhotra (1986) (25).

### SILICA FUME HYDRATION REACTIONS

The ultra-fine particle size of silica fume brings the potential of being much more reactive than other supplementary cementing materials. Silica fume particles when properly dispersed fill the interstices of the fresh cement paste structure, where they are available to react with the alkali hydroxide and  $\text{Ca(OH)}_2$  liberated by the hydrating portland cement, forming insoluble C-S-H. When used in proportions to replace up to 10% of cement, it significantly reduces bleeding and segregation of the mixtures, and may be used in higher proportions. Aqueous slurries of silica fume may be prepared without superplasticizing admixtures, but the resulting cementitious mixtures usually require higher w/c ratios. Because of their very high surface area, early reaction of the fume takes place with the alkaline cement pore solution.

Since silica fume contains particles as fine as  $0.1 \mu\text{m}$  or less and has high surface energy, it partially dissolves in saturated  $\text{Ca(OH)}_2$  solution in a time as early as 5 to 15 minutes, and a  $\text{SiO}_2$ -rich hydrate is deposited in layers or films on the silica fume particles. C-S-H having a C/S ratio of about 1 has been reported to form at  $20^\circ\text{C}$  in 24 hours after mixing with water and at  $38^\circ\text{C}$  in only 6 hours (Grutzeck et al., 1982b). The reaction of silica fume with  $\text{Ca(OH)}_2$  is affected by the specific surface area, and the surface energy. Typically the C-S-H produced has a lower C/S ratio than that of fly ash. Since C-S-H with a C/S ratio of less than 0.8 is considered to be thermodynamically unstable, calcium silicate hydrate once produced is converted to a C-S-H variety having the lower limit of C/S, which coexists with excess silica containing very little calcium. This lower C/S ratio tends to be confirmed in recent reports of Taylor (1986) (42a), Diamond (1983) (6), Glasser (1987) (11), and Roy (1986) (36) have described the changing composition of pore solutions with longer time periods, which reflect the hydration processes occurring beyond the early ages.

Despite the early rapid reaction, much silica fume remains for later slow reaction. For example, Li et al. (1985) (23) showed from selective dissolution experiments that, while much SF is reacted in a SF-OPC mixture at 7 days, considerable unreacted SF remains. The early heat of hydration of silica fume-containing mixtures is frequently equivalent to that of high-early-strength cement, although the rate at which heat is liberated depends upon the proportions, and the w/c ratio. The fume

particles surround each cement grain, densifying the matrix, filling the voids with strong hydration products, and improve the bonding with aggregates and reinforcing material such as glass fiber. Silica fume by reacting with alkali also affords protection against the alkali-aggregate type reaction occurring between a cement pore solution and glass fiber [Kumar and Roy, 1986 (20); Diamond, 1986 (7)].

The heat evolution calorimeter curves of cement with different proportions of silica fume (with  $\text{SiO}_2 = 94.5\%$ ,  $\text{Fe}_2\text{O}_3 = 0.25\%$ ,  $\text{Al}_2\text{O}_3 = 3.40\%$ , and BET specific surface area =  $17 \text{ m}^2/\text{g}$ ) are shown in Fig. 7, expressed per gram of cement. The early hydration of alite in Stages I, II, and III is accelerated by the addition of silica fume. The hydration of the interstitial phase is also accelerated. Silica fume depressed the  $\text{Ca}(\text{OH})_2$  content of the liquid phase of paste immediately after mixing with water, but the concentration is sharply raised to the maximum earlier than in cement paste without silica fume, as shown in Fig. 8. There is also a pronounced decrease in the  $\text{CaSO}_4$  content with time.

Soon after mixing with water the  $\text{Ca}^{2+}$  ions from the liquid phase of fresh paste are adsorbed on silica fume and tend to initiate nucleation of C-S-H on the surface (Grutzeck et al., 1983) (14). The Ca ion is actively dissolved from alite, its adsorption on the silica surface lowers the Ca ion concentration in the liquid phase, and the hydration of alite in the early stage is accelerated. At the same time, the  $\text{CaSO}_4$  content is also lowered and the hydration of the interstitial phases  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  is therefore accelerated. C-S-H formation by pozzolanic reaction is initiated at around ten hours and it progresses in the period from 1 to 7 days. C-S-H with a low C/S ratio is produced, and the amount of  $\text{Ca}(\text{OH})_2$  remaining in the hardened paste is decreased.

#### COMPARISONS IN REACTIVITY OF FLY ASH AND SILICA

Based on determination of  $\text{Ca}(\text{OH})_2$  content of the products, the reaction rates of silica fume added to  $\text{C}_3\text{S}$  and cement appear to be lower, in some cases, than when added to  $\text{Ca}(\text{OH})_2$ , similar to the observed behavior in the case of slag and fly ash. The amount of  $\text{Ca}(\text{OH})_2$  combined in the reaction products of cement mixed with 30% silica fume was found to be 3g/100g of silica fume in 10 hours, and 13g in 3 days (Cheng-Yi and Feldman, 1985) (4). The degrees of reaction of silica fume were reported to vary (Uchikawa, 1986) (42b), though few accurate measurements have been found in the literature. Li and Roy (1988) (24) have found in  $\text{C}_3\text{S}$ -SF mixtures that approximately equal total reaction (of  $\text{C}_3\text{S} + \text{SF}$ ) occurs with C/S ratios of 1.5 to 0.83.

The degree of reaction of low-calcium fly ash (51%  $\text{SiO}_2$ , 27%  $\text{Al}_2\text{O}_3$ , 2%  $\text{CaO}$ ), and silica fume (95%  $\text{SiO}_2$ ) with  $\text{Ca}(\text{OH})_2$  and with Type I cement were determined by selective dissolution methods (Li et al., 1985) (23), and compared. It was found (Table II), not surprisingly, that the degree of reaction of silica fume is much greater than the low-calcium fly ash, even at 90 days, primarily due to the very high specific surface area of the silica fume. Half of the silica fume (with 10% SF - 90% cement) was hydrated in one day, and two-thirds during the first three days, although thereafter the hydration proceeded slowly. Between 28 and 90 days, additional hydration took place, although the fume was still

only 75% hydrated at 90 days. In the latter study the early SF reaction (1-3 days) was more rapid with the cement than with  $\text{Ca(OH)}_2$ . Reaction of very low w/c mixtures of  $\text{C}_3\text{S-SF}$ , having C/S ratios of 1.5-0.83, showed only about 55% reaction of the total system after 28 days (Li and Roy, 1988) (24), as shown in Fig. 6.

### HYDRATION PRODUCTS

Blending material additions may significantly affect the size, distribution, and structure of the individual flocs comprising fresh cement paste. Observed decreases in water demand most likely result from the modifications, particularly when superplasticizers are used. We expect that future studies will more specifically address the nature of the change in floc structure, and its relation to the dispersion efficiency and consequent homogeneity of hardened cements pastes and concrete.

The changed floc structure is reflected in changes in structure of the hardened paste, including its pore size distribution and resultant permeability. Kumar and Roy (1986b) (21), and Kumar et al. (1987) (22) have determined cumulative pore size distributions in pastes containing blends of cement made with increasing content of FA and silica fume. The total porosity is controlled by the w/s volume ratio, but the pore size distribution varies with the material and stage of reaction. The median pore size generally is much diminished in mature blended materials compared with OPC paste. As shown in Table III, which gives typical values obtained with FA, SF, and BFS, the reduced value of the mean pore size also results in lower ionic diffusion rates (Kumar and Roy, 1986 (21); Kumar et al., 1987) (22); it also produces lower water permeabilities (Hooton, 1986 (19); Li et al., 1985 (23); Roy, 1986) (36).

As indicated previously, the chemical composition of the C-S-H formed in blended hardened cement pastes differs from that of OPC hydration products. During early hydration there appears to be an almost epitaxial effect of the silica rich "substrates" on which cement hydration products are precipitated. The EMPA analyses given in Table IV illustrate the compositional differences found in four-year-old pastes (Uchikawa, 1986) (42b), showing that not only is the lower C/S ratios of the blended material maintained at longer times, but also higher amounts of alkalis are retained. The C/S ratio of the C-S-H in cement pastes with silica fume is clearly lower in proportion to the amount of silica added, and the paste is poor in Al bearing hydrates (Uchikawa, 1986) (42b).

The differences in the microstructural characteristics of the hydration products from cement-fly ash and cement-silica fume are apparent in the scanning electron microscopy images of Figs. 9 and 10. (23). A fracture surface of a cement-fly ash paste (Table II) cured for 90 days is shown in Fig. 9(a), showing a dense well-developed microstructure. However, Fig. 9(b) shows the residue after selective dissolution of the cementitious hydrate (C-S-H), revealing that there is much unreacted residual fly ash remaining as apparent both from rounded and irregular shapes. Fig. 10(a) shows a similar fracture surface for a cement-silica fume paste (Table II) cured for 28 days, while Fig. 10(b) is a similar sample after selective dissolution. The residue shown is consistent with the findings indicated in Table II; only 65% of



the silica fume is reacted after 28 days. Very fine, regular particles and elongated fine siliceous agglomerates are apparent in the largely unreacted residue.

### SUMMARY

The hydration reactions in cement pastes incorporating fly ash and silica fume are responsible for the microstructural development. These complex reactions involve phase solubility, accelerating and retarding effects of a multiphase, multi-particle material, and surface effects at the solid-liquid interface. The initial degree of dispersion of cement and blending agents in the paste strongly influences the development of final hardened paste microstructure. Surface charge, as measured by the zeta-potential at the solid-liquid interface (Roy, 1986) (36) reflects the dispersion of the system. The floc structure of fresh cement paste affects its workability, and the incorporation of ash affects the floc structure, generally interrupting the structure, creating smaller units, thereby imparting greater fluidity. Adequately dispersed silica fume can provide a similar effect and also, due to its ultra-fine particle size, fill the intergranular interstices and produce a denser paste structure, reflected in very high strength.

Both physical and chemical characteristics influence the hydration kinetics of each of the blended cement materials in a specific manner. Silica fume ordinarily accelerates the early portland cement hydration, largely because of its very high surface area, accelerating and increasing the heat development resembling a high early strength cement. Fume also disperses the hydration product, provides for deposition of C-S-H, and thereby fills the pore interstices with fine hydration products. Its optimal use is with superplasticizers to minimize the water demand and adequately disperse the fine particles. Dense products with fine pore size, very low permeability, and low ionic diffusivity commonly are the result. Despite the rapid early hydration, much silica fume remains unreacted until a later stage.

While cement setting is commonly retarded by fly ash, Class C fly ash usually causes greater retardation than Class F. The overall reaction after a few days, however, is greater with Class C fly ash than Class F fly ash. Much residual unreacted unhydrated Class F fly ash and even Class C fly ash will remain even at later ages in the hydration products.

In sum, the hydration (rates and mechanisms, and microstructural development of blended cement pastes) is a complex process. Recent research has contributed much understanding to the hydration behavior of these materials, which is useful in providing additional guidelines for their proper selection and use of each material. When adequately characterized materials are used within the appropriate guidelines, the resulting blended cement pastes will frequently impart superior properties to the matrices of the concretes which they form.

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## REFERENCES

1. Aitcin, P.-C., Pinsonneault, P., and Roy, Della M. "Physical and Chemical Characterization of Various Condensed Silica Fumes," Bull. Am. Cer. Soc. 63, 1487-1491, 1984).
2. Barnes, P., Ghosh, A., and Mackay, A.L. Cem. Concr. Res. Vol. 10, 639-646. 1980.
3. Byfors, K., Hansson, C.M, and Trihart, J. Cem. Concr. Res. Vol. 16, 760, 1986.
4. Cheng-Yi, H., and Feldman, R.F. "Hydration reaction in portland cement-silica fume blends," Cem. Conc. Res. Vol. 15 (4) 585-592 , 1985.
5. Dalgleish, B.J., Ghosh, A., Jennings, H.M., and Pratt, P.L. Proc. RILEM Conf. Concr. at Early Ages, Paris, vol. 1, pp. 137-143, 1982.
6. Diamond, S. "Effects of Microsilica (Silica Fume) on the Pore Solution Chemistry of Cement Pastes," J. Am. Ceram. Soc. Vol. 66, C82-C84, 1982.
7. Diamond, S., ed. Proc. Durability of Glass Fiber Reinforced Concrete Symposium, Prestressed Concr. Inst., Chicago, IL, 1986.
8. Diamond, S., Ravina, D., and Lovell, J. "The occurrence of duplex film on fly ash surface," Cem. Conc. Res. Vol. 10 (2) 297-300, 1980.
9. Ghosh, A., and Pratt, P.L. "Studies of the hydration reaction and microstructure of cement-fly ash paste," Proc. Ann. Mtg. of Materials Research Society, Boston, Effect of Fly Ash Incorporation in Cement and Concrete, 82-91, 1981.
10. Glasser, F.P., and Marr, J. "Effect of Mineral Additions on the Composition of Cement Pore Fluids," 419-430 in The Chemistry and Chemically Related Properties of Cement, Brit. Cer. Proc. #35, Sept. 1984.
11. Glasser, F.P., Diamond, S., and Roy, D.M. "Hydration Reactions in Cement Pastes Incorporating Fly Ash and other Pozzolanic Materials," Mat. Res. Soc. Proc. Vol. 86, 139-158, 1987.
12. Grutzeck, M.W., Roy, D.M., and Scheetz, B.E. "Hydration Mechanisms of High-Lime Fly Ash in Portland Cement Composites," Proc., Symposium N, Effects of Fly Ash Incorporation in Cement and Concrete, Ed. S. Diamond, pp. 92-101, Materials Research Society, Secretariat, 110C Materials Research Laboratory, University Park, PA 16802 , 1982a.

13. Grutzeck, M.W., Roy, D.M., and Wolfe-Confer, D. "Mechanism of Hydration of Portland Cement Composites Containing Ferrosilicon Dust," A3-202, Proc., 4th Intl. Cement Microscopy Assn. Mtg., Las Vegas; Intl. Cem. Micr. Assn., Duncanville, TX, 1982b.
14. Grutzeck, M.W., Atkinson, S.D., and Roy, D.M. "Mechanism of Hydration of Condensed Silica Fume in Calcium Hydroxide Solutions," Proc. CANMET/ACI First Intl. Conf. on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-products in Concrete, Vol. II, Ed. V.M. Malhotra, pp. 643-664; ACISP-79, ACI, Detroit, 1983.
15. Grutzeck, M.W., Fajun, Wei, and Roy, D.M. "Retardation Effects in the Hydration of Cement-Fly Ash Pastes," Fly Ash and Coal Conversion By-Products: Characterization, Utilization, and Disposal I, Mat. Res. Soc., Proc. Symp., Vol. 43, Eds. G.J. McCarthy and R.J. Lauf, 65-72, Boston, 1985.
16. Gumtz, G., Perri, J.S., Roy, D.M., White, E.L., and Dunstan, E. "Fly Ash Classification and Model Development Study," EPRI Proj. Rept. RP 2422-10, June, 1986.
17. Harrison, A.M., Winter, N.B., and Taylor, H.F.W. 8th Int. Congr. Chem. Cem., V. IV 176-182, 1986.
18. He, Jun-Yuan, Scheetz, B.E., and Roy, D.M. "Hydration of Fly Ash Cements," Cem. Concr. Res. Vol. 14(4), 505-512, 1984.
19. Hooton, R.D. "Permeability and Pore Structure of Cement Pastes Containing Fly Ash, Slag and Silica Fume," pp. 128-143 in Blended Cements, ASTM STP 897, Ed. G. Frohnsdorf, ASTM, Philadelphia, PA, 1986.
20. Kumar, A., and Roy, D.M. "Microstructure of Glass Fiber/Cement Paste Interface in Admixture Blended Portland Cement Pastes," Proceedings. Durability of Glass Fiber Reinforced Concrete Symposium, Ed., S. Diamond, 147-156, Prestressed Concrete Institute, Chicago, IL, 1986a.
21. Kumar, A., and Roy, D.M. "Pore Structure and Ionic Diffusion in Admixture Blended Portland Cement Systems," Proc. 8th Intl. Congr. Chem. Cement, Brazil, V. V, 73-79, 1986b.
22. Kumar, A., Komarneni, S., and Roy, D.M. "Diffusion of Cs<sup>+</sup> and Cl<sup>-</sup> Through Sealing Materials," Cem. Concr. Res. Vol. 17, 1, 153-160, 1987.
23. Li, S., Roy, D.M., and Kumar, A. "Quantitative Determination of Pozzolanas in Hydrated Systems of Cement or Ca(OH)<sub>2</sub> with Fly Ash or Silica Fume," Cem. Concr. Res. Vol. 15, 1079-1086, 1985.
24. Li, S., and Roy, D.M. "Preparation and Characterization of High and Low CaO/SiO<sub>2</sub> Ratio "Pure" C-S-H for Chemically Bonded Ceramics," J. Mat. Res. Vol. 3 (2), 380-386, 1988.

25. Malhotra, V.M., ed. Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, ACI SP-91, American Concrete Inst., Detroit, MI, 1986.
26. Meland, I. "Influence of condensed silica fume and fly ash on the heat evolution in concrete," 1st Int. Conf. The use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete, Montebello, IL, 665-676, 1983.
- 27a. Malek, R.I.A., and Roy, D.M. "Electrokinetic Phenomena and Surface Characteristics of Fly Ash Particles," Fly Ash and Coal Conversion By-Products: Characterization, Utilization, and Disposal I, Mat. Res. Soc. Symp. Proc., Vol. 43, Eds. G.J. McCarthy and R.J. Lauf, 41-50, 1985.
- 27b. Malek, R.I.A., and Roy, D.M. "Self-Cementing Characteristics of Cement Pastes," MRS Symp. Proc., Vol. 113, Ed. G.J. McCarthy, D.M. Roy, F.P. Glasser, and R.T. Hemmings (1988).
28. McCarthy, G.J., Glasser, F.P., and Roy, D.M., eds. Fly Ash and Coal Conversion By-Products: Characterization, Utilization, and Disposal I, Mat. Res. Soc. Proc. V. 65, Mat. Res. Soc., Pittsburgh, PA, 1986.
29. McCarthy, G.J., Glasser, F.P., Roy, D.M. and Diamond, S. eds. Fly Ash and Coal Conversion Byproducts: Characterization, Utilization and Disposal III, Mat. Res. Soc. Symp. Proc. Vol. 86, 25-264, 1987.
30. McCarter, W.J., and Curran, P.N. "Electrical Response Characteristics of Setting Cement Paste," Mag. Concr. Res. Vol. 36 42-49, 1985.
31. Perez-Pena, M. Electrical Conductivity and Dielectric Studies of Hydraulic Cements, Ph.D. Thesis, The Pennsylvania State University, 1986.
32. Perez-Pena, M., Roy, D.M., Bhalla, A.S., and Cross, L.E. "Dielectric Properties of Densified Hardened Cementitious Materials," Cem. Concr. Res. Vol. 16, 951-966, 1986.
33. Perez-Pena, M., Roy, D.M., and Tamas, F.D. "Influence of Chemical Composition and Inorganic Additives on the Electrical Conductivity of Hydrating Cement Pastes" (in press), 1988.
34. Pratt, P.L., and Jennings, H.M. Ann. Rev. Mater. Sci. Vol. 11, 123-149, 1985.
35. Roy, D.M. "Properties of Blast-Furnace Slag Cements," York Workshop, Oct. 1985.
36. Roy, D.M. "Mechanisms of Cement Paste Degradation Due to Chemical and Physical Factors," Proc. 8th Intl. Congr. Chem. Cement, Brazil, V. I, 362-380, 1986.

- 37a. Roy, D.M. "New Strong Cement Materials: Chemically Bonded Ceramics," Science, 651-658, Feb. 6, 1987a.
- 37b. Roy, D.M. "Hydration of Blended Cements Containing Slag, Fly Ash, or Silica Fume," Institute of Concrete Technology, Coventry, U.K., 1987.
- 38. Roy, D.M., Luke, K., and Diamond, S. "Characterization of Fly Ash and its Reactions in Concrete," Fly Ash and Coal Conversion By-Products: Characterization, Utilization, and Disposal, Mat. Res. Soc. Symp. Proc. Vol. 43, Eds., G.J. McCarthy and R.J. Lauf, 3-20, 1985a.
- 39. Takemoto, K., and Uchikawa, H. "Hydration of Pozzolan Cement," 7th Int. Cong. Chem. Cem., Paris, Vol. I, IV-2/1-2/29, 1980.
- 40. Tamas, F., Farkas, E., and Roy, D.M. "Electrical Conductivity of Pastes Made with Clinker and Gypsum", in The Chemistry and Chemically Related Properties of Cement, F.P. Glasser, Ed., British Ceramic Proc. #35, Sept. 1984.
- 41. Tamas, F.D., Farkas, E., Voros, M., and Roy, D.M. "Low Frequency Electrical Conductivity of Cement, Clinker and Clinker Mineral Phases," Cem. Concr. Res. Vol. 17, 153-160, 1987.
- 42a. Taylor, H.F.W., "Chemistry of Cement Hydration, Paper 2.1, pp. 82-110 in Vol. 1, Proc. 8th Intl. Conf. on the Chemistry of Cement, Rio de Janeiro, 1986.
- 42b. Uchikawa, H. "Effect of Blending Components on Hydration and Structure Formation," Paper 3.2, pp. 249-280 in Vol. 1, Proc. 8th Intl. Conf. on the Chemistry of Cement, Rio de Janeiro, 1986.
- 43. Wei, Fajun, Grutzeck, M.W., and Roy, D.M. "The Retarding Effects of Fly Ash Upon the Hydration of Cement Paste: The First 24 Hours," Cem. Conc. Res., Vol. 15 (1), 174-184, 1985.

TABLE 1--SUMMARY OF CHARACTERISTICS OF SLAG,  
FLY ASH AND SILICAS

Designation	Mineralogical and Chemical Feature	Particle Characterization
Fly Ash (Class F) (low-Ca)	(Alkali) aluminosilicate glass matrix with mullite, Fe-rich spinel, hematite, quartz, unburned C*. Possible alkali sulphate condensates on surface.	Size partly dependent on collection efficiency. May contain hollow or thin-walled spheres.
Fly Ash (Class C) (high-Ca)	Calcium-rich glass matrix with C3A, C4A3S, C4AF, Ca2SiO4, (C2S), Ca-Mg silicates (e.g., merwinite).	Spherical and irregular, size according to collection efficiency.
Silica Fume	Mainly amorphous SiO2, some unburned C*.	Mainly extremely fine high surface spheres.

C\* = carbon

TABLE 2--REACTED FRACTION OF CLASS F FLY ASH,  
SILICA FUME, AND BLAST FURNACE SLAG

Specimens	Hydration Time					
	1D	3D	7D	28D	90D	complete hydration
70 C* - 30 FA	3.98	4.80	8.10	28.60	35.00	56.83
90 C* - 10 SF	50.50	64.60	65.40	65.70	74.70	95.20
63 CH - 37 FA	0	~0	~0	9.80	17.60	
67 CH - 33 SF	29.0	49.0	70.3	72.7	79.7	
50 C* - 50 BFS	1-3**	8-16	24-30	30-37		

\*Type I +Type II  
superplasticizer.

\*\*Range depends on presence or absence of

TABLE 3--POROSIMETRY AND DIFFUSION DATA FOR DIFFERENT MATERIALS CURED AND DIFFUSED AT 38 C+

Material	w/s*	Curing Age (days)	Porosity (%)	Median Pore Size (mm)	Diffusion Coefficient $\times 10^{13}$ m <sup>2</sup> /sec	
					Cl <sup>-</sup>	Cs <sup>+</sup>
Portland cement (P.C.)	0.40	28	23.5	15.0	227	8.6
P.C. + silica fume	0.40	28	27.5	7.5	15.6	>0.07
P.C.	0.35	28	22.0	15.0	129	5.2
P.C. + blast furnace slag	0.35	28	26.0	9.5	18.2	9.6**
P.C. + fly ash	0.35	28	11.5	2.75	13.5	1.4

+Ref: Kumar et al. (1987) (ref. 22).

\*w/s = water/solid

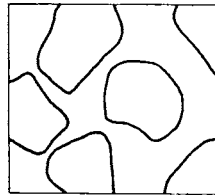
\*\*7-day value given; 28-day data erroneous

TABLE 4--CHEMICAL COMPOSITION OF C-S-H IN THE HARDENED CEMENT PASTE WITH AND WITHOUT 40 PERCENT BLENDING COMPONENT (W/C = 0.40, 293 K, AGE 4 YEARS) BY EMPA (42b)

	C/S	A/C	C/(S+A)	Na <sub>2</sub> O	K <sub>2</sub> O (%)
OPC	2.03	0.06	1.81	0.03	0.11
fly ash cement	1.01	0.21	0.84	0.24	0.33
slag cement	1.62	0.44	0.96	0.23	0.33

## NORMAL CEMENT HYDRATION

(1)  
CEMENT  
GRAINS  
DISPERSED  
IN WATER

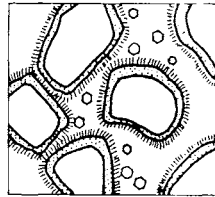


$\text{C}_3\text{SIO}_5$ ,  
 $\text{C}_2\text{SIO}_4$ ,  
 $\text{C}_3\text{AL}_2\text{O}_6$ ,  
 $\text{C}_2\text{FE}_x\text{AL}_{2-x}\text{O}_5$ ,  
 $\text{CASO}_4 \cdot 2\text{H}_2\text{O}$   
(+  $\text{H}_2\text{O}$ )

( a )

4-12 HOURS

(2)  
SET  
CEMENT  
PASTE

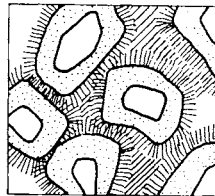


15-20% HYDRATION  
"C-S-H"  $< 1 \mu\text{m}$  NON-  
CRYSTALLINE FIBROUS,  
RETICULATE STRUCTURE;  
CRYSTALLINE HYDRATES;  
LOOSE BINDING ANHYDROUS  
CORES (HIGH POROSITY)

( b )

1-4 WEEKS

(3)  
FULLY  
HARDENED  
CEMENT  
PASTE  
 $\sim 50 \text{ MPa}$   
COMPR.  $\sigma$



$\sim 60-75\%$  HYDRATION  
"C-S-H" FILLS MOST  
LARGE PORES; "C-S-H",  
CRYST. HYDRATES BIND  
GRAINS (SMALLER ANH.  
CORES); MOD POROSITY  
(MACRO AND MICRO)  
REMAINS

( c )

Fig. 1--Schematic representation of Portland cement hydration steps



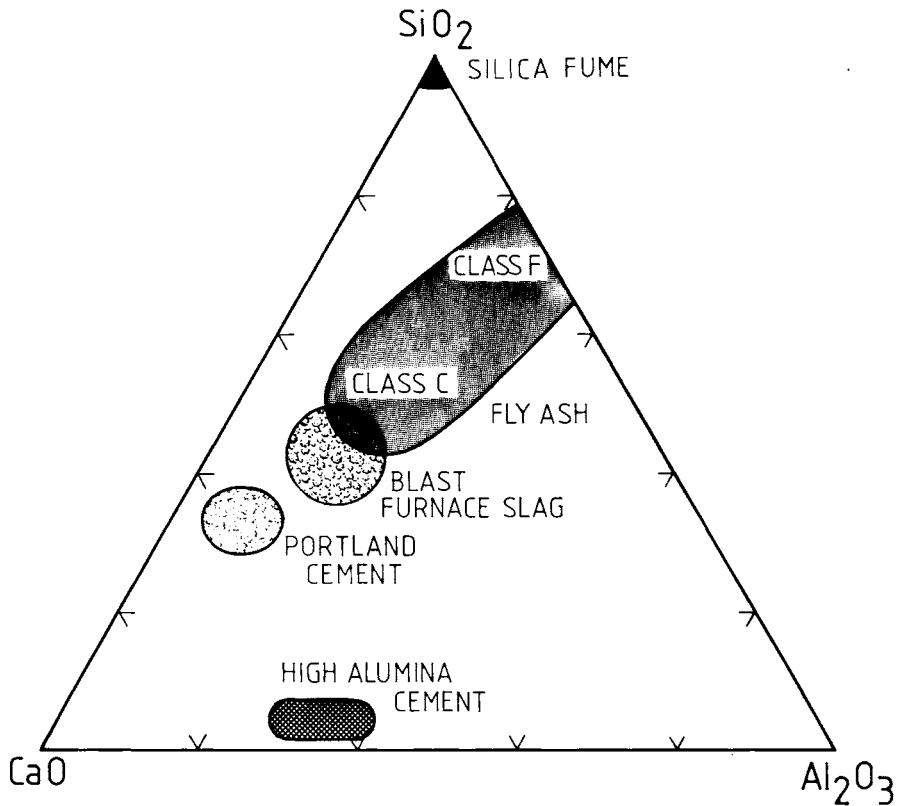


Fig. 2--Compositions of cements and blending materials; simplified representation of components as  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  compositions

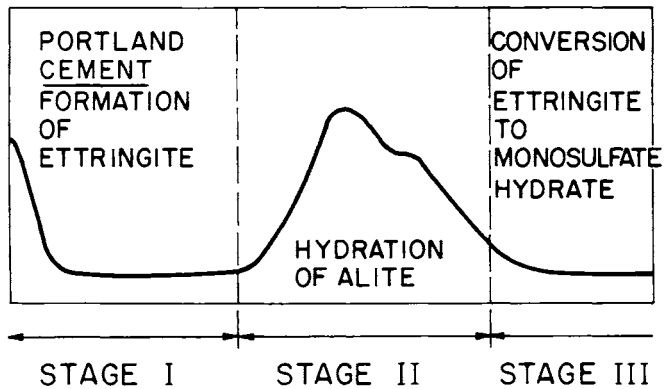


Fig. 3--Classification of hydration stages by isothermal calorimetry

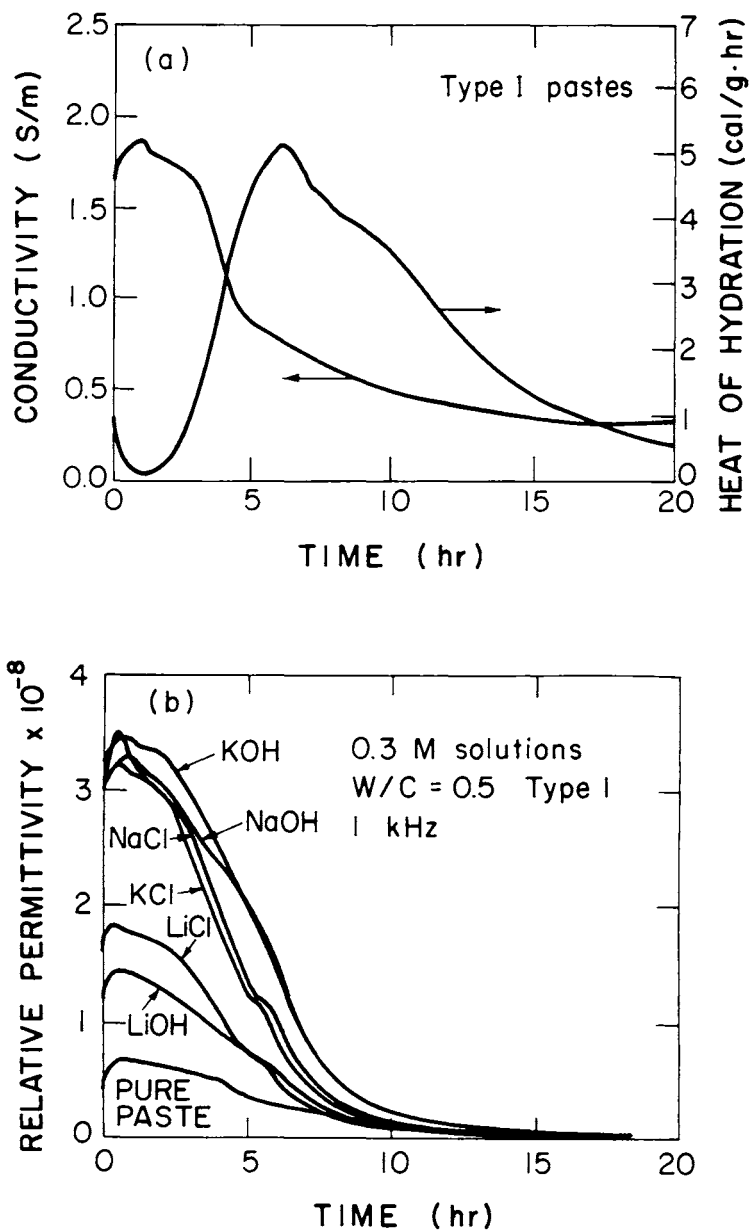


Fig. 4--a) Early hydration of cement as reflected in electrical conductivity (at 1 KHz) and heat of hydration measurements of 0.50 w/c ASTM Type 1 cement pastes, at 40 C  
 b) Effect of chlorides and hydroxides on relative permittivity

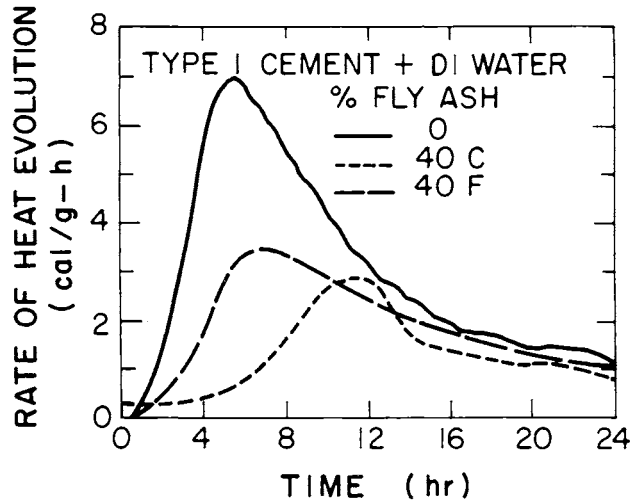


Fig. 5--Rate of heat evolution of OPC, (ASTM Type 1 cement), and OPC blends with 40 percent fly ash, at 38 C

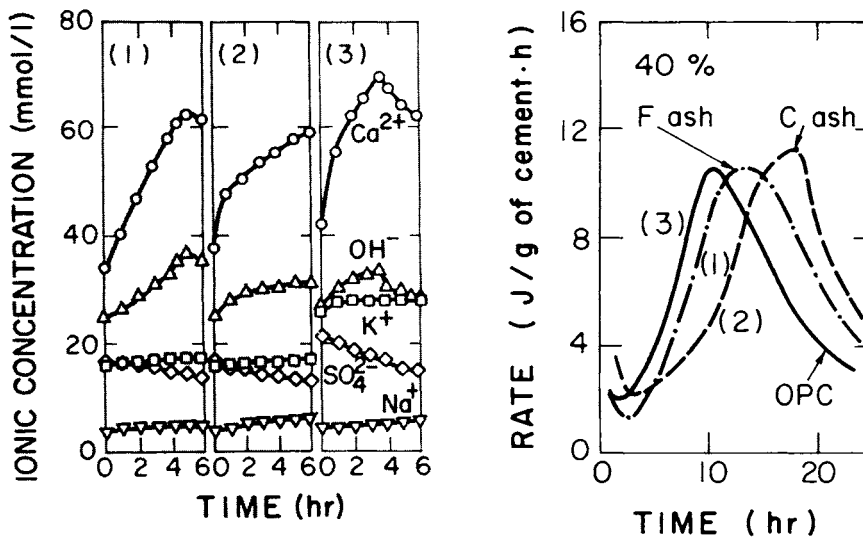


Fig. 6--Ionic concentration in the liquid phase and heat evolution curves of the hydration of fly ash cement at 20 C (Reference 39) -- (1) OPC + 40 percent Class F ash; (2) = OPC + 40 percent Class C fly ash; (3) = OPC

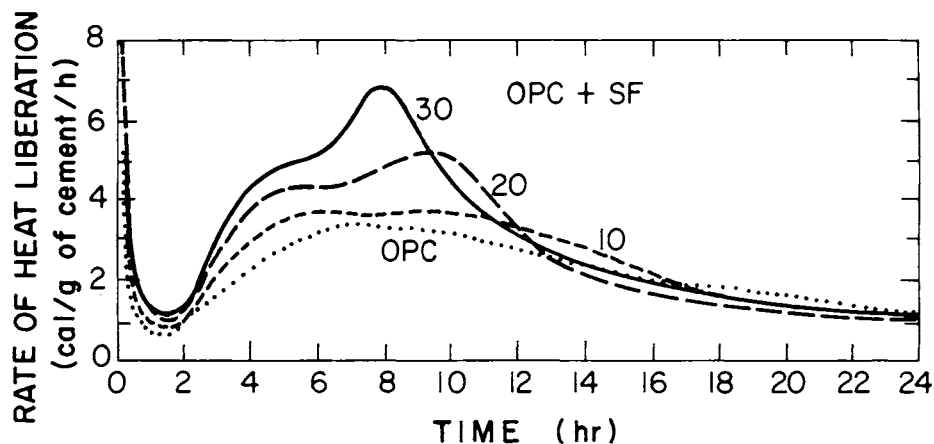


Fig. 7--Heat evolution curves of the hydration of cement with 0, 10, 20, and 30, percent silica fume (Reference 4)

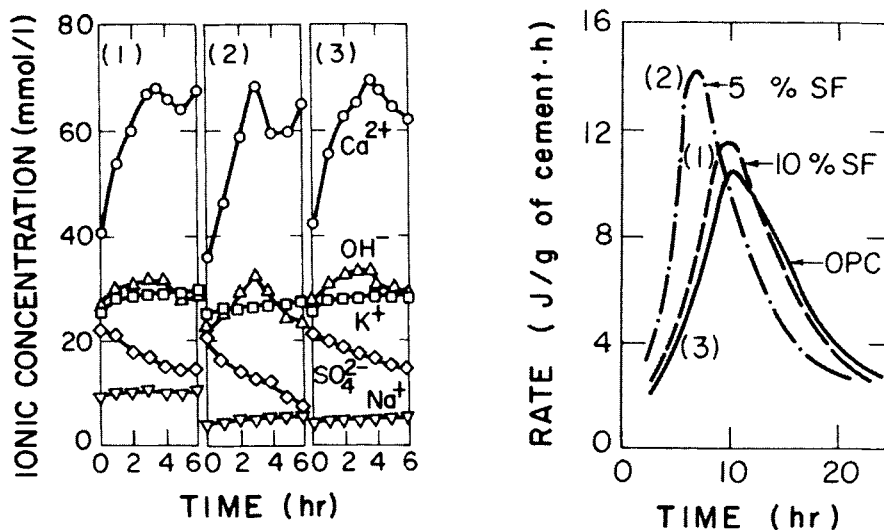


Fig. 8--Ionic concentration in the liquid phase and heat evolution curves of the hydration of containing silica fume cements compared with OPC at 20 C (Reference 42b) --  
(1) = 10 percent SF; (2) = 50 percent aerosil; (3) = OPC

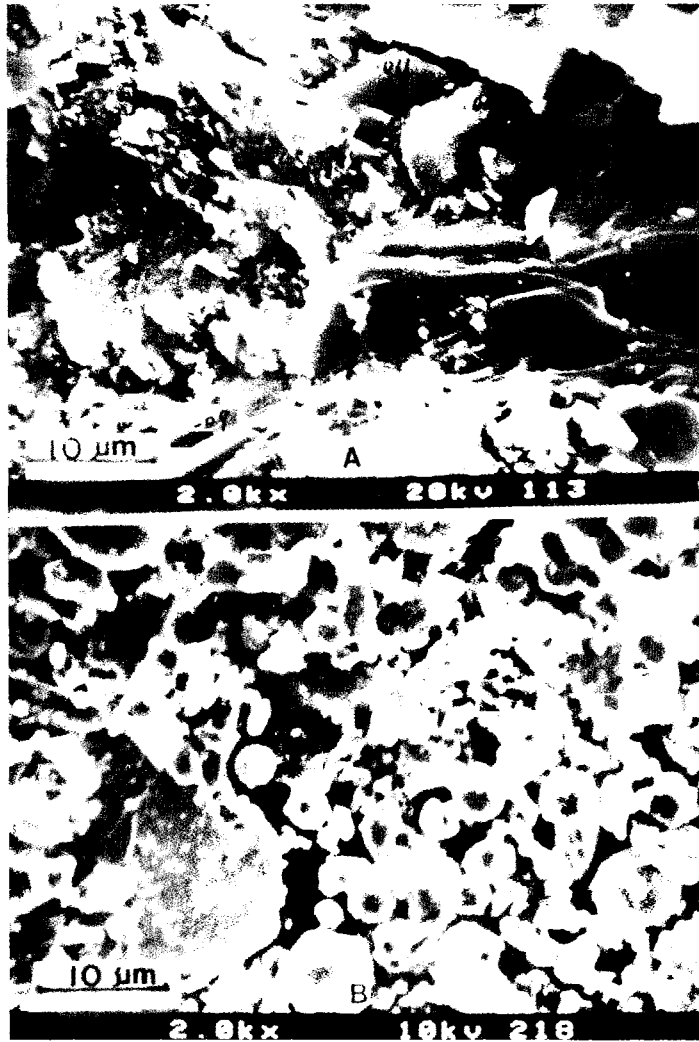


Fig. 9--SEM of 70 percent cement-30 percent fly ash mixture after curing 90 days; a) fracture surface, b) after selective dissolution

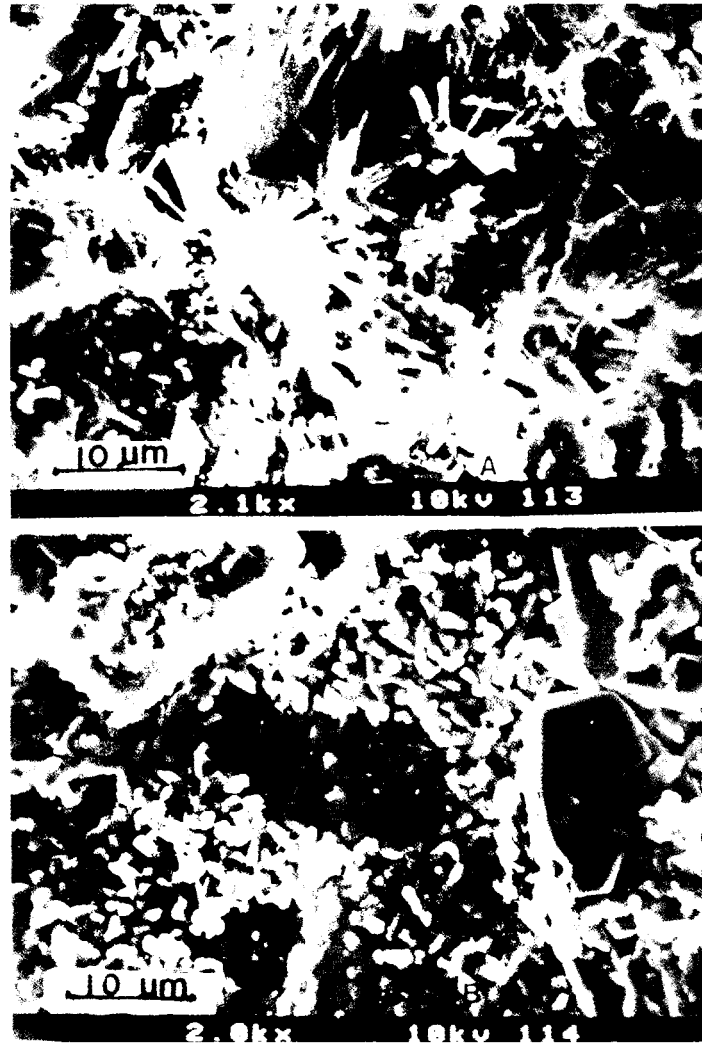


Fig. 10--SEM of 90 percent cement-10 percent silica fume mixture after curing 28 days; a) fracture surface, b) after selective dissolution