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Chemical Evolution of Cementitious Materials with High Proportion of Fly Ash and Slag

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management



Westinghouse
Hanford Company Richland, Washington

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CHEMICAL EVOLUTION OF CEMENTITIOUS MATERIALS WITH HIGH PROPORTION OF FLY ASH AND SLAG

Evolution of alkali activated cementitious materials

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Abstract

Cement mixtures containing high proportions of slag and fly ash were tested to assess their suitability to immobilize simulated off-gas waste solutions after vitrification of low-level radioactive tank wastes stored at Hanford. Materials were mixed with carbonated or alkaline solutions and cured initially adiabatically, then at 70°C. Chemical changes were monitored for 7 months using X-ray diffraction, selective dissolution and SEM; NMR was utilized to follow the polymerization of silicate species. The process of hydration during the first months of curing was characterized by formation of quite crystalline Al-substituted C-S-H structurally related to 1.1 nm tobermorite and traces of zeolites in some materials. A low content of calcium hydroxide was found in all materials after 1 month of curing. The SEM examination demonstrated rapidly decreasing porosity, making the mixtures favorable for long-term durability.

Keywords: hydration, chemistry, cement, fly ash, slag, wastefoms.

1 Introduction

To predict the performance of cementitious waste forms in different environments, it is necessary to consider the development of phase composition and microstructure due to hydration reactions. The main product of hydration, calcium silicate hydrate (C-S-H), is the matrix-forming phase in cementitious systems. Its properties determine to a large extent the properties of the matrix itself (permeability, diffusivity, and thermodynamic stability). The research presented here is part of a study of the chemistry, microstructure and durability of cement-stabilized low level radioactive wastes. A companion paper on durability is included in this symposium [1].

Several factors make these wastefoms quite different from ordinary portland cement paste hydrated at room temperature. The liquid phase contains appreciable alkali and hydroxide ions. These provide early activation of slag and fly ash. Such activation

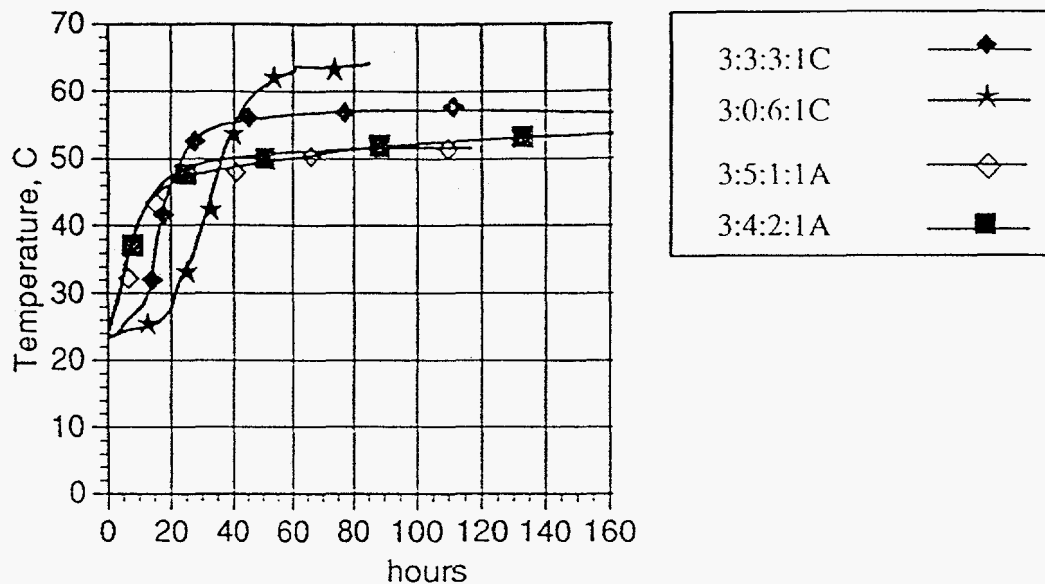


Figure 1. Adiabatic calorimetry.

served. The method is not suitable for quantitative determination of unreacted cement phases. The calculations were based on ignited weight. The procedure utilized can be found in [2, 3].

Specimens for ^{29}Si MAS NMR spectroscopy were ground to a powder and packed into zirconia rotors. The single-pulse ^{29}Si MAS NMR spectra were acquired using a GE WD-300 spectrometer equipped with an Oxford Instruments superconducting magnet (magnetic field 7 T and operating frequency of 59.62 MHz for ^{29}Si). The ^{29}Si chemical shifts are given relative to tetramethylsilane (TMS) at 0 ppm.

3 Results

3.1 XRD

Powder XRD spectra for hydrated materials are shown in Figures 2–3. The main hydration products at 1 month were C–S–H(I), hydrotalcite, AFm (which appears to be hemi-carboaluminate), and calcite; trace amounts of calcium hydroxide, a sodalite and Na–P1 were present in some of the mixtures. The rate of pozzolanic reaction was observed to be different for the two solutions. The maximum intensity for the calcium hydroxide peaks for the carbonated solution was observed at 3 days, while for the alkaline solution it was observed at 7 days. At 28 days only trace amounts of calcium hydroxide were present in all materials. Traces of a sodalite were observed in 3:4:2:1A and 3:5:1:1A at early ages (3–5 days). Later traces of Na–X and Na–P1 zeolite (gismondine) were also observed (Figures 2–3). Crystallization of zeolites in the matrix of materials 3:4:2:1A and 3:5:1:1A did not cause loss of strength [1]. In most samples, the C–S–H appeared to be largely amorphous. More crystalline C–S–H, structurally related to 1.1 nm tobermorite, was observed in 3:4:2:1A and in 3:3:3:1C after 2 months (Figure 3).

3.2 SEM

The examination of fracture surfaces of 3:3:3:1C and 3:0:6:1C at 1 month showed a considerable amount of the AFm and hydrotalcite-type phases. The back scattered electron

Table 1. Composition of solutions

	A, g/l	C, g/l
$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	7.03	7.03
$\text{Na}_3(\text{PO}_4) \cdot 12\text{H}_2\text{O}$	24.53	24.53
NaNO_2	12.17	12.17
NaOH	53.76	—
NaNO_3	32.73	32.73
Na_2CO_3	—	39.97

Table 2. Oxide composition (% weight) of dry materials by XRF

Oxide	Cement ¹	Fly ash ²	Slag ³	Clay ⁴
SiO_2	22.17	46.13	37.0	59.71
Al_2O_3	3.24	25.02	8.0	9.05
Fe_2O_3	4.24	7.25	0.2	3.17
CaO	64.48	8.02	39.0	3.13
MgO	1.13	1.81	11.0	11.2
K_2O	0.52	0.63	0.4	0.83
Na_2O	0.15	4.74	0.3	0.07
TiO_2	0.23	4.70	0.4	0.42
P_2O_5	0.12	0.42	0.01	1.47
MnO	0.06	0.03	0.5	0.05
SO_3	2.14	0.12	2.8	<0.1
Loss on ignition	1.20	0.53	0.39	10.64

1 Type I/II, Ash Grove, Durkee, OR

2 Type F, Centralia, Ross Sand and Gravel Co., Portland, OR

3 Koch Minerals Co., Chicago, IL

4 Attapulgit, Engelhard Co., Iselin, NJ

plus adiabatic curing conditions produce quite high reaction temperatures. These factors cause considerable changes in hydration chemistry.

2 Experimental

The solid materials (cement, fly ash, slag and clay) were mixed at room temperature with either alkaline (A) or carbonated (C) solution. Solids were mixed with liquid at w/s ratio of 1 (1 liter of liquid mixed with 1 kg of solid). The compositions of solutions are shown in Table 1. The mixtures tested are designated by their proportion (by weight) of cement, fly ash, slag and clay. For example, the material 3:3:3:1 contains 30% cement, 30% fly ash, 30% slag and 10% clay. The oxide compositions of the cement, fly ash, slag and attapulgit clay are shown in Table 2.

The materials were sealed in tubes and cured adiabatically for the first 4 days, after which they were cured isothermally at 70°C for 7 months. Adiabatic calorimetry results are shown in Figure 1. At the desired age hydration was stopped by crushing the pastes and immersing in methanol for 7 days. The samples were then dried in vacuo and kept under vacuum until analyzed.

The weight percent of slag and fly ash reacted at different ages was determined by selective dissolution of materials in salicylic acid and methanol. In this method C-S-H and cement are largely dissolved, while ~97% of fly ash and ~85% slag are pre-

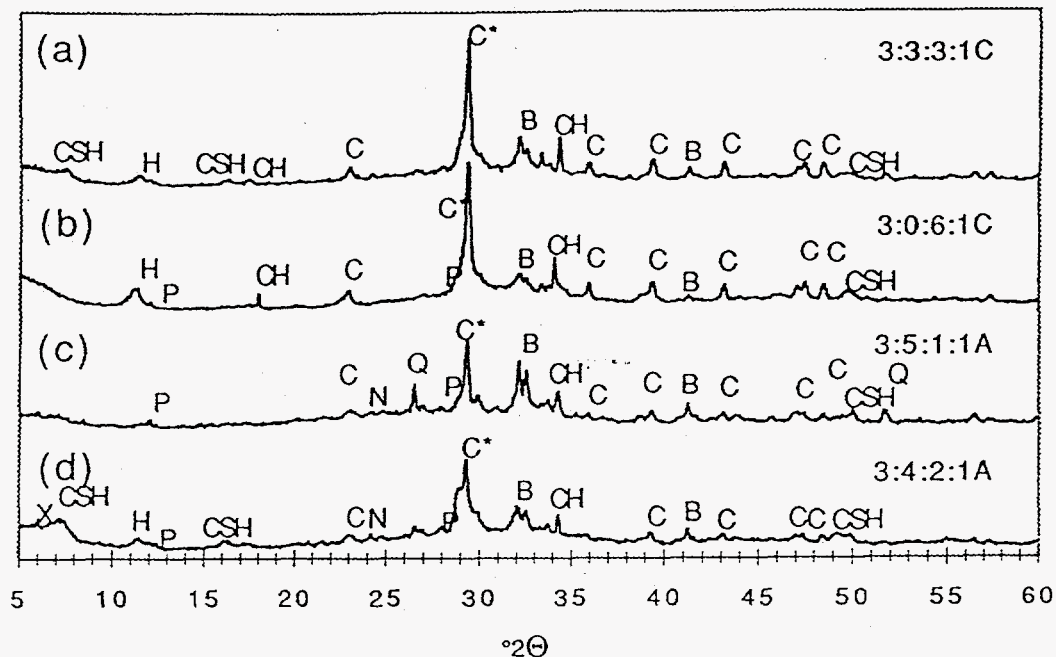


Figure 2. Powder XRD spectra of samples hydrated for one month, acquired with Cu K α radiation; B=belite, C-S-H=calcium silicate hydrate, C=calcium carbonate (calcite), C*=overlapping C-S-H and calcite, H=hydrotalcite ($[\text{Mg}_6\text{Al}_2(\text{OH})_{16}] \cdot \text{CO}_3 \cdot 4\text{H}_2\text{O}$) and AFm-type phase, hemicarbonate ($\text{C}_4\text{A}\bar{\text{C}}_{1/2}\text{H}_{12}$), N=a sodalite type zeolite, P=Na-P1, zeolite (gismondine), Q=quartz, X=Na-X zeolite; (a) 3:3:3:1C, (b) 3:0:6:1C, (c) 3:5:1:1A, (d) 3:4:2:1A.

image (BEI) of these materials showed a reaction rim surrounding slag and fly ash particles, and in the space between them plate-like AFm and hydrotalcite were crystallized (Figure 4). There was much unreacted material and unfilled space between the particles. Examination at later ages showed that the course of reaction differed between the two solutions. In the alkaline solution (A), slag and fly ash were activated earlier and dissolved from the surface more rapidly than in the carbonated solution (C) (for example, see Figure 5 at 2 months). In the latter we observed precipitated C-S-H on the surface of particles (Figure 6). Dissolution of fly ash in the carbonated case occurred only at 4 months, when the glassy phase of some of fly ash particles has dissolved leaving distorted shells of outer product C-S-H, which had presumably formed earlier (see Figure 7). A lot of reaction seams to take place in the hardened matrix through dissolution and precipitation. As a result of the continuing hydration a finer porosity and more uniform matrix is observed at later ages in all the materials (for example, see Figure 8 at 7 months).

3.3 Selective Dissolution

Table 3 shows the weight percent of slag and fly ash reacted at different ages determined by selective dissolution. The results are consistent with other investigations of blended cements [2, 3, 7]. The total amount of fly ash and slag was ~60% in all mixtures. The results show that hydration continued throughout the time period.

3.4 NMR

Figure 9 shows the Si MAS NMR spectra for 3:3:3:1C and 3:0:6:1C at the ages of 1 month and 7 months. We observed considerable intensity of $Q^2(1\text{Al})$ at ~82 ppm and

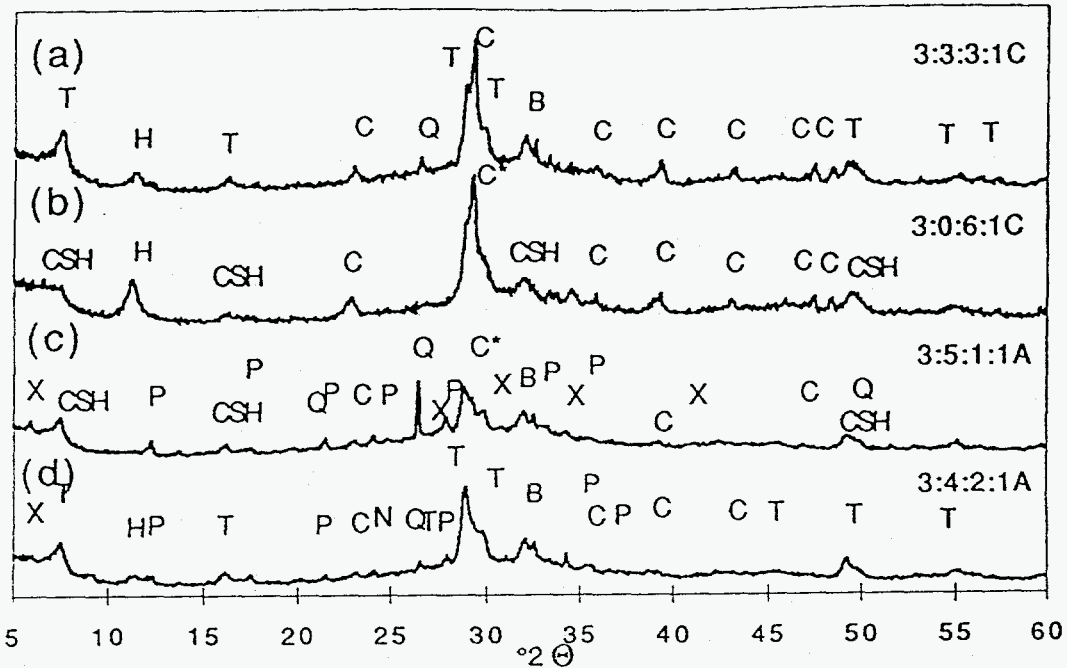


Figure 3. Powder XRD spectra of samples hydrated for seven months, acquired with Cu K α radiation; B=belite, C-S-H=calcium silicate hydrate, C=calcium carbonate (calcite), C*=overlapping C-S-H and calcite, H=hydrotalcite ($[\text{Mg}_6\text{Al}_2(\text{OH})_{16}] \cdot \text{CO}_3 \cdot 4\text{H}_2\text{O}$) and AFm-type phase, hemicarbonate ($\text{C}_4\text{A}\bar{\text{C}}_{1/2}\text{H}_{12}$), N= a sodalite type zeolite, P= Na-P1, zeolite (gismondine), Q=quartz, T= more crystalline C-S-H, X=Na-X zeolite; (a) 3:3:3:1C, (b) 3:0:6:1C, (c) 3:5:1:1A, (d) 3:4:2:1A.

$\text{Q}^2(0\text{Al})$ at ~ 85.5 ppm for all the samples. The results are in agreement with observations of other authors for ordinary Portland cement [4], alite [5] and slag hydration [6].

4 Discussion

As expected, the course of reaction was different in the carbonate and alkaline solutions. Larger amounts of portlandite were observed in the alkaline solution and were consumed later. The amounts of AFm and hydrotalcite were found to relate to the amount of slag, because slag is activated more rapidly than fly ash and releases Al and Mg. In 3:4:2:1A and 3:5:1:1A some Al crystallized in sodalite, Na-P1 and Na-X zeolites instead of AFm due to

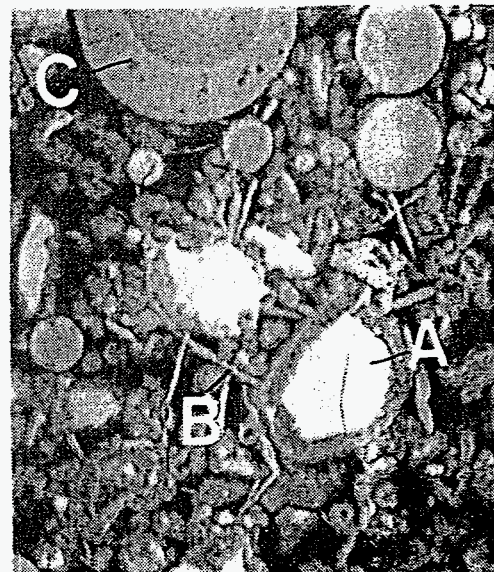
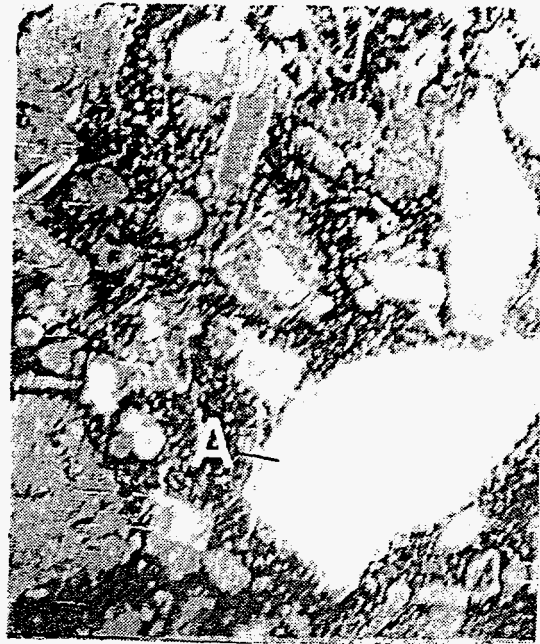


Figure 4. BEI of 3:3:3:1C at 1 month; A-slag, B-hydrotalcite and AFm phases, C-fly ash particle.



20 μm

Figure 5. BEI 3:5:1:1A at 2 months;
A—activated slag particle.



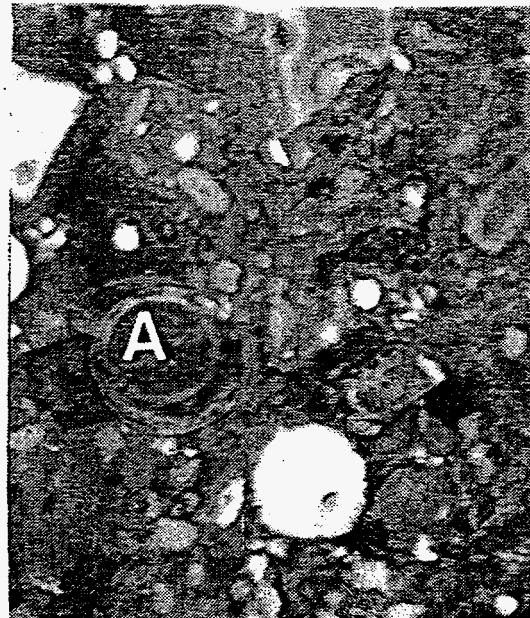
25 μm

Figure 6. BEI 3:3:3:1C at 4 months;
A—slag particle.



50 μm

Figure 7. BEI 3:3:3:1C at 4 months;
A—activated fly ash sphere.



50 μm

Figure 8. BEI of 3:3:3:1C at 7 months;
A—fully reacted fly ash sphere.

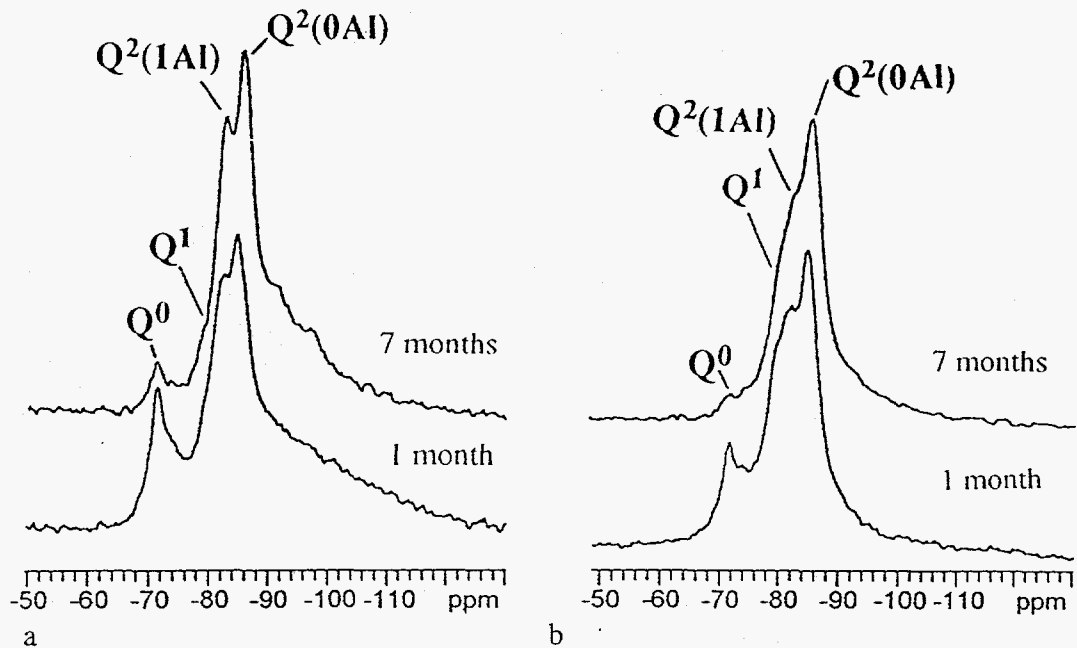


Figure 9. ^{29}Si MAS NMR spectra for waste materials (a) 3:3:3:1C, (b) 3:0:6:1C. The single pulse spectra were acquired (~ 4000 scans) using a pulse recycle delay of 10 s and a flip angle of 90° .

the low C/S ratio of solids and the presence of considerable alkali. At early ages we observed traces of a sodalite, and later a combination of sodalite, Na-P1 and Na-X zeolites, although Na-P1 was prevailing.

By NMR high intensity of $\text{Q}^2(1\text{Al})$ at ~ -82 ppm was observed for all materials from the early stage of hydration, showing that the precipitated C-S-H had a considerable substitution of Al. For all the samples at 7 months we observed a high intensity of $\text{Q}^2(1\text{Al})$ and $\text{Q}^2(0\text{Al})$, and very little intensity for Q^1 at ~ -79.9 ppm (chain terminating groups), which indicates the formation of C-S-H with quite long chains. The 3:0:6:1C spectrum had the highest intensity of Q^1 (~ -79.9 ppm), so the average chain length in 3:0:6:1C was the lowest.

Table 3. Weight percent of slag and fly ash reacted determined by selective dissolution

Age	3:3:3:1C	3:0:6:1C	3:5:1:1A	3:4:2:1A
10 days	29	49	24	42
1 month	42	62	36	55
5 month	nd*	nd	42	65
7 month	54	75	nd	nd

* not determined

5 Conclusions

The reactions observed in alkali activated cementitious materials cured at elevated temperatures resulted in the formation of Al-substituted C-S-H structurally related to 1.1 nm tobermorite, and traces of sodalite, Na-P1, and Na-X zeolites. The Na-P1 zeolite was found to replace a sodalite at later ages. A considerable substitution of Al in C-S-H was observed from a very early age. In some samples considerable crystallinity was found in C-S-H at 7 months. These reactions can be explained by the low C/S ratio of the mix and the large amount of Al that was activated by alkaline solution. The rates of fly ash and slag activation were found to depend on the initial pH and composition of the solution. The system is moving to a more stable phase assemblage that is characterized by crystallization of Al substituted C-S-H that has quite long chain lengths and is more crystalline and structurally related to 1.1 nm tobermorite. From SEM and dissolution work it is evident that the degree of reaction is increasing with time, creating more fine microporosity and filling the larger pores. As the microstructure becomes more uniform, its permeability is decreasing, improving the resistance of these materials to deterioration.

6 Acknowledgement

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