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Sodium Polyphosphate-Modified Class C/Class F Fly Ash Blend Cements for Geothermal Wells

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Abstract

We investigated the usefulness of the coal-combustion by-products, Class C fly ash (C) and Class F fly ash (F), in developing cost-effective acid-resistant phosphate-based cements for geothermal wells. In the temperature range of 20-100°C, sodium polyphosphate (NaP) as the acidic cement-forming solution preferentially reacted with calcium sulfate and lime in the C as the base solid reactant through the exothermic acid-base reaction route, rather than with the tricalcium aluminate in C. This reaction led to the formation of hydroxyapatite (HOAp). In contrast, there was no acid-base reaction between the F as the acidic solid reactant and NaP. After autoclaving the cements at 250°C, a well-crystallized HOAp phase was formed in the NaP-modified C cement that was responsible for densifying the cement's structure, thereby conferring low water permeability and good compressive strength on the cement. However, the HOAp was susceptible to hot CO_2-laden H_2SO_4 solution (pH 1.1), allowing some acid erosion of the cement. On the other hand, the mullite in F hydrothermally reacted with the Na from NaP to form the analcime phase. Although this phase played a pivotal role in abating acid erosion, its generation created an undesirable porous structure in the cement. We demonstrated that blending fly ash with a C/F ratio of 70/30 resulted in the most suitable properties for acid-resistant phosphate-based cement systems.

1. Introduction

In our previous studies on the hydrothermal synthesis and characterization of sodium polyphosphate-modified Class F fly ash/calcium aluminate blend (SFCB) geothermal well cement, we found that four crystalline hydrothermal reaction products, the hydroxyapatite [($Ca_3(PO_4)_3(OH)$; HOAp], boehmite (γ-AlOOH), hydrogarnet ($3CaO.Al_2O_3.6H_2O$), and zeolite [(Na-P type; $Na_3Al_3Si_5O_{16}.6H_2O$ and analcime, $NaAlSi_2O_6.H_2O$)] phases, were responsible for strengthening the cement autoclaved at temperatures from 100 to 300°C; they also were instrumental in alleviating carbonation by CO_2 (> 40,000 ppm), and erosion by mild acid brine (pH ~ 5) [1-4]. The HOAp phase was formed in a two-step reaction pathway: The first step was an exothermic acid-base reaction between calcium cation (Ca^{2+}) liberated from the calcium aluminate cement (CAC) as the proton-accepting cation-leachable solid base reactant, and sodium dihydrogen phosphate, $Na^+H_2(PO_4)^-$, derived from the hydrolysis of the sodium polyphosphate (NaP) as the proton-donating acid reactant at room temperature, to generate amorphous dibasic calcium phosphate hydrate, $Ca(HPO_4).xH_2O$. The second step was the hydrothermal reaction of $Ca(HPO_4).xH_2O$ with additional Ca^{2+} and $Na^+H_2(PO_4)^-$ hydrolysate species, thereby yeilding HOAp. Concurrently, the decalcified CAC was converted into amorphous aluminum oxide hydrate at room temperature, followed by its hydrothermally induced transformation into crystalline boehmite. The chemical affinity of amorphous aluminum oxide hydrate with two hydrolysate species, Ca^{2+} and OH^-, also yielded the hydrogarnet phase.

Meanwhile, the uptake of Na^+ dissociated from NaP by the mullite ($3Al_2O_3.2SiO_2$) reactant in the Class F fly ash generated an additional crystalline Na-P type zeolite phase at the hydrothermal temperature of 150°C. Raising the temperature to 300°C led to the Na-P type → analcime phase transition.

Regarding the chemistry of CAC as the starting material, two calcium aluminate compounds, monocalcium aluminate ($CaO.Al_2O_3$, CA) and calcium bialuminate ($CaO.2Al_2O_3$, CA_2), and one calcium aluminate silicate, gehlenite ($2CaO.Al_2O_3.SiO_2$, C_2AS), in the CAC played an important role in promoting the generation of these reaction products. However, one intriguing question remained unanswered: Are other calcium aluminate compounds, such as tricalcium aluminate ($3CaO.Al_2O_3$, C_3A) in the cement, as

effective in deriving these reaction products as are CA and CA_2. As is well documented [5,6], in Class C fly ash as the coal combustion by-products, C_3A coexists with other chemical compounds, such as quartz, lime, and calcium sulfate. We deemed it worthwhile to investigate the usefulness of Class C fly ash as replacement for CAC because not only does this confer an economical advantage in making the SFCB cement, but it also abates an ash-disposal problem.

Thus, the current study was directed toward investigating the characteristics of the sodium polyphosphate-modified Class F fly ash/Class C fly ash bend cements after autoclaving them at 250°C for their use as acid-resistant geothermal well cements. Among the characteristics to be investigated were the pH values of the pore solution in the cement slurries, the total energy generated in exothermal acid-base reactions of cement slurries along with a quantitative analysis of reaction product responsible for the total output of this reaction energy, the porosity, water permeability and compressive strength of autoclaved cements. We also identified the crystalline phases assembled in autoclaved cement bodies. All the data obtained were integrated and correlated directly with the information on the resistance of autoclaved cements to a CO_2-laden H_2SO_4 solution (pH 1.1) at 90°C.

2. Experimental procedure

2.1. Materials

The Boral Material Technologies Inc supplied both the Class C fly ash (C) and Class F fly ash (F). The chemical constituents of the oxides for these fly ash reactants were as follows: 36.2 % SiO_2, 19.1 % Al_2O_3, 6.7 % Fe_2O_3, 24.6 % CaO, 5.4 % MgO, 1.7 % SO_3, 1.7 % Na_2O, 0.5 % K_2O, 3.7 % loss in ignition for C; and, 38.6 % SiO_2, 38.6 % Al_2O_3, 12.0 % Fe_2O_3, 0.5 % CaO, 1.4 % MgO, 1.9 % SO_3, 1.5 % Na_2O, 1.9 % K_2O and 3.4 % loss in ignition for F. The x-ray diffraction (XRD) analysis of these fly ashes showed that the crystalline components of C consisted mainly of four major phases, quartz (SiO_2), tricalcium aluminate ($3CaO \cdot Al_2O_3$), calcium sulfate anhydrate ($CaSO_4$), and lime (CaO), while F had three major phases, quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), and hematite (Fe_2O_3). Granular sodium polyphosphate, -[-(-$Na^+PO^-_3$-)$_n$-, NaP], was obtained from the Aldrich Chemical Company Inc. The NaP then was dissolved in water

to make a 25wt% solution for use as the cement-forming acid aqueous reactant. The base reactants, mixed in a twin shell dry blender, had five C/F ratios, 100/0, 90/10, 70/30, 50/50, and 30/70 by weight. In preparing the cement slurries, a 66.7wt % base reactant for each C/F ratios then was mixed thoroughly with the acid reactant of 33.3wt% (25wt% NaP solution) at room temperature.

2.2. Measurements

The pore solutions were extracted from 3 min-aged cement slurries placed in a centrifugal device to measure their pH. Also, three references, C/water (c/w ratio of 0.35) and F/water (same ratio) slurries, and 25wt% NaP solution, were used to expedite the interpretation of the changes in pH value by varying the C/F ratios. A non-isothermal different scanning calorimeter (DSC) with heating rate of 10°C/min. in N_2 gas was employed to obtain the total energy generated in an acid-base exothermic reaction. Fourier transform infrared spectroscopy (FT-IR) gave information on which reactant, C or F, preferentially reacts with NaP at temperatures between 20-100°C. For measuring the compressive strength, water permeability, and porosity, the neat cement slurries were cast in two cylindrical molds, 30 mm diam. and 70 mm long, for compressive strength testing, and 30 mm diam. and 30 mm long for the other measurements, and allowed to harden at room temperature for 20 hours. The hardened cements were removed from the molds and autoclaved for 24 hours at 250°C. Their porosity was measured by helium comparison pyconometry. Water permeability through the cylindrical cements under a pressure of 202.65 kNm^{-2} was determined by the Ruska liquid permeameter. Compressive strength test was performed using Instron. The results of these tests and measurements are the average from three specimens. The crystalline phases formed in the autoclaved cements were identified by XRD. For the acid resistance test, the autoclaved cements (30 mm diam. by 60 mm long) were immersed for 15 days in the H_2SO_4 solution (pH 1.1) containing 0.5wt% sodium hydrogen carbonate ($NaHCO_3$) as a source of ~3000 ppm CO_2 at 90°C, $H_2SO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + 2CO_2 + 2H_2O$. To maintain the pH at 1.1, the H_2SO_4 solution was replenished with a fresh solution every 5 days. The volume proportion of the cements was 1 to 25. After exposure, the rate of acid erosion of cements

was determined from their loss in weight. This result directory provided information on the effectiveness of phases formed in the cement bodies in minimizing acid erosion.

3. Results and discussion

3.1. Cement Slurry

Before mixing the NaP solution with F-blended C, and C alone, we surveyed the pH value of the three references, the NaP solution, and the pore solutions extracted centrifugally from water-mixed C and F slurries (Table 1). The NaP solution was acidic, pH 4.9. The pore solution of C slurry was basic, pH 10.78; in contrast, the pH of F was 4.81, rendering the acidic slurry. From this information, it is possible to assume that an acid-base reaction would take place between NaP and C, but not between NaP and F. Correspondingly, the pore solution of a slurry made from a mix of 66.7wt% C and 33.3wt% (25wt% NaP) denoted as the 100/0 C/F ratio, had a nearly neutral pH of 6.76, reflecting the occurrence of an acid-base reaction. When 10 % of the total weight of C was replaced by F, pH fell to 6.53. A further drop in pH was seen as the content of F was increased. With a 30/70 C/F ratio, the pH of 5.95 was tantamount to a decrease of ~ 12 % compared with that of the 100/0 ratio slurry.

To obtain the information about the degree of acid-base reaction, our focus centered on computing the total energy generated in the exothermic acid-base reaction between the NaP and C or C/F mixtures. Figure 1 shows the non-isothermal DSC curves over temperature range of 20° - 90°C for the slurries made with 100/0 and 70/30 C/F ratios. In this test, these two reactants were separately left for 24 hours at 5°C before mixing them. Although the features of both curves highlight the onset temperature of the reaction at ~ 40°C and its peak at nearly 60°C, one difference between them was the enclosed area of the curve with the baseline, which represents the total heat energy generated during the exothermic acid-base reaction. Computer programs were prepared to calculate theoretical exothermic energy, ΔH, J/g, from the enclosed area. The computed ΔH value of the 100/0 ratio slurry was 8.18 J/g, which was almost two-fold higher than that of the 70/30 ratio. Figure 2 plots the changes in ΔH as a function of C/F ratio. As seen, the ΔH value depended on C/F ratio; namely, a decrease in this ratio that means the incorporation of more F into the blended slurry resulted in the decline of the ΔH value.

This finding strongly underscored the fact that NaP preferentially reacted with the C via acid-base activity at temperatures from 20° to 90°C, rather than the F.

To support this information, FT-IR study over the frequency range of 1800-400 cm^{-1} was carried out for 100/0-, 50/50-, and 30/70 ratio cements hardened at room temperature, followed by heating at 100°C (Figure 3). As discussed in the introduction, in our study, the hydroxyapatite (HOAp) phase commonly formed through a two-step reaction pathway, acid-base and hydrothermal hydration. Thus, the HOAp obtained from Aldrich Science Corp. also was used as the reference sample. The FT-IR spectrum of 100/0 ratio encompassed six representative bands at 1167, 1085, 1040, 794, 604, and 566 cm^{-1}. From the reference spectrum of the HOAp (Figure 4), the three bands at 1040, 604, and 566 cm^{-1} appears to belong to this compound. The major contributor to the remaining other three bands is the silica [7]. In contrast, the specific features of the spectrum for the 50/50 ratio were as follows: First was the decline of peak intensity at 1040, 604, and 566 cm^{-1} bands attributed to HOAp, compared with those of the silica-related bands; second was the appearance of new band at 911 cm^{-1}. We assumed that this new band is due to F. Since the F reactant included three major chemical components, silica, mullite, and hematite, we inspected the FT-IR spectra of the last two components as reference samples to definite the assignment of this new band; our results suggested that the band at 911 cm^{-1} was associated with mullite. With the 30/70 ratio cement, the intensity of HOAp-related bands had strikingly decayed, while the peak for mullite had intensified.

The above information strongly supported the findings from the DSC study; namely, NaP preferentially reacted with C, rather than F at ≤ 100°C.

3.2 Autoclaved Cement

An important factor governing the mechanical and physical properties of autoclaved cements, and their resistance to hot acid is the identity of the crystalline phases formed as hydrothermal reaction products in the cement bodies, and also that of the non-reaction products. To obtain this information, we inspected the 100/0, 50/50, and 30/70 ratio cements after autoclaving for 24 hours at 250°C, by XRD tracings over the diffraction range of 0.444-0.225nm (Figure 5). The "as-received" C was used as the reference sample. As expected, the pattern (a) of the C base reactant revealed the

presence of four crystalline components, quartz (SiO_2), calcium sulfate anhydrate ($CaSO_4$), lime (CaO), and tricalcium aluminate ($3CaO.Al_2O_3$, C_3A). When C was mixed with NaP, followed by autoclaving it, the features of XRD pattern (b) differed from that of C; in particular, there was the appearance of hydroxyapatite [($Ca_5(PO_4)_3(OH)$, HOAp)]-related *d*-spacing lines and the elimination of the *d*-spacing lines associated with $CaSO_4$ and CaO, while the prominent lines of quartz and C_3A remained unchanged. Accordingly, HOAp as the hydrothermal reaction product is more likely to be formed by the interaction between the NaP and CaO or $CaSO_4$, rather than one between NaP and C_3A. Incorporating F into the NaP/C system led to the formation of an additional reaction product. The pattern (c) from the 50/50 ratio cement can be accounted for the generation of the zeolitic analcium ($NaAlSi_2O_6.H_2O$) phase as an additional reaction product resulting from the interaction between the Na from NaP and the mullite ($3Al_2O_3.2SiO_2$) in the F. However, the XRD tracing (not shown) of this cement made at room temperature did not verify the formation of any zeolitic phases; therefore, the analcime crystals seem to be assembled at high hydrothermal temperature. Again, non-reacted quartz and C_3A components were detected, while the intensity of HOAp-related lines declined because of the decrease in the amounts of available $CaSO_4$ and CaO base reactants due to the reduction in the proportion of C to F. A further decrease in this proportion to 30wt% C to 70wt% F displayed two specific features in the pattern (d): One was a considerable attenuation of the intensity of HOAp- *d*-spacing lines; the other was a conspicuous growth of the intensity of the analcime-related line in conjunction with the presence of some non-reacted mullite phases.

Table 2 summarizes the phase compositions for 250°C-autclaved NaP-modified 100/0-, 70/30-, 50/50-, and 30/70-C/F ratio cements. The crystalline phase of the reaction products formed in the autoclaved cements depended primarily on the C/F ratio; namely, the major crystalline phase in cements with 100/0 and 70/30 ratios of C/F was HOAp; the 50/50 ratio revealed the generation of the analcime phase as another major reaction product. With the 30/70 ratio, analcium became the principal phase, while the formation of the HOAp phase was poor.

Table 3 lists the changes in porosity, water permeability, and compressive strength of autoclaved cements as a function of C/F ratio. The data revealed that porosity

tends to decline with the decrease in C/F ratio. In fact, the porosity of 27.5 % for the 100/0 ratio cement rose ~23 % to 33.9 % as 30wt% of total amount of the C was replaced by F. Its further replacement by F to 70wt% created a porous structure with 41.6% pores. Relating this finding to the results from the XRD study, a well-formed HOAp phase contributes to densifying the structure of cement. In contrast, the development of the analcime phase, coexisting with HOAp by adding F to C led to increasing numbers of pore in the cement. Thus, when analcime became the most dominant phase, as more F was added to C, the dense structure of the HOAp-associated cement was converted into a porous one. As expected, the porous structure not only impaired the compressive strength, but also increased the rate of transportation of water through the cement. In fact, the value of compressive strength for the 30/70-ratio cement was more than twice as low as that of the 100/0 ratio, while its water permeability of 2.3 x 10^{-3} Darcy was equivalent to two orders of magnitude higher than that of the 100/0 ratio.

3.3. Acid erosion

Based upon the information described above, our focus now shifted to assessing the resistance of F-blended and non-blended C phosphate cements to CO_2-laden H_2SO_4 solution at 90°C for 15 days: weight loss of the cements caused by its acid erosion was measured to evaluate their ability to mitigate the acid erosion. Acid corrosion products formed over a superficial layer of the cement were brushed off before weighting them. Figure 6 depicts the loss in weight for the 100/0-, 70/30-, 50/50-, and 30/70- ratio cements. Interestingly, the 100/0 ratio cement possessing the densest structure and the highest compressive strength in this series was most vulnerable to hot acid attack, loosing 13.1 % of its weight. Incorporating F into the C remarkably reduced this amount of acid erosion. With the 70/30 ratio, weight loss was only a 3.1 %, which was equivalent to a decrease of ~76 % compared with that of the 100/0 ratio. A further reduction of weight loss to 1.9 % was measured from the 50/50 ratio, while the incorporation of more F into the C (30/70 ratio) resulted in a weight loss of only 1.5 %. In addition, the acid corrosion product brushed off from the top surfaces of all eroded cements was identified as bassanite ($CaSO_4.1/2H_2O$) by XRD.

As a result, the following important statement can be drawn: the HOAp phase, which plays a pivotal role in conferring a good strength and minimum water permeability of the 100/0 ratio cement, is susceptible to reaction with sulfuric acid and sodium sulfate to form crystalline bassanite as the corrosion product. In contrast, the extent of susceptibility of the analcime phase formed in the C/F blend cements to hot strong acid is mush less than that of the HOAp, strongly suggesting that analcime-rich cement has excellent resistance to hot acid.

4. Conclusion

In sodium polyphosphate (NaP)-modified Class C fly ash (C)/Class F fly ash cement systems, the basic nature of C promoted exothermic acid-base reactions with the NaP solution as an acidic cement-forming reactant. This reaction, followed by hydration, at temperature range of 25-100°C, led to the formation of hydroxyapatite [($Ca_3(PO_4)_3(OH)$, HOAp] as the reaction derivative. In contrast, F being acidic underwent no acid-base reaction with the NaP. Correspondingly, the total exothermic energy generated by the acid-base reaction depended on the proportion of C to F; namely, incorporating more F into this cement system reduced the output of reaction energy. The x-ray diffraction analysis for the 250°C-autoclaved cement systems revealed that the NaP preferentially reacted with two chemical ingredients in the C, calcium sulfate and lime to form the HOAp, rather than tricalcium aluminate (C_3A). Thus, autoclaved cement made with a C/F ratio of 100/0 included well-formed HOAp as the major crystalline phase coexisting with two remaining non-reacted reactants, C_3A and quartz. The HOAp phase provided the following three properties needed for geothermal well cement, 1) lowering of porosity, 2) development of good compressive strength, and 3) minimum water permeability. When some amount of C was replaced with F, the analcime ($NaAlSi_2O_6.H_2O$) phase in the zeolitic mineral family was formed as the other crystalline reaction product. Analcime was synthesized by hydrothermal reactions between the Na from NaP and the mullite ($3Al_2O_3.2SiO_2$) in F at 250°C. In fact, the phase composition in cement made with 70/30 ratio consisted of HOAp as the major phase and analcime as the minor phase. The 50/50 ratio cement made by adding more F had two major phases,

HOAp and analcime, and with the 30/70 ratio, the analcime phase became a single major reaction product, while HOAp was poorly formed.

Although the HOAp phase played a pivotal role in conferring good strength and minimum water permeability of the cement, it was susceptible to reactions with sulfuric acid and sodium sulfate, leading to the formation of crystalline bassanite as the acid corrosion products in CO_2-laden H_2SO_4 solution (pH 1.1) at 90°C. In contrast, the extent of susceptibility of the analcime phase formed in the C/F blend cements to hot strong acid was much less than that of the HOAp; therefore, analcime-rich cement displays an excellent resistance to hot acid.

Overall from the viewpoints of having minimum water permeability, a good strength, and a low rate of acid erosion, the most effective C/F ratio cement was 70/30 in this series. Thus, cost-effective acid-resistant geothermal well cement could be formulated by a combination of the coal combustion by-products, C and F.

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Table 1. Formulation of NaP-modified C/F blend and non-blend cements' slurries, and the pH of pore solutions extracted from their slurries.

Formulation, No.	C/F ratio	C, wt%	F, wt%	25% NaP solution, wt%	Water, wt%	Pore solution, pH
Reference 1	-	-	-	100	-	4.90
Reference 2		74.1	-	-	25.9	10.78
Reference 3	-	-	74.1	-	25.9	4.81
1	100/0	66.7	-	33.3	-	6.76
2	90/10	60.0	6.7	33.3	-	6.53
3	70/30	46.7	20.0	33.3	-	6.38
4	50/50	33.3	33.3	33.3	-	6.14
5	30/70	20.0	46.7	33.3	-	5.95

Table 2. Phase compositions for the 250°C-autoclaved phosphate-based cements with C/F ratios of 100/0, 70/30, 50/50, and 30/70.

C/F ratio	Reaction products		Remaining non-reacted reactant
	Major phase	Minor phase	
100/0	HOAp	-	Quartz, C_3A
70/30	HOAp	Analcime	Quartz, C_3A, mullite
50/50	HOAp, Analcime	-	Quartz, C_3A, mullite
30/70	Analcime	HOAp	Quartz, C_3A, mullite

Table 3. Changes in porosity, water permeability, and compressive strength of the 250°C-autoclaved cements as a function of C/F ratio.

C/F ratio	Porosity, %	Water permeability, Darcy	Compressive strength, MPa
100/0	27.5	5.7×10^{-5}	22.3
70/30	33.9	1.2×10^{-4}	20.5
50/50	37.7	8.4×10^{-4}	19.4
30/70	41.6	2.3×10^{-3}	10.0

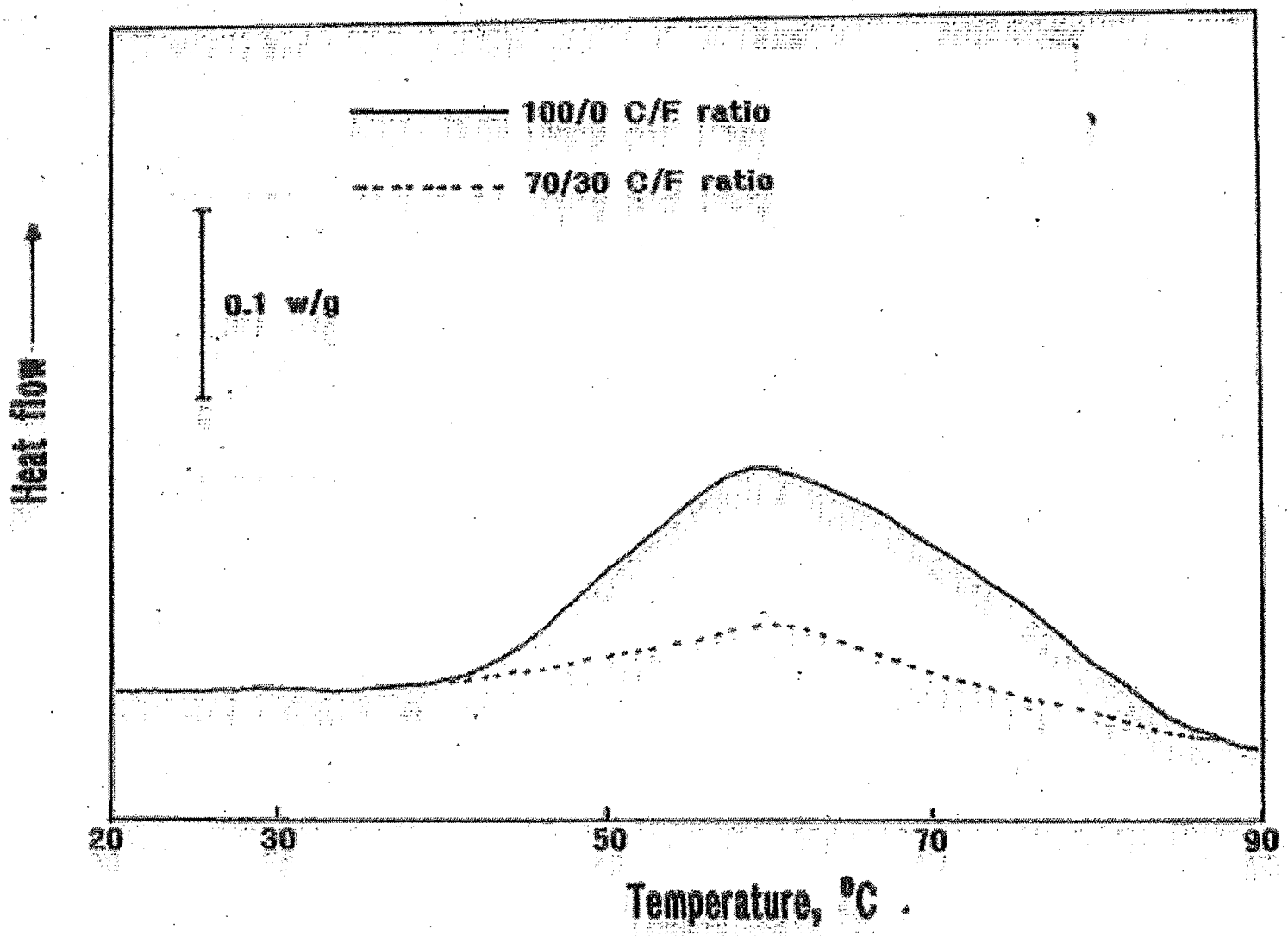

Figure 1. DSC exothermic curves for cement slurries made with C/F ratios of 100/0 and 70/30.

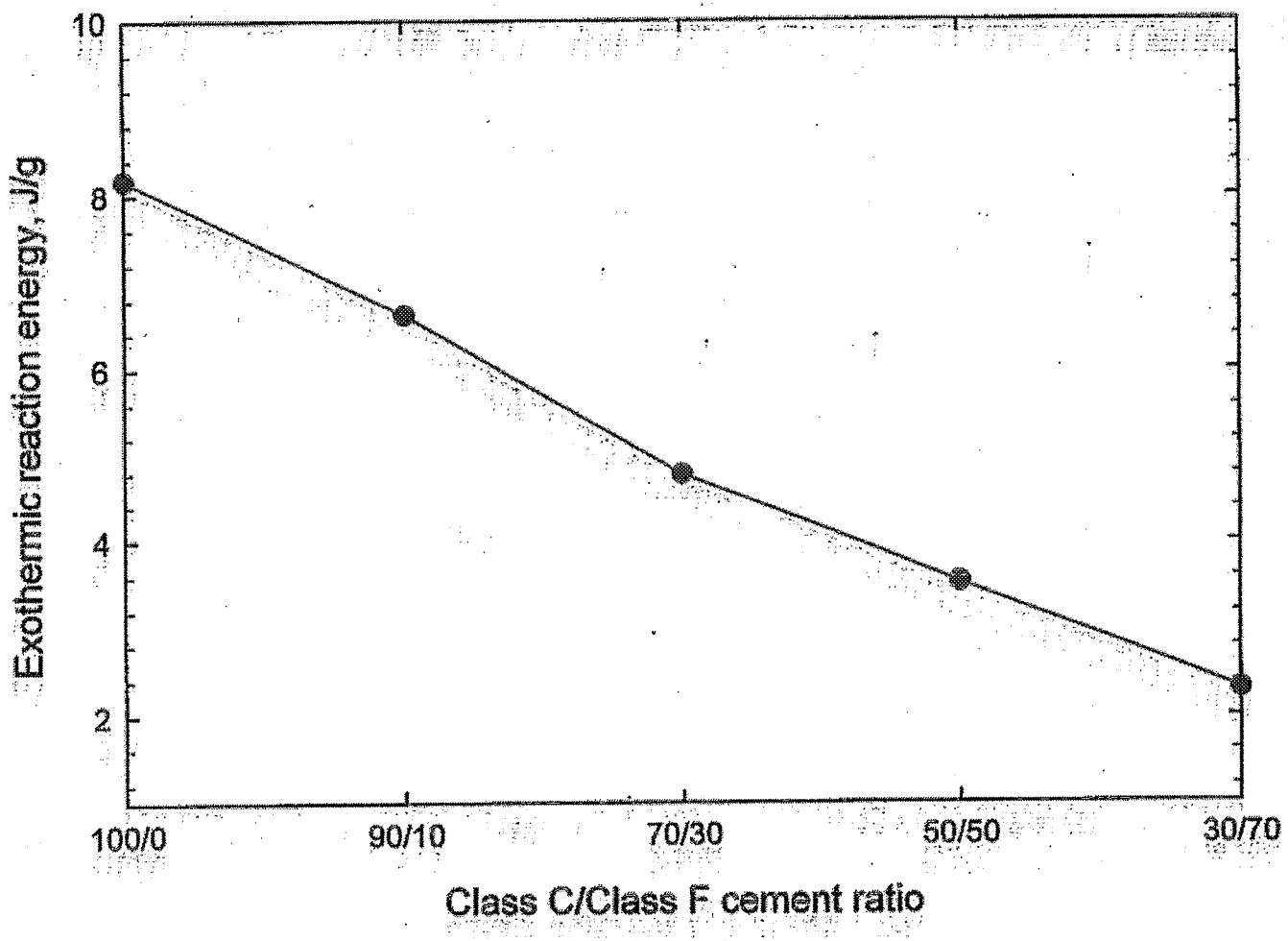

Figure 2. Changes in exothermic reaction energy of cement slurries as a function of C/F ratio.

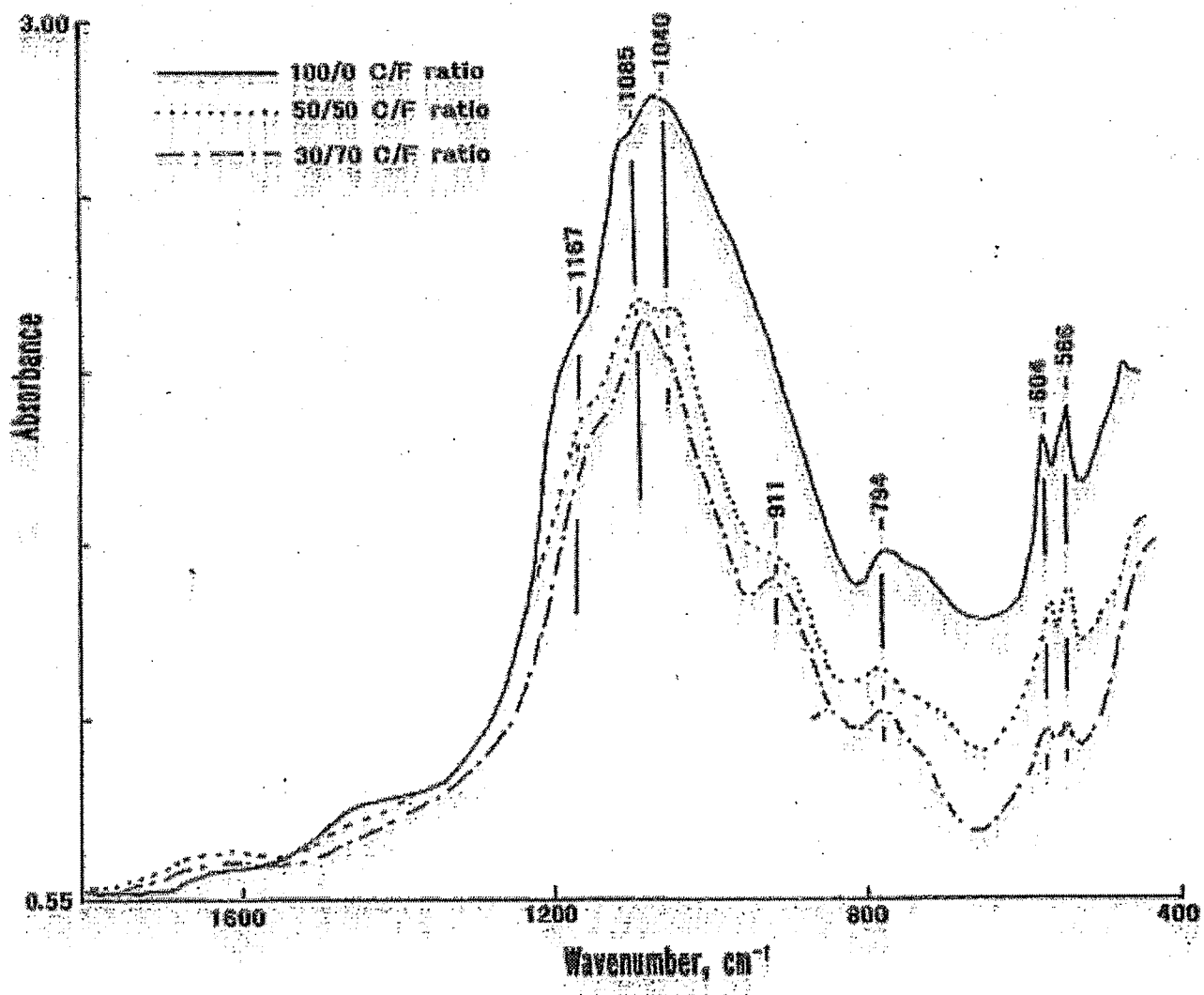

Figure 3. Comparison of FT-IR spectral features for cements made with C/F ratios of 100/0, 50/50, and 30/70.

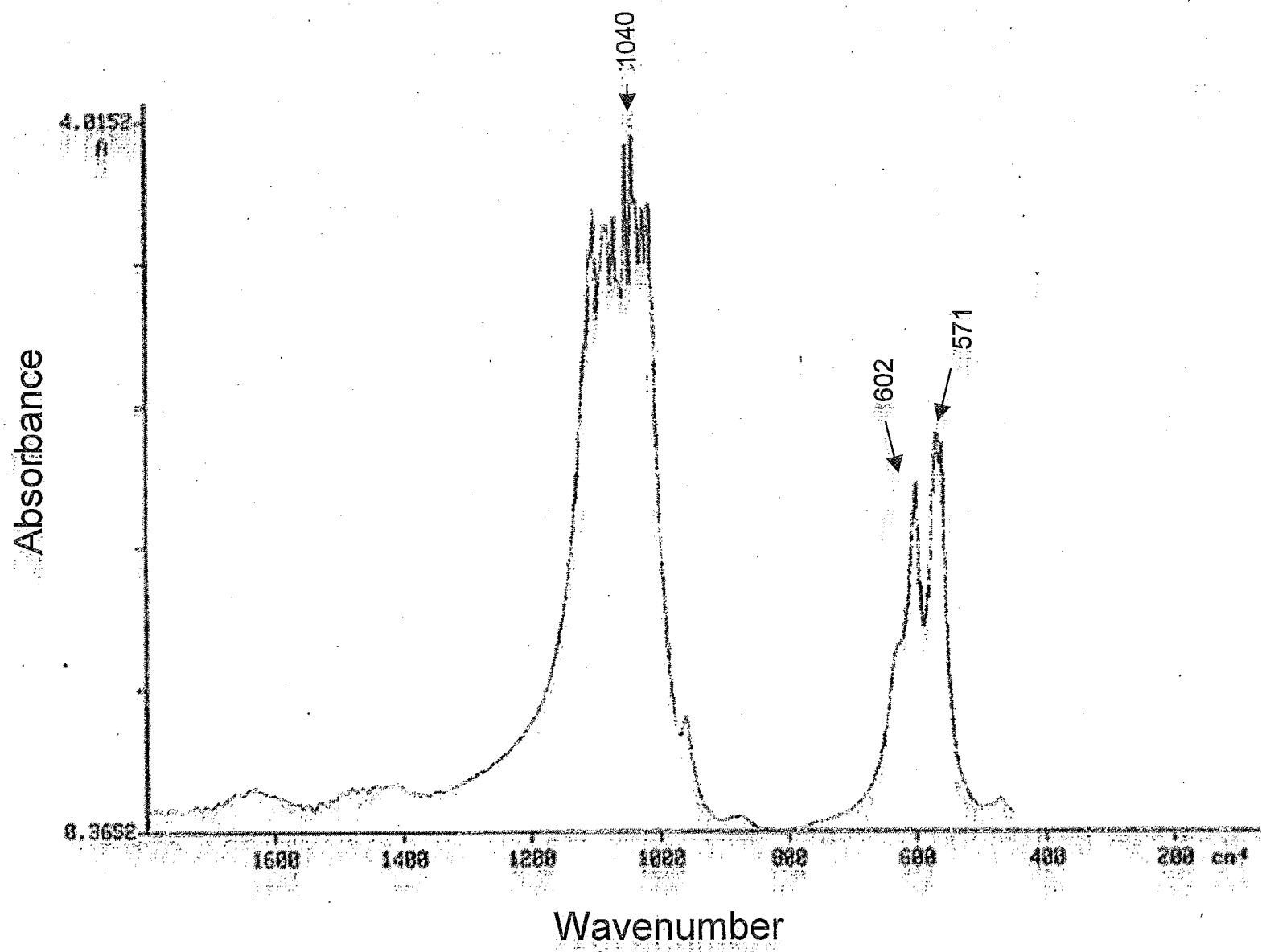

Figure 4. FT-IR spectrum of HOAp reference sample.

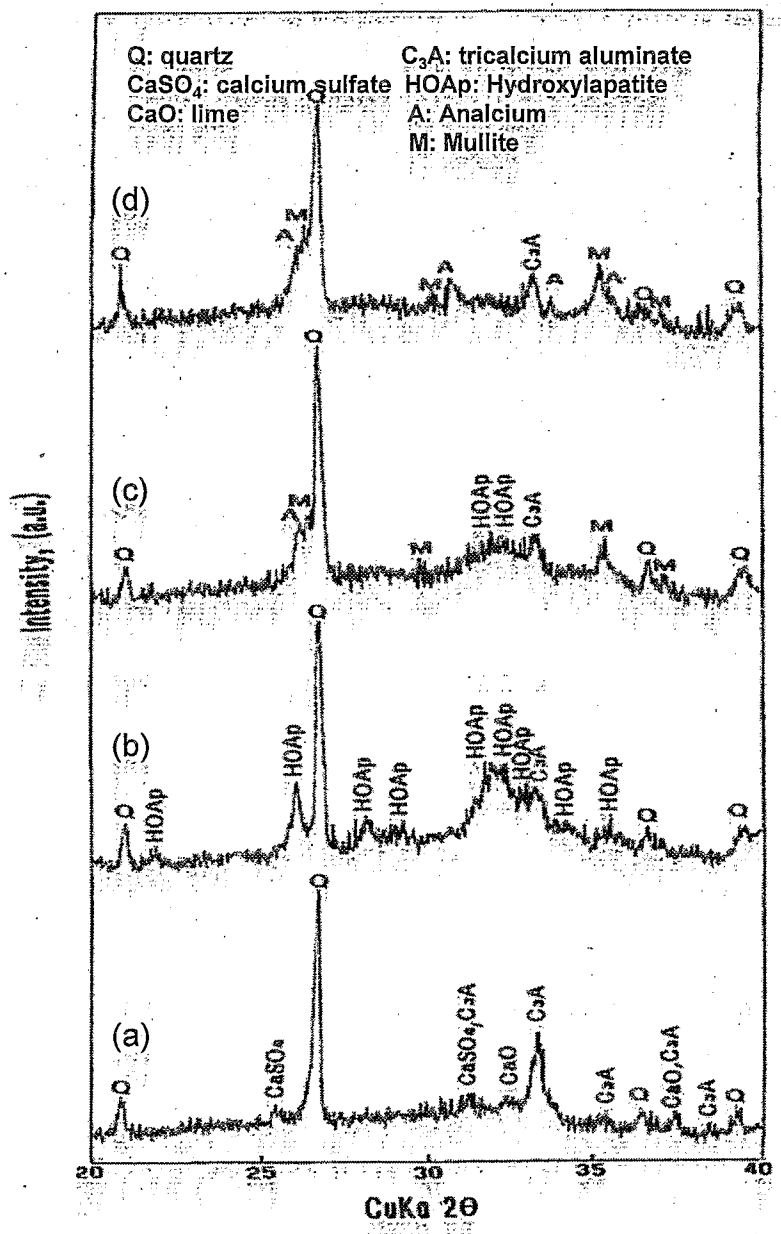

Figure 5. XRD patterns for (a) Class C fly ash, and (b)100/0-, (c) 50/50-, and, (d) 30/70-ratio C/F cements after autoclaving at 250°C.

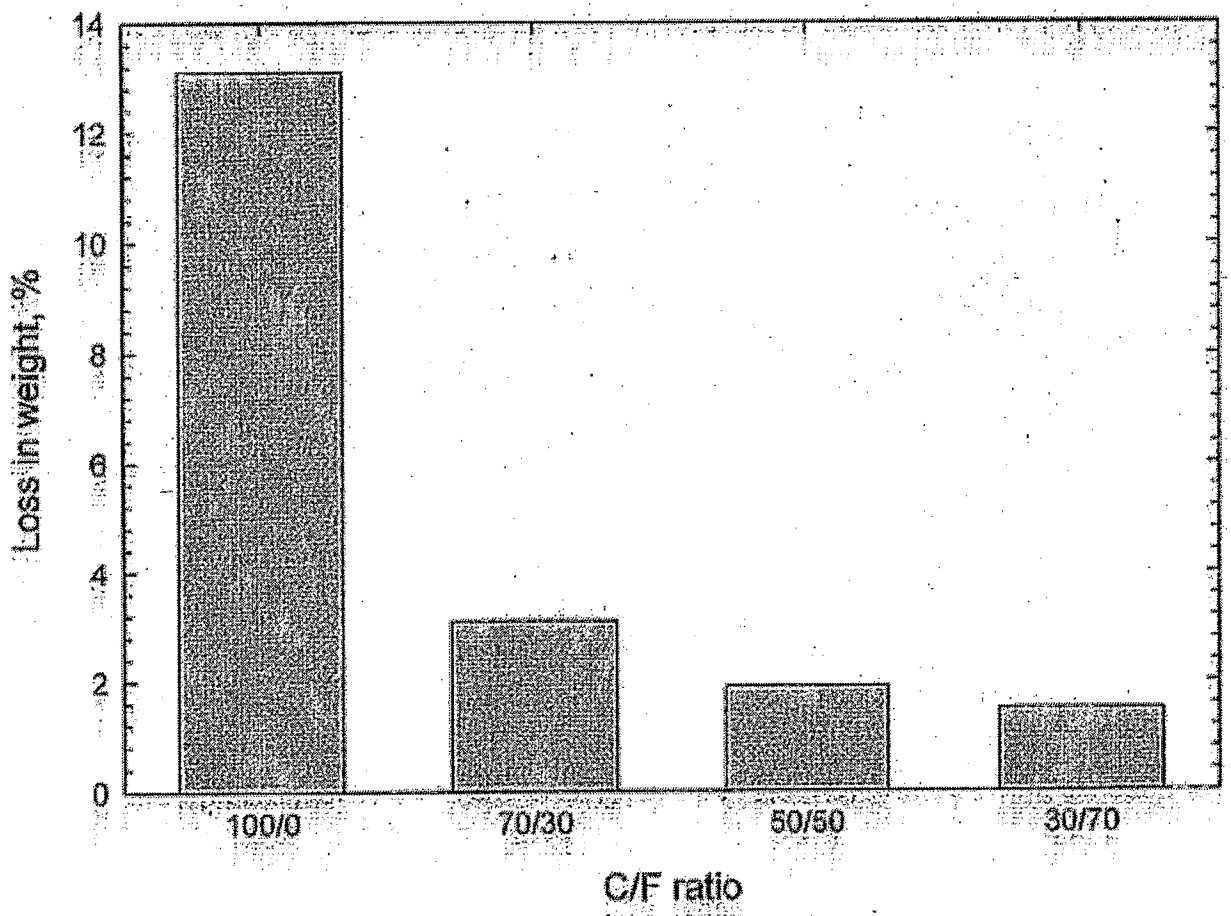

Figure 6. Acid erosion of autoclaved cements made with 100/0-, 70/30-, 50/50-, and 30/70-C/F ratios after exposure for 15 days to CO_2-laden H_2SO_4 solution (pH, 1.1) at 90°C.