

# Solidification/stabilization of a synthetic electroplating sludge in cementitious binders containing NaOH

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## Abstract

Solidification/stabilization of a highly concentrated synthetic electroplating waste sludge by cementitious mixtures containing NaOH was studied. The sludge contained 86.2 mg/g Ni, 84.1 mg/g Cr, 18.8 mg/g Cd, and 0.137 mg/g Hg and before mixing was dewatered to 25% solids. It was stabilized by ordinary Type I portland cement (OPC), an OPC/Class F fly ash mixture (referred to as CFA), and a lime/Class C fly ash mixture (referred to as LFA). Mix ratios of OPC: sludge of 0.3:1, OPC:fly ash:sludge of 0.2:0.5:1, and lime:fly ash:sludge of 0.3:0.5:1 were used, respectively. NaOH was added to each mix at 0 (control sample), 2, 5 and 8% by weight of solidified binder. A set of binder samples without sludge, but containing 8% NaOH, was also prepared. The microstructure, microchemistry, and component phases present in the binders after curing were determined by scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffractometry. The chemical species present in the sludge were not significantly affected by the high pH produced by NaOH; the sample showing the least effect was CFA/sludge. Ettringite was formed in CFA/sludge samples containing up to 5% NaOH, and in CFA/sludge and LFA/sludge containing up to 2% NaOH. NaOH reacted with the binders to produce phases containing Na plus minor amounts of Cr and Ni.

## 1. Introduction

The disposal of hazardous wastes in cementitious binders is common practice [1] and is called solidification/stabilization (S/S). The cementitious binder is usually ordinary Type I portland cement (OPC), but additives such as Class F fly ash, Class C fly ash, and lime are also used. Solidification/stabilization is particularly attractive for heavy-metal wastes which precipitate as insoluble hydroxides when in pH environments such as those produced by lime or hydrating cement.

Recently, Roy et al. [2–4] studied S/S of a synthetic heavy metal waste in three cementitious binders: OPC, OPC and Class F fly ash mixtures (CFA), and

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lime and Class C fly ash mixtures (LFA). Wastes containing nitrates of Ni, Cr, Cd, and Hg were pre-treated with lime to induce precipitation. The sludge contained complex, impure salts of the heavy metals, which is not surprising as heavy metal-lime mixtures contain other anions apart from hydroxides (such as nitrates from the waste and carbonates from atmospheric carbon dioxide [4]). The synthetic (pre-treated) sludge formed a simple mixture of sludge and binder (for example, sludge and OPC). Thus physical encapsulation was the principal mechanism of S/S when a lime-treated heavy metal waste was mixed with a cementitious binder.

A waste stream from an industrial facility usually contains more than one component, and mixing of several waste streams can create very complex mixtures. NaOH is such a common wastewater treatment material that its presence in waste streams is not unusual. When the pH increases beyond 10, the solubility of many metals increases [5]. As NaOH can drastically affect the pH of a system, the leaching rates of many metals are expected to increase if NaOH is present in appreciable amounts. In addition, NaOH can affect the unconfined compressive strength of cementitious binders by interfering with the setting process [6].

The present study reports the results of a microstructural and microchemical study of the solidification/stabilization of a synthetic electroplating sludge (EPA classification F006, 40 CFR 261.31) containing Ni, Cr, Cd, and Hg. Solidification/stabilization was promoted by OPC, an OPC/Class F fly ash mixture, and a lime/Class C fly ash mixture; furthermore, all were solidified with varying amounts of NaOH added to the mixture as an interference compound.

## 2. Experimental procedure

A synthetic, heavy-metal sludge was prepared by adding lime to water containing nitrates of Cr, Ni, Cd, and Hg. The sludge was dewatered to 25% solids, poured into three 567 L (150 gallon) drums, and mixed with OPC, CFA, or LFA (see Table 1). Water, necessary for the hydration of binders, only came from sludge.

Details of the preparation of the sludge were discussed by Cullinane et al. [7]. Sludge was mixed with each binder, divided into four subequal parts, and NaOH was added at concentrations of 0, 2, 5, and 8% by weight of binder and sludge. Samples of binders with 8% NaOH, but without sludge, were prepared for comparison. After curing from six months to one year, each sample was studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffractometry (XRD) using methods which were previously described [8, 9]. Scanning electron microscopy and semiquantitative energy dispersive X-ray analysis were performed with an ISI-60A scanning electron microscope equipped with an EDAX 9100 energy dispersive X-ray spectrometer. The SEM samples were coated with gold, and EDX samples were coated with carbon.

TABLE 1

Solidification/stabilization mixtures<sup>a</sup>

Binder	OPC	CFA	LFA
Sludge <sup>b</sup>	Ni-86.2 mg/g, Cr-84.1 mg/g, Cd-18.8 mg/g, Hg-0.137 mg/g Sludge was dewatered to 25% solids		
Binder/sludge ratio	0.3:1 (OPC:sludge)	0.2:0.5:1 (OPC:fly ash:sludge)	0.3:0.5:1 (Lime:fly ash:sludge)
Liquid/binder ratio <sup>c</sup>	2.5	1.07	0.94
NaOH	0, 2, 5, and 8%	0, 2, 5, and 8%	0, 2, 5, and 8%

<sup>a</sup> See Cullinane et al. [7] for details of sample preparation.<sup>b</sup> Wet weight before dewatering.<sup>c</sup> Calculated on the basis that the sludge is 75% liquid.

TABLE 2

Symbols used for phases identified in XRD patterns

Symbol	Name and chemical formula
A	Alumina (Al <sub>2</sub> O <sub>3</sub> )
Cc	Calcium carbonate (CaCO <sub>3</sub> )
CAH	Calcium aluminate hydrate (xCaO·zAl <sub>2</sub> O <sub>3</sub> ·yH <sub>2</sub> O)
CH	Calcium hydroxide (Ca(OH) <sub>2</sub> )
C <sub>2</sub> S	Dicalcium silicate (2CaO·SiO <sub>2</sub> )
C <sub>3</sub> S	Tricalcium silicate (3CaO·SiO <sub>2</sub> )
Et	Ettringite (3CaO·Al <sub>2</sub> O <sub>3</sub> ·3CaSO <sub>4</sub> ·Al <sub>2</sub> O <sub>3</sub> ·32H <sub>2</sub> O)
Gyp	Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)
Mag	Magnetite (Fe <sub>3</sub> O <sub>4</sub> )
Ml	Melilite (a solid solution between two end members, Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> and Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub> )
Ms	Monosulfate (3CaO·Al <sub>2</sub> O <sub>3</sub> ·CaSO <sub>4</sub> ·13H <sub>2</sub> O)
Mu	Mullite (3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> )
Pe	Periclase (MgO)
Qu	Quartz (SiO <sub>2</sub> )
Sp	Spinel ((Mg,Cr,Fe)AlO <sub>4</sub> )

<sup>a</sup> Cement chemist's notation: A = Al<sub>2</sub>O<sub>3</sub>; C = CaO; S = SiO<sub>2</sub>; H = H<sub>2</sub>O.

X-ray diffractometry (XRD) was performed on samples which were ground in porcelain or agate mortars. Very few samples could be sieved because of a high moisture content. Patterns by XRD were obtained with a Scintag Pad-V automated diffractometer using Cu K<sub>α</sub> radiation. The operating conditions for X-ray examinations were: 45 keV accelerating voltage, 35 mA current, 3 to 70° 2θ scanning range, 0.02° step-width, and a minimum of 3 s counting time or 3,000 counts. The widths of slits positioned before the sample were 2° and 4°,

and those after the sample were  $0.5^\circ$  and  $0.3^\circ$ . The sample holder was spun on its vertical axis to minimize the effects of compositional heterogeneity, grain size, orientation, and texture. Synthetic corundum ( $5\ \mu\text{m}$ ) and quartz from fly ash were used as internal standards in sludge and fly-ash-containing binders, respectively. Abbreviations used for phases identified in XRD patterns and their chemical composition are given in Table 2.

### 3. Results

#### 3.1 Type I portland cement

At low magnifications ( $100\text{--}1000\times$ ), OPC/sludge had a slightly granular appearance. Rounded grains, tens of micrometers in diameter, were common. The grains were often surrounded by a void space and the number of grains per unit volume of matrix increased as the NaOH concentration increased. Samples containing 2% NaOH also showed a granular matrix, and contained small, stubby ettringite needles and a phase in the form of hexagonal plates. As the concentration of NaOH exceeded 2%, ettringite disappeared, but the concentration of hexagonal platelets increased. At increased NaOH concentrations, an additional phase, in the form of flat, elongated platelets, was observed as shown in Fig. 1.

In the absence of sludge, OPC with 8% NaOH contained randomly oriented layers, consisting of thin crystalline plates tens of micrometers in width. Particles with an elliptical core were also observed, as shown in Fig. 2.

An energy dispersive X-ray (EDX) analysis of C–S–H in OPC is shown in Fig. 3(a). Calcium and Si were the principal elements, but minor amounts of Fe, K, and Al were also present. Elements lighter than Na could not be detected by EDX. Figure 3(b) is an analysis of crystalline plates in OPC containing 8%

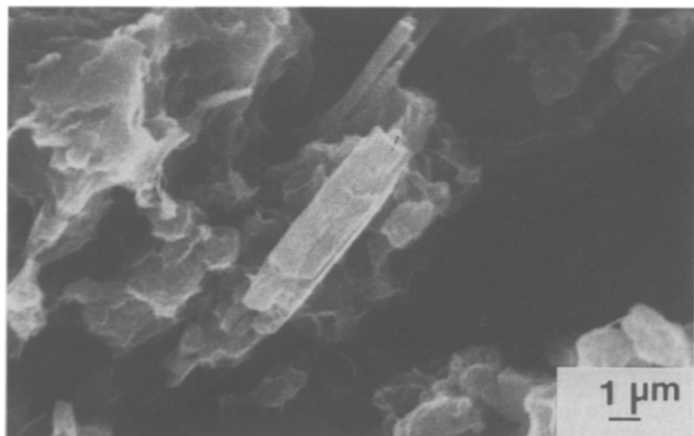


Fig. 1. OPC with sludge and 5% NaOH. A crystalline form with elongated tabular shape.

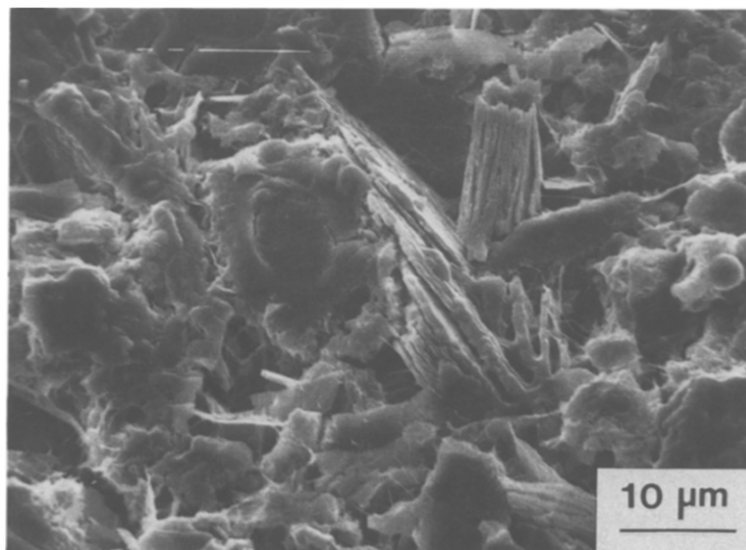


Fig. 2. OPC containing 8% NaOH, without sludge. Thick stacks of platelets are present.

NaOH but no sludge. The same sample is shown in Fig. 2. The plates were calcium silicate containing Na.

An analysis of an ellipsoidal particle from an OPC/sludge sample containing 0% NaOH is shown in Fig. 3(c). Ca, Cr, Ni, and Si were the principal elements. Aggregates of elongated platelets, similar to those seen in Fig. 1 from OPC/sludge samples containing 5% NaOH, were calcium aluminosilicates with minor amounts of S. No waste elements were detected, as seen in Fig. 3(d), but the ellipsoidal particles in OPC/sludge containing 8% NaOH contained highly variable amounts of Ni and Cr as shown in the spectra of Figs. 3(e) and 3(f).

Figure 4 shows XRD patterns from (a) sludge, (b) hydrated OPC, (c–f) OPC/sludge samples containing 0 to 8% NaOH, and (g) OPC containing 8% NaOH but no sludge. The patterns contained several peaks, but only  $\text{CaCO}_3$  and  $\text{Ca(OH)}_2$  could be identified with certainty. Heavy metals existed as impure complexes [4]. The OPC pattern, Fig. 4(b), showed peaks from the expected hydration products of OPC, including  $\text{Ca(OH)}_2$  and ettringite.  $\text{Ca(OH)}_2$  was present in all OPC/sludge samples, regardless of the amount of NaOH. Some di- and tri-calcium silicates were also present. Ettringite was not detected when the NaOH concentration exceeded 2%; but when ettringite was absent, gypsum was present. The amount of calcite varied from sample to sample.

The most intense peak in pure sludge occurred at 0.781–0.750 nm, and was present in all sludge/OPC samples. A 0.863 nm sludge peak was strongest in control samples (0% NaOH), but absent in others. Two peaks, at 0.438 and 0.292 nm, were found only in the control sample, and peaks at 1.247–1.043 nm were also observed.

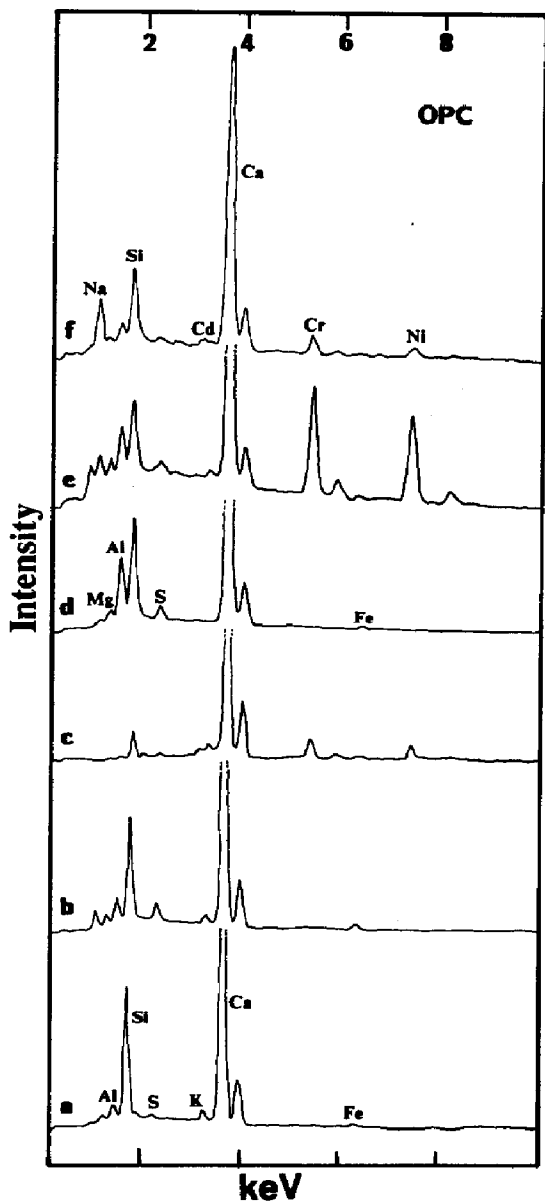


Fig. 3. EDX of (a) OPC, (b) OPC containing 8% NaOH, (c) OPC/sludge containing 0% NaOH, (d) OPC/sludge containing 5% NaOH, and (e-f) OPC/sludge containing 8% NaOH.

An elongated, tabular crystalline phase was observed in the OPC/sludge sample containing 5% NaOH. Large hexagonal plates in OPC/sludge samples containing 8% NaOH were identified as  $\text{Ca}(\text{OH})_2$ . These plates were frequently observed.

The microstructure of OPC containing 8% NaOH differed from the microstructure in samples containing sludge. It was dense, layered, homogeneous, and did not contain detectable amounts of ettringite. Layering was produced by stacks of calcium aluminosilicate sheets, tenths of a micrometer thick. The abundance of calcium silicate grains surrounded by prominent reaction rims suggested that NaOH retarded the hydration of OPC.

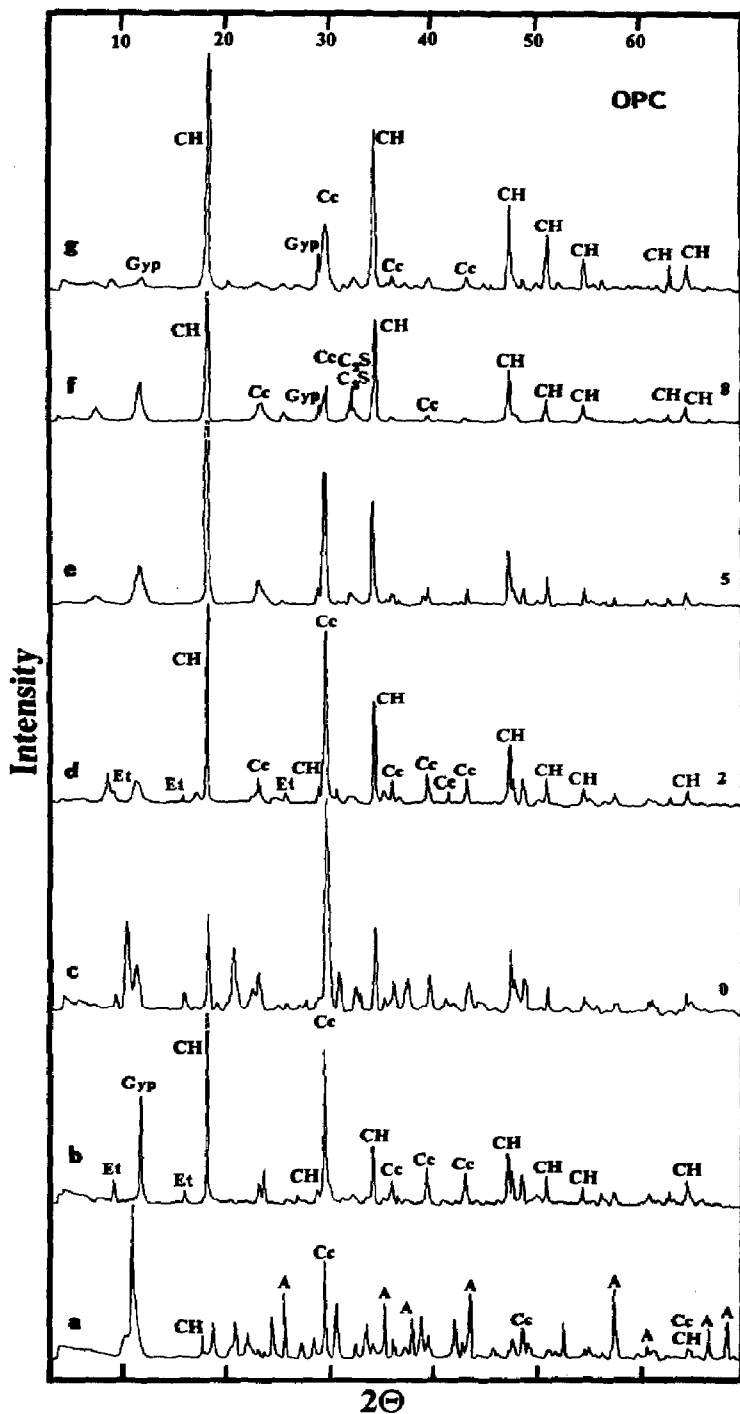


Fig. 4. XRD patterns of (a) the sludge, (b) OPC, (c-f) OPC/sludge containing 0 to 8% NaOH, and (g) OPC with 8% NaOH.

### 3.2 Type I portland cement and Class F fly ash (CFA)

The bulk matrix of CFA/sludge was massive and crudely layered. Fly ash spheres, easily recognizable in all samples, showed reaction to widely varying degrees with some ash completely reacted leaving only highly inert phases

such as mullite or quartz. Thin hexagonal plates, tens of micrometers in diameter, were common in CFA/sludge samples containing no NaOH, but the number of such plates was less in samples containing 2% NaOH.

Additional crystalline phases were found in CFA/sludge samples containing 5 and 8% NaOH. One phase, shown in Fig. 5, was fibrous and grew in radial bundles perpendicular to the wall of spherical cavities. Another was blocky and equ-dimensional, with partially developed octahedral faces. These phases were usually found in the cavities. Ellipsoidal particles, as long as 100  $\mu\text{m}$  along the long axis and 30–40  $\mu\text{m}$  along the short axis, were common in all samples, particularly those containing 2%, or more, NaOH. The particles were morphologically different from the surrounding matrix, composed of finely crystalline materials, surrounded by a thin void rim. Class F fly ash containing 8% NaOH had more hexagonal plates, in parallel stacks or in a honeycomb pattern, as shown in Fig. 6.

Energy dispersive X-ray analyses of fly ash spheres indicated that they were a form of calcium aluminosilicate with variable, but minor, amounts of Cr and Ni. The new phases described above were also calcium aluminosilicates, and their compositions were similar to the composition of fly ash. Nickel and Cr were also present in the matrix at low levels.

X-ray diffraction patterns of (a) sludge, (b) Class F fly ash, (c) CFA, (d–g) CFA/sludge with increasing amounts of NaOH, and (h) CFA containing 8% NaOH are shown in Fig. 7. The phases identified from XRD patterns of CFA/sludge containing 0 to 8% NaOH were of four types: (1) phases found in Class F fly ash; (2) hydration products of OPC and fly ash; (3) phases associated with pure sludge; and (4) reaction products due to the presence of

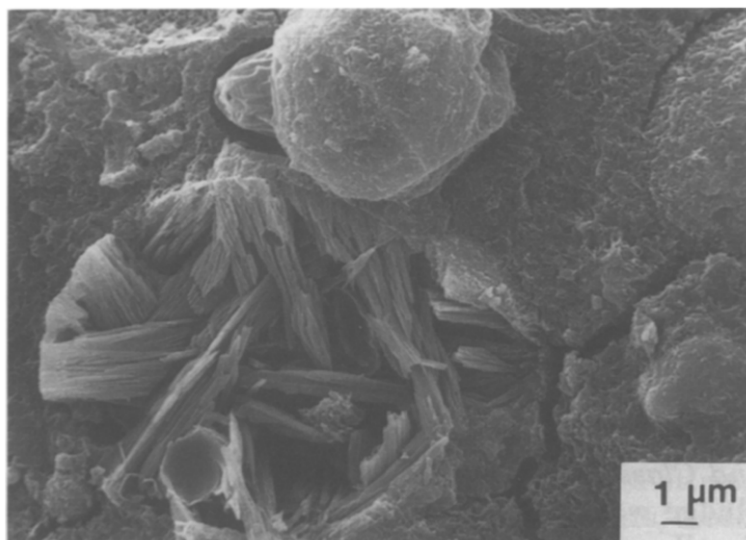


Fig. 5. CFA/sludge with 8% NaOH. A closeup of the fibrous form seen in the 5% sample.



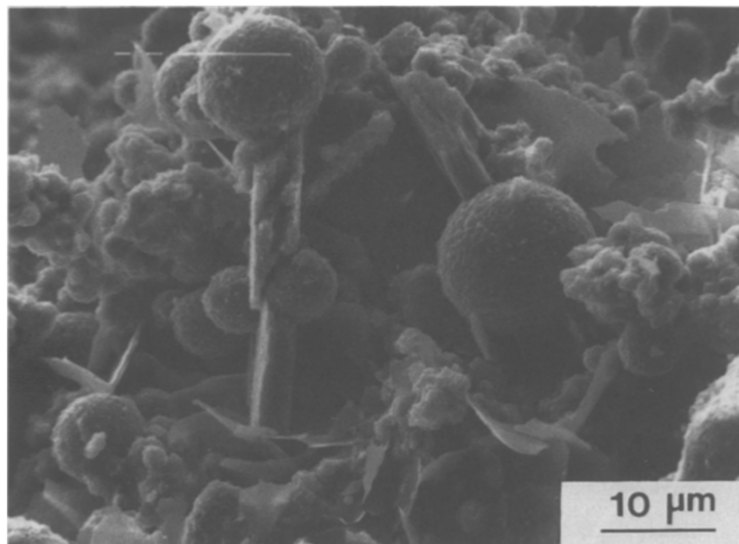


Fig. 6. CFA containing 8% NaOH. Fly ash spheres surrounded by reaction products were common. A hexagonal platelike form was also found.

NaOH. Quartz, mullite, magnetite or hematite, came from the fly ash. In all CFA/sludge samples  $\text{Ca}(\text{OH})_2$ , common in hydrated portland cement, was absent. Ettringite was observed in all CFA/sludge samples except those containing 8% NaOH. Calcium silicates from OPC were found in most samples. A few new, unidentifiable peaks, such as 0.411 and 0.317 nm, were observed in CFA/sludge 8% NaOH. In contrast to CFA/sludge, CFA containing 8% NaOH contained  $\text{Ca}(\text{OH})_2$ , and gypsum was present instead of ettringite (Fig. 7h).

### 3.3 Lime and Class C fly ash

The matrix of LFA/sludge was composed of randomly oriented platelets. The boundaries (crystal edges) of the platelets were sharper as the NaOH concentration increased. Fly ash spheres were sometimes surrounded by a distinct reaction product which grew radially, as shown in Fig. 8. Two additional phases were present in LFA/sludge containing 5 and 8% NaOH: thin and tabular crystals with wavy boundaries shown in Fig. 9; and elongated, tabular crystals with prismatic and pyramidal faces shown in Fig. 10. LFA containing 8% NaOH, but without the sludge, was composed of abundant hexagonal platelets a few micrometers in diameter (Fig. 11). Random orientation of these platelets produced a honeycomb structure. The fly ash spheres often merged into the matrix due to their high reactivity, but a few unreacted ones remained.

An analysis of a hexagonal plate from LFA is shown in Fig. 12(a). The analysis shows that the plates were calcium aluminosilicates. Figure 12(b) shows an analysis of a similar hexagonal plate from LFA containing 8% NaOH. Calcium was partially replaced by Na. Furthermore, EDX indicated that Na was uniformly distributed throughout LFA containing 8% NaOH.

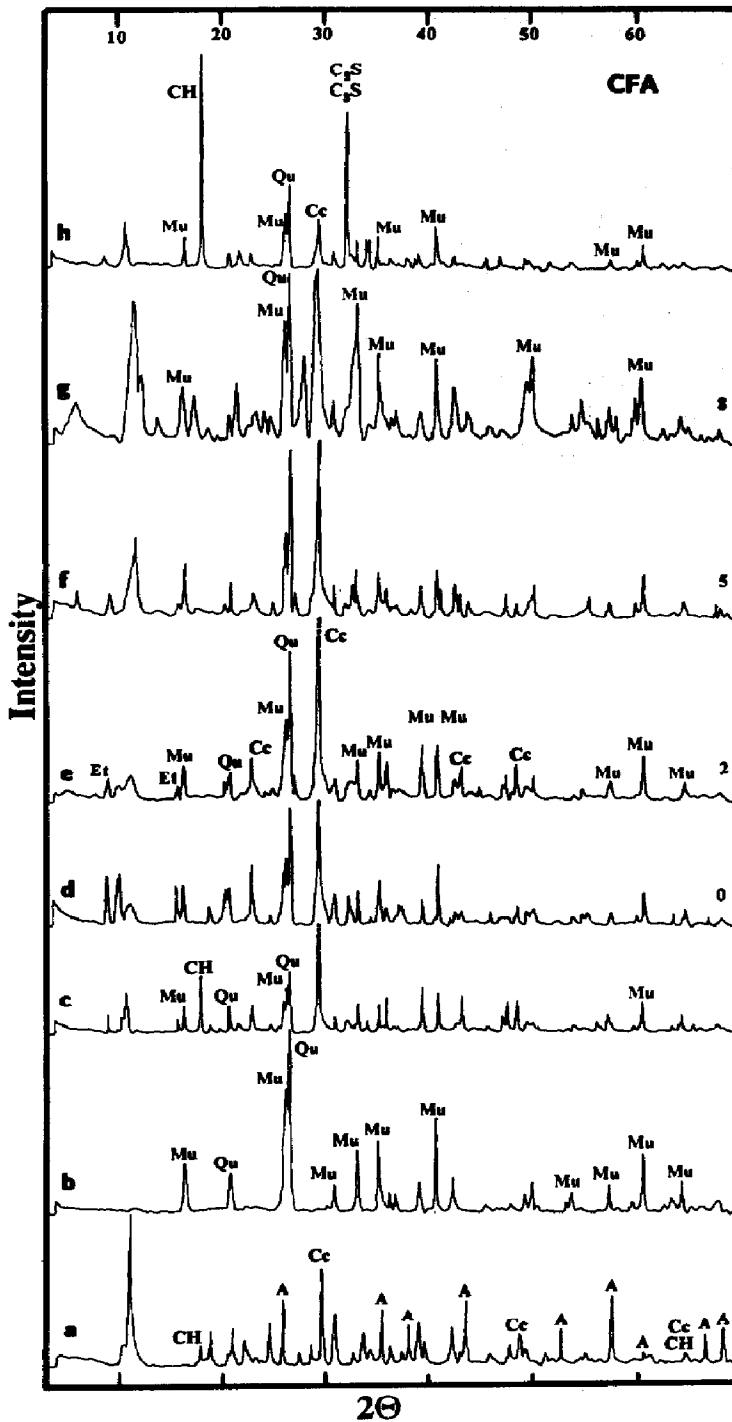


Fig. 7. XRD patterns of (a) the sludge, (b) Class F fly ash, (c) CFA, (d-g) CFA/sludge containing 0 to 8% NaOH, and (h) CFA with 8% NaOH.

Figure 12(c) shows an analysis of the radial reaction products around a fly ash sphere from LFA/sludge containing 2% NaOH, similar to Fig. 8. The radial crystallites were also calcium aluminosilicate, but containing Ni and Cr. An analysis of the platy matrix from LFA/sludge containing 5% NaOH is shown in Fig. 12(d). Figure 12(e) through 12(g) show analyses of the tabular crystalline

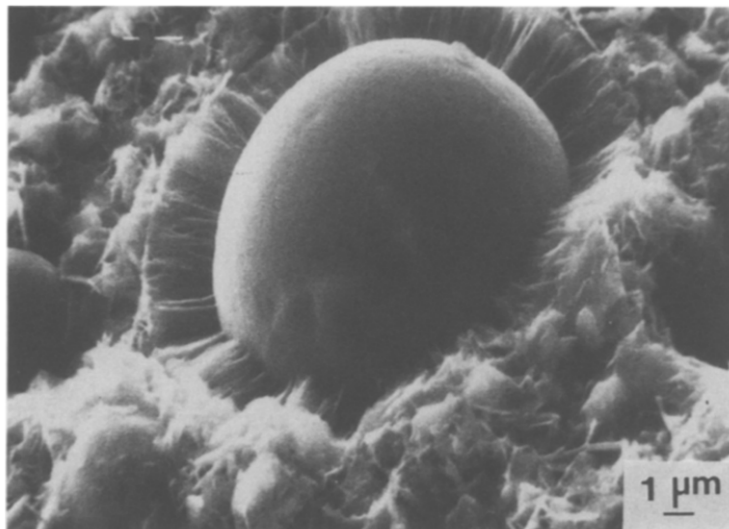


Fig. 8. LFA/sludge containing 2% NaOH. Fly ash spheres surrounded by radial reaction products.

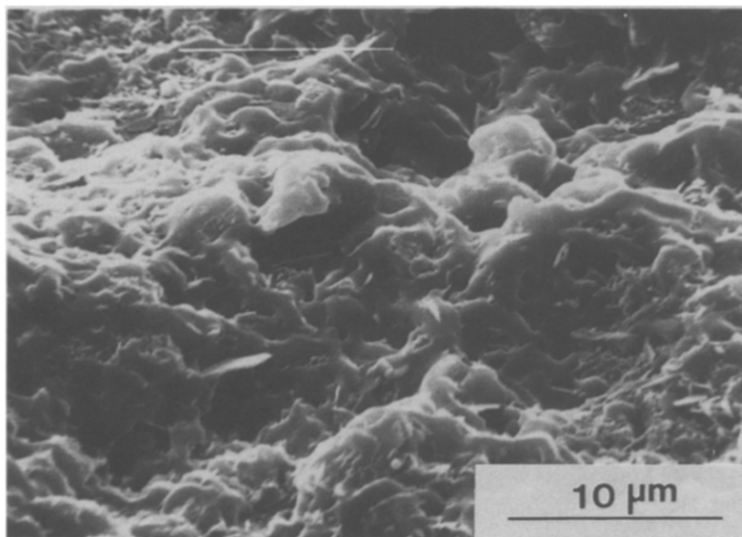


Fig. 9. LFA/sludge containing 5% NaOH. A new crystalline form with wormy boundaries.

phase observed in LFA/sludge containing 8% NaOH (as shown in Fig. 10). Energy dispersive X-ray analysis of fly ash spheres indicated that they were calcium aluminosilicates, overlapping in composition with the matrix platelets. Minor, but variable, quantities of Cr and Ni were always present.

X-ray diffraction patterns of the (a) sludge, (b) Class C fly ash, (c) LFA, (d-g) LFA/sludge containing increasing amounts of NaOH, and (h) LFA containing 8% NaOH are shown in Fig. 13. Quartz, periclase, melilite, anhydrite, and magnetite were identified in the XRD pattern of the Class C fly ash (Fig. 13(b)).

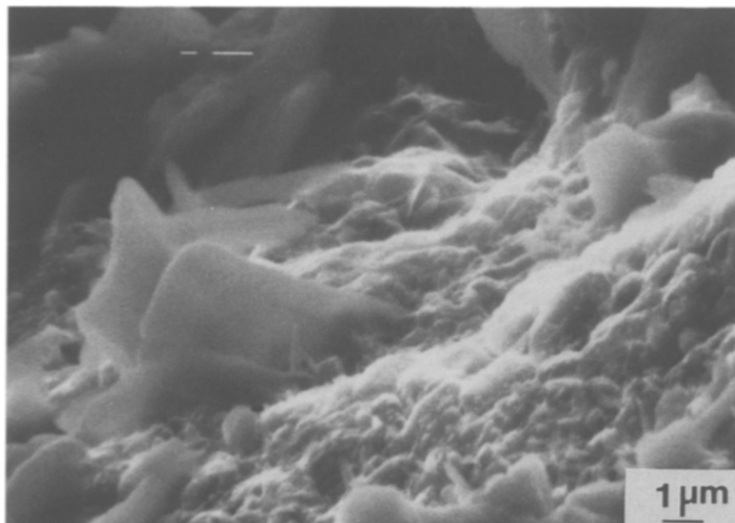


Fig. 10. LFA/sludge containing 8% NaOH. A new crystalline form with a flat, tabular shape.

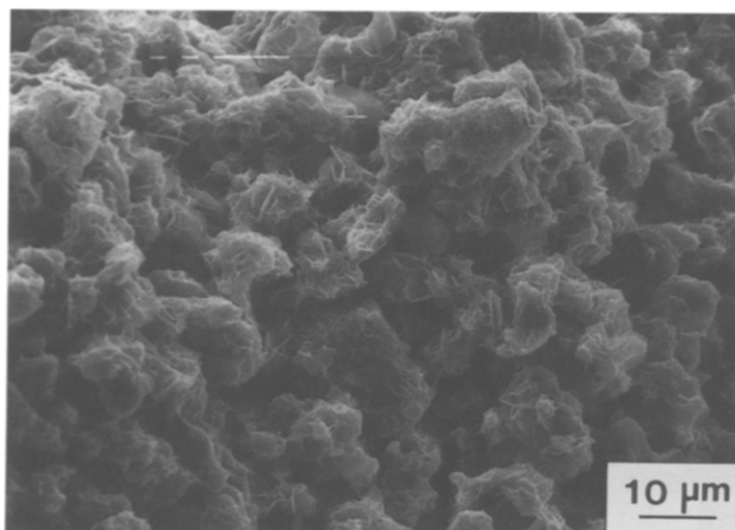


Fig. 11. LFA containing 8% NaOH. Abundant platelets are found in the matrix.

The phases identified in LFA/sludge containing increasing amounts of NaOH were of three types: (1) binder material, lime and Class C fly ash; (2) hydration products; and (3) the sludge. Lime, quartz, periclase, and some form of iron oxide were present in the binder. Gypsum was present, and ettringite absent when the NaOH concentration was 5% or greater. Strätlingite was found in LFA/sludge containing 5 or 8% NaOH. Several sludge peaks could be identified in each pattern. In the 8% sample, new peaks appeared at 1.280 and 0.505 nm. The amount of calcite was variable.

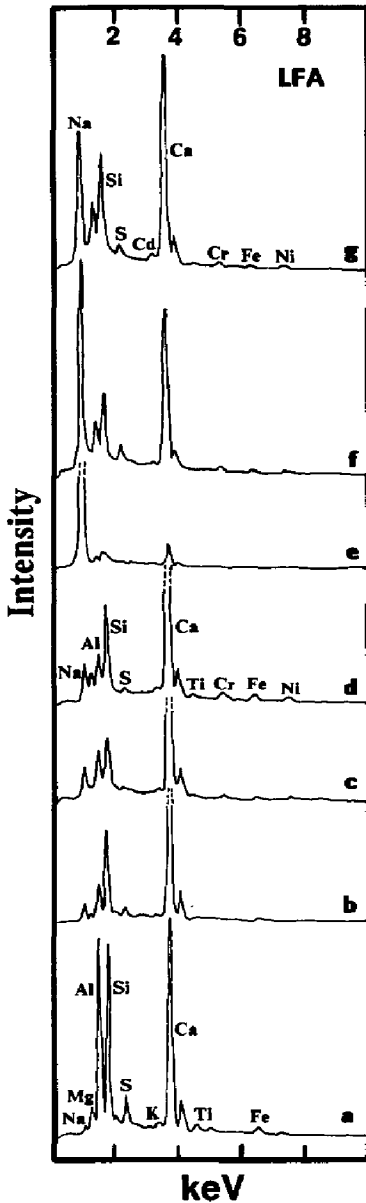


Fig. 12. EDX of (a) LFA, (b) LFA containing 8% NaOH, (c) radial reaction products of fly ash from LFA/sludge containing 2% NaOH, (d) plate-like matrix from LFA/sludge containing 5% NaOH, and (e-g) tabular crystalline form from LFA/sludge containing 8% NaOH.

#### 4. Discussion

Hydration of a cement or a pozzolanic mixture is affected by the presence of many inorganic and organic compounds [10], commonly called interference compounds. Davies and Alexander [6] reported that when the alkali content in OPC increased from 0.15 to 2.8% (by weight), the unconfined compressive strength was reduced by more than 50%. Dorsch [11], in contrast, found that the strength of certain OPC/sand mortars was not significantly affected by the addition of a 10% NaOH solution. The effect of an interfering compound on the

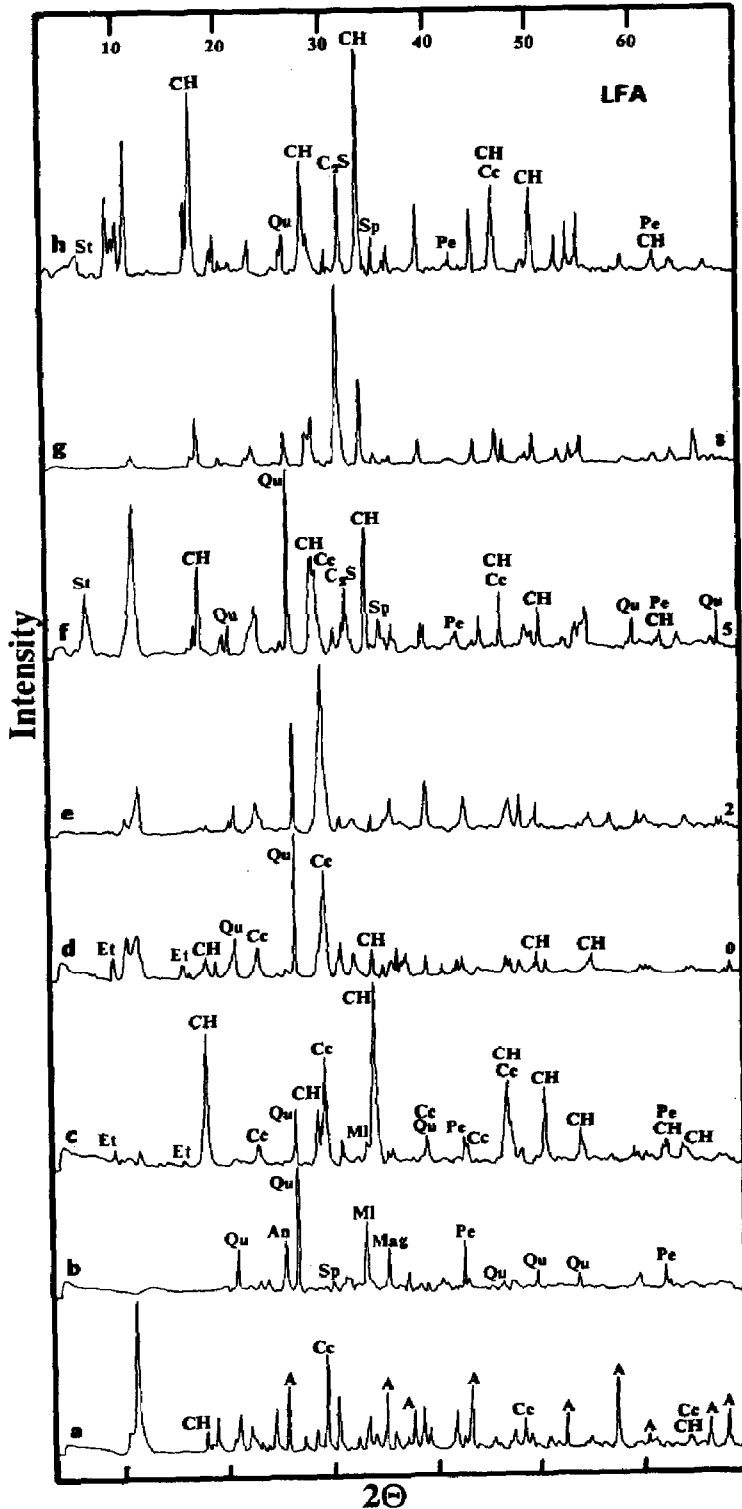


Fig. 13. XRD patterns of (a) the sludge, (b) Class C fly ash, (c) LFA, (d-g) LFA/ sludge containing 0 to 8% NaOH, and (h) LFA containing 8% NaOH.

unconfined compressive strength of a S/S binder is of lesser importance since a commercial vendor usually anticipates a decrease in strength, and therefore, increases the amount of binder. Previous studies of S/S usually considered a model system of a binder and a simple waste, but the effects of other compounds present in a complex waste stream on S/S of metals has not been satisfactorily evaluated. Roy et al. [12] recently presented the results of a study which evaluated the effect of sodium sulfate on the same electroplating waste-binder systems used in this study. They found that physical encapsulation was the dominant mechanism of S/S, and that the interfering compound only affected the binders. Similar to the Na sulfate study, the effect of NaOH on S/S of a synthetic electroplating waste in these binders can be discussed separately in terms of its effect on the binders and the waste.

A considerable body of work exists on the effect of alkalis in cement [13]. Excess alkalis in cement dissolve in the pore water and the resultant pH is in the range 13 to 14 [14]. Way and Shayan [15] from their experiments found that the pH of the extracted aqueous phase was proportional to the amount of NaOH added to the mixing water and the concentration of the  $\text{OH}^-$  ions was 1750 mmol/kg after 20 hours when 4.5 M sodium hydroxide mixing solution was used. If NaOH added to the cementitious binders is first dissolved in water and then mixed, the pH of that water for OPC, CFA, and LFA containing 8% NaOH, without sludge, is about 14.17, 14.14, and 14.21, respectively. The exact pH of the sludge-containing binders cannot be predicted, as some complexation is likely to take place. The solubility-pH relationship of most metals suggests that they should redissolve in the pore-water. However, XRD did not provide any evidence that the sludge species were significantly affected by NaOH. The peak from the sludge pattern persisted in all binders, irrespective of NaOH concentration. Of course, these XRD observations are qualitative. Other minor peaks, however, disappeared when the NaOH concentration increased. CFA was the least affected binder.

Patterson [5] noted that the minimum solubility obtained for a given metal from an experiment depended on kinetic factors. Early and Cannon [16] observed that clear solutions of Cr(III) did not precipitate in basic solutions for years. Thus it is not totally surprising that we see no evidence that NaOH has a significant short term effect on the chemical species of the heavy metal sludge.

The binder matrices contained small quantities of the waste elements. From this we conclude that some amount of chemical entrapment may have occurred. Pretreatment of the original solution with lime presumably did not precipitate all the heavy metals and some remained in the liquid portion of the sludge. During subsequent mixing of sludge with binder, the liquid supplied the necessary water for hydration. Some of the newly crystallized phases, and the poorly crystalline matrix of the binders trapped the heavy metals present in the liquid portion of the sludge.

The addition of NaOH to the binders containing sludge produced more plate-like calcium alumino-silicate phases containing Na plus minor amounts

of the waste elements (Ni and Cr). Cd was detected in almost all EDX analyses, but Hg was not because it was below the detection limit of the technique. The platelike phase was similar to the calcium sulfo-aluminate hydrate phase commonly observed in cementitious binders. Tashiro and Oba [17] suggested that this phase could be used for chemical entrapment of waste elements.

Several other crystalline phases were found in LFA/sludge. These phases were types of calcium alumino-silicates, but could not be matched with any compound from the powder diffraction files [18]. When NaOH was added, Na was detectable throughout the binder, but NaOH was not. In CFA/sludge and LFA/sludge, fly ash spheres were a form of calcium alumino-silicate, quite similar in composition to the matrix platelets. A new phase in LFA/sludge contained large amounts of Na and Ca. An appreciable amount of Na from NaOH was bound in these phases; the binders chemically reacted with the interfering compound. They also help to lessen the corrosivity of NaOH, as even a 2% NaOH solution (pH 13.7) is hazardous by the RCRA definition.

Not all crystalline phases, however, incorporated the waste elements. Large  $\text{Ca}(\text{OH})_2$  crystals that formed late in the cavities of OPC/sludge containing 8% NaOH did not contain Ni, Cr, or Na.

X-ray diffraction and SEM showed that in the presence of NaOH, more unhydrated calcium silicates were in OPC and CFA, with or without the sludge. Spiering and Stern [19] found that  $> 0.1 N$  NaOH retarded hydration of tricalcium aluminate. It may also retard overall hydration of OPC. In the present study, ettringite was present in CFA/sludge containing 5% NaOH, but in OPC/sludge and LFA/sludge only up to 2% NaOH. Way and Shayan [15] reported that crystallization of ettringite in OPC was inhibited when NaOH concentration was 2 M (pH 14.30). Continuation of ettringite crystallization in CFA/sludge up to 5% NaOH indicates that a pH increase in CFA/sludge did not occur. Gypsum was present when ettringite was absent. Fraay et al. [20] noted that with increasing pH the solubility of sulfate ions in pore water decreased. Gypsum in OPC, along with gypsum formed from anhydrite in Class C fly ash, did not dissolve further due to the high pH produced by NaOH.

The effect of alkalis in portland cement has been reviewed [13]. The evidence is somewhat conflicting, but in general, it was observed that NaOH increased the fraction of crystalline phases in the hydration product. Mori et al. [21, 22] in a series of papers observed that C-S-H, forming from the interaction of NaOH with calcium silicate, was coarse and also incorporated  $\text{Na}^+$ . In contrast, Suzuki et al. [23], in their study on the effect of NaOH and NaCl on the formation of pure C-S-H, found that  $\text{Na}^+$  ions were incorporated in C-S-H during crystallization, but after being immersed in water for several days,  $\text{Na}^+$  ions could be easily removed from the C-S-H. Sodium ions therefore do not effect a permanent change in the crystal structure of C-S-H. Our study, particularly SEM observations, suggests that the addition of NaOH led to new crystalline phases containing Na.

Fly ash is suitable for reducing the effect of pH increases in S/S systems. Fly ash is mainly glassy with minor amounts of crystalline phases [24]. The



pozzolanic property of fly ash is due to the reactive nature of the glassy phase with respect to lime (pH 12.6). Glass is unstable at high pH [25]. Being less polymerized, the glass in Class C fly ash is more reactive than in Class F. A lime saturated solution reacts with Class C fly ash immediately, but takes a very long time to react with Class F fly ash. This study indicates that when NaOH is added to LFA, or CFA with the sludge, it is likely to react selectively with the fly ash component, but not affect the sludge. Analyses of fly ash spheres by EDX in the present study indicate that with the addition of NaOH the amount of Na on fly ash spheres increased. Minor amounts of the heavy metals were also found on their surfaces. Fly ash is then effective in neutralizing NaOH, and can counteract the pH increase. This study shows that Class F fly ash can be more effective in resisting the pH change than Class C fly ash.

A comparison of the binders shows that CFA altered the sludge the least. The absence of  $\text{Ca}(\text{OH})_2$  in CFA/sludge, irrespective of the amount of NaOH, was due to the sludge [2].  $\text{Ca}(\text{OH})_2$  was present in CFA and in CFA containing 8% NaOH. CFA resisted the pH increase due to NaOH, as ettringite appeared in samples containing up to 5% NaOH compared to OPC/sludge or LFA/sludge where it was found in samples containing only up to 2% NaOH. Among the binders studied, CFA tolerated a wider range of pH and had the least effect on the chemical species of the sludge.

All binders containing sludge showed an initial increase in unconfined compressive strength with the addition of NaOH, followed by a decrease with further additions (Fig. 14). The decrease in unconfined compressive strength is related to the increase in the crystalline fraction in the binders [26, 27]. The

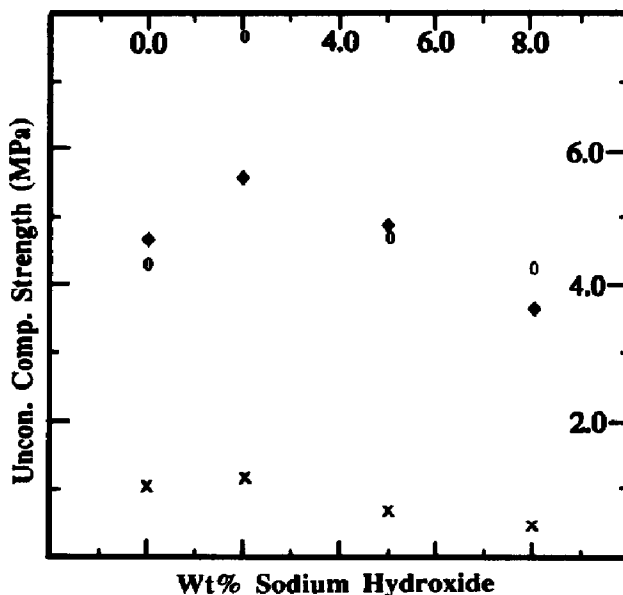


Fig. 14. Unconfined strength of the binders with the sludge and increasing amounts of NaOH. (x) OPC/sludge, (O) CFA/sludge, and (◆) LFA/sludge [7].

change was minimal in CFA/sludge. The continued high unconfined compressive strength of LFA/sludge was possibly due to the radial fibers that grew from the fly ash spheres producing a stronger bond with the surrounding matrix.

## 5. Conclusions

Synthetic electroplating sludge and binders formed a mechanical mixture, irrespective of the NaOH concentration (and therefore pH). This suggests that physical encapsulation is the principal mechanism of solidification/stabilization. The matrix and the newly crystallized phases of the binders effected some degree of chemical entrapment.

NaOH reacted with the binders to produce new phases containing Na and minor amounts of the heavy metals. The hazardous (corrosive) nature of the interfering compound was mitigated by the binders. Class F fly ash was more effective than Class C in resisting the pH increase with increasing NaOH concentration. The addition of NaOH to the binders with the sludge led to increasing crystalline fractions, and ultimately, lower strengths.

## References

- 1 J.R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990, 692 pp.
- 2 A. Roy, H.C. Eaton, F.K. Cartledge and M.E. Tittlebaum, *Hazard. Waste Hazard. Mater.*, 8 (1991) 33.
- 3 A. Roy and H.C. Eaton, *Cem. Concr. Res.*, 22 (1992) 589.
- 4 A. Roy, H.C. Eaton, F.K. Cartledge and M.E. Tittlebaum, *Environ. Sci. Technol.*, 26 (1992) 1349.
- 5 J.W. Patterson, *Industrial Wastewater Treatment Technology*, Butterworth Publishers, Boston, MA, 1985, pp. 467.
- 6 K.M. Alexander and C.E.S. Davis, *Aust. J. Appl. Sci.*, 11 (1960) 1.
- 7 J.M. Cullinane, R.M. Bricka and N.R. Francingues, 13th Annual EPA Research Symp., Cincinnati, OH, 1987, p. 64.
- 8 M.B. Walsh, H.C. Eaton, M.E. Tittlebaum and F.K. Cartledge, *Hazard. Waste Hazard. Mater.*, 3 (1986) 1.
- 9 D.G. Skipper, H.C. Eaton, F.K. Cartledge and M.E. Tittlebaum, *Cem. Concr. Res.*, 17 (1987) 851.
- 10 F.M. Lea, *The Chemistry of Cement and Concrete*, Chem. Publishing, New York, 1987, 727 pp.
- 11 K.E. Dorsch, *Cement*, 6 (1933) 381.
- 12 A. Roy, H.C. Eaton, F.K. Cartledge and M.E. Tittlebaum, *J. Hazardous Mater.*, 30 (1992) 297.
- 13 I. Jawed and J. Skalny, *Cem. Concr. Res.*, 8 (1978) 37.
- 14 R.S. Barneyback and S. Diamond, *Cem. Concr. Res.*, 11 (1981) 279.
- 15 S.J. Way and A. Shayan, *Cem. Concr. Res.*, 19 (1989) 759.
- 16 J.E. Earley and R.D. Cannon, *Aqueous Chemistry of Chromium (III)*, In: R.L. Carlin (Ed.), *Transition Metal Chemistry*, Marcel Dekker, New York, Vol. 1, 1965, p. 34.
- 17 C. Tashiro and J. Oba, *Cem. Concr. Res.*, 9 (1979) 253.

- 18 JCPDS, Powder Diffraction File, Published by the International Center for Diffraction Data, Swarthmore, PA, 1986.
- 19 G.A.C.M. Spierings and H.N. Stein, *Cem. Concr. Res.*, 6 (1976) 265.
- 20 A.L.A. Fraay, J.M. Bijen and Y.M. Haan, *Cem. Concr. Res.*, 19 (1989) 235.
- 21 H. Mori, G. Sudoh, K. Minegishi and J. Ohta, 25th Gen. Mtg. Cem Assoc. Japan, 1971, p. 33 (unpublished).
- 22 H. Mori, G. Sudoh, K. Minegishi and J. Ohta, Proc. 6th Int. Cong. Chem. Cem., Moscow, 1974, pp. II-3, 4, 5.
- 23 K. Suzuki, T. Nishigawa, H. Ikenaga and T. Ito, *Cem. Concr. Res.*, 16 (1986) 333.
- 24 R. Helmuth, Fly Ash in Cement and Concrete, Portland Cem. Assoc., Skokie, IL, 1987, 202 pp.
- 25 A. Paul, Chemistry of Glasses, Chapman and Hall, London, 1982, 293 pp.
- 26 R.F. Feldman and J.J. Beaudoin, *Cem. Concr. Res.*, 6 (1976) 389.
- 27 J.J. Beaudoin and R.F. Feldman, *Cem. Concr. Res.*, 15 (1985) 105.