

## Chemical characteristics and leachability of organically contaminated heavy metal sludge solidified by silica fume and cement

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**Abstract** This paper discusses the development of mixtures with silica fume as a stabilization/solidification agent and binder for industrial wastewater residue containing organic and heavy metal contaminants. The UCS (Unconfined Compressive Strength) gradually increased to 66.7% as the silica fume content increased to 15%. The leaching of TOC and chromium decreased as more OPC was substituted with silica fume. When the mix had 5% silica fume, it retained about 85% TOC, and chromium leached out 0.76mg-Cr/g-Cr in acidic solution. Also, microstructural studies on the solidified wastes through the scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and X-ray diffraction analysis showed that the silica fume caused an inhibition to the ettringite formation which did not contribute to setting, but coated the cement particles and retarded the setting reactions. The results indicated that the incorporation of silica fume into the cement matrix minimized the detrimental effects of organic materials on the cement hydration reaction and contaminant leachability.

**Keywords** Heavy metal; leachability; microstructure; silica fume; sludge; solidification

### Introduction

Although cement-based stabilization/solidification of wastewater residue that contains heavy metal and organic contaminants seems attractive, it can be problematic due to the detrimental effect of organic material upon cement hydration and strength development. The addition of adsorbents and/or pozzolanic materials to eliminate the adverse effects of organic contaminants has been discussed for a long time. It is necessary to know the effects of adsorbent and pozzolanic materials, those are additives to the cement, on the physical and chemical containment properties of cement paste and the behavior of the final solidification product.

This paper discusses the cement based stabilization/solidification with silica fume as a pozzolanic agent and binder for industrial wastewater residue containing organic and heavy metal contaminants. Also, it includes the effects of silica fume on the leachability of contaminants from cement based solidified matrix and the microstructural analyses of matrices before and after the extraction procedure.

Silica-fume used as a pozzolanic material in this study is a by-product of the smelting process for silicon metal and ferrosilicon alloy production. It contains more than 75% silicon, and shares the following main characteristics: SiO<sub>2</sub> contents 85–98%, spherical shape with particle size of smaller than 1 mm and mean size in the range of 0.1–0.2 mm, large surface area (about 20m<sup>2</sup>/g) and amorphous structure. Its amorphous structure, high SiO<sub>2</sub> content and large surface area make it reactive with calcium hydroxide produced by cement hydration to produce the binder calcium-silicate-hydrate (C-S-H) faster and in greater magnitude than coarser and more impure pozzolans such as pulverized fly ash (Sellevold, 1987; Atkins, *et al.*, 1989; Roy, 1989; Mehta, 1989). The extreme fineness of

silica fume could make it an efficient filler which probably serves to distribute the binder phase (C-S-H) in a more homogenous fashion in the available space. It would divide the pore volume into finer pores leading to very slow moisture transport (Sellevold, *et al.*, 1982).

## Material and methods

### Sample preparation

Type I Ordinary Portland Cement (OPC) was used as a major binder for solidification. The wastewater residue in the mix was kept at 50%, and the OPC was replaced with silica fume up to 15% of total material as shown in Table 1. The Blank, Control and Sample 1 were used for microstructural analysis as well as compressive strength and leaching test. The blank sample was prepared to investigate the effect of organically contaminated sludge on the cement hydration and microstructural properties in comparison with the control. Samples for analyses were cured in a sealed curing box of saturated moisture at 20°C for 7 and 28 days.

The sludge used in this work was obtained from chrome tannery processes, which contained up to 1.2% chromium and 1.5% organic carbon that was oil and grease, fibrous and non-fibrous protein, hydrocarbons, surfactant, and other organic matter (Table 2). These organic materials were known to have setting/curing inhibitory effects on cementitious reactions by composing complexing agents and coating reactive particles. Also, the high concentration of  $\text{SO}_4^{2-}$  in the chrome tanning sludge was known to interfere with cement hydration causing delayed initial setting and curing (Conner, 1990; Lea, 1971).

### UCS (Unconfined Compressive Strength) and leachability test

The UCS (Unconfined Compressive Strengths) of the samples cured for 7 days and 28 days were determined. The physical integrity measured by UCS was used as one of the parameters to assess the effects of silica fume on the physical properties of solidified matrix. After testing UCS, the samples were crushed and sieved to make a particle size of 2–9.5 mm for the leaching test. For the organic leachability test, a crushed subsample of 40 g was extracted with 400 ml of distilled water. Also, 640 ml acetic acid solution of 0.1 N was added to the same subsample of 40 g for heavy metal leachability in another bottle. The bottles were shaken for 24 hrs on a shaker table with a 2.5 cm stroke at 120 cycles per minute, then filtered for the analyses of TOC and heavy metal concentrations.

**Table 1** Mixing ratio of each sample

	Sludge	OPC	Silica fume	Water/Cement
Blank	–	1	–	0.4
Control	0.5	0.5	–	0.8
Sample 1	0.5	0.45	0.05	0.89
Sample 2	0.5	0.4	0.1	1
Sample 3	0.5	0.35	0.15	1.14

**Table 2** Properties of sludge

PH	10.1
Moisture content (%)	80
Ignitable matter (%)	4.6 (23.2)*
TOC (mg/L)	15,400
Total Cr (mg/L)	12,200
Cl <sup>-</sup> as NaCl (mg/L)	34,500
SO <sub>4</sub> <sup>2-</sup> as Na <sub>2</sub> SO <sub>4</sub> (mg/L)	33,000
Total nitrogen (mg/L)	480

\* Dry weight base

### Microstructural analysis

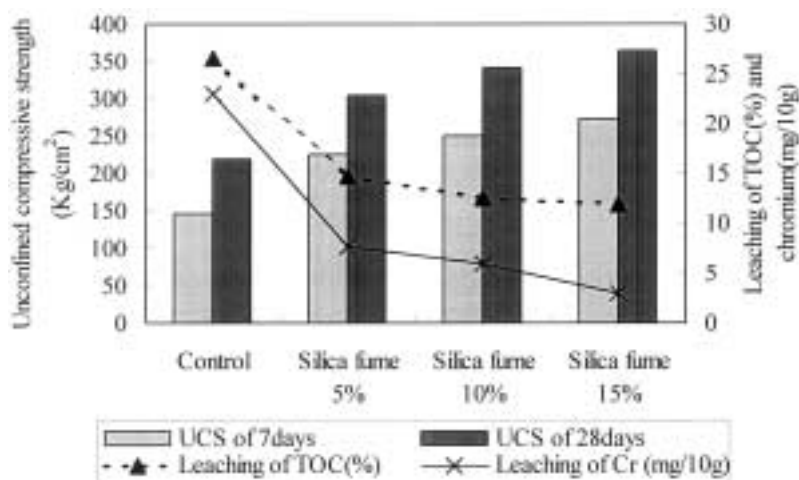
All samples for microstructural analysis were dried in a vacuum desiccator for 24 hrs. MIP (Mercury Intrusion Porosimetry) analysis was done with the dried samples leached in acidic solution as well as unleached samples. The mercury intruding pressure was increased to approximately 30,000 psi to determine the distribution pore size of 0.006–1,000  $\mu\text{m}$ . XRD (X-ray Diffraction) analysis was performed using a Rigaku G/MAX-IIIC X-ray powder diffractometer with a Cu  $K\alpha$  radiation source. Morphological analysis was performed by a Philips 535 Scanning Electron Microscope (SEM) fitted with an energy dispersive system. The dried solid samples were carefully fractured and representative sections were mounted on examination stubs using epoxy resin. The leached samples for XRD and SEM/EDS analyses were extracted for 60 days with distilled water, which was changed every 5 days during the period.

## Results and discussion

### UCS and leachability of solidified matrix

The effect of replacing the OPC with silica fume is shown in Figure 1. The UCS of the samples showed that the mix with 5% silica fume had considerably higher strength, resulting in a 38.8% increase, than the mix without silica fume in control. The UCS gradually increased to 66.7% as the silica fume content increased to 15%.

Also, the results of the leaching test on the 28-day old solidified samples are shown in Figure 1, in terms of TOC and chromium leaching, respectively. The results of the leaching test showed that the retention of TOC and chromium increased as more OPC was substituted with silica fume, similar to the UCS test results. When the mix had 5% silica fume, it retained about 85% TOC, and chromium leached at the rate of 0.76 mg/g in acidic solution. The leaching of chromium from the mix with 5% silica fume had decreased by 66.8% compared with the Control (50% OPC), however, the TOC retention increased only by 16% despite the 38.3% UCS increase. It suggests that the retention of chromium depended more upon fixation on OPC hydration products than TOC. The leaching of TOC and chromium were reduced by 55.6% and 87.2% compared with the control when the OPC was replaced with silica fume up to 15%.



**Figure 1** Unconfined compressive strengths and leaching of TOC and chromium of solidified matrices

### Mercury intrusion and pore structure

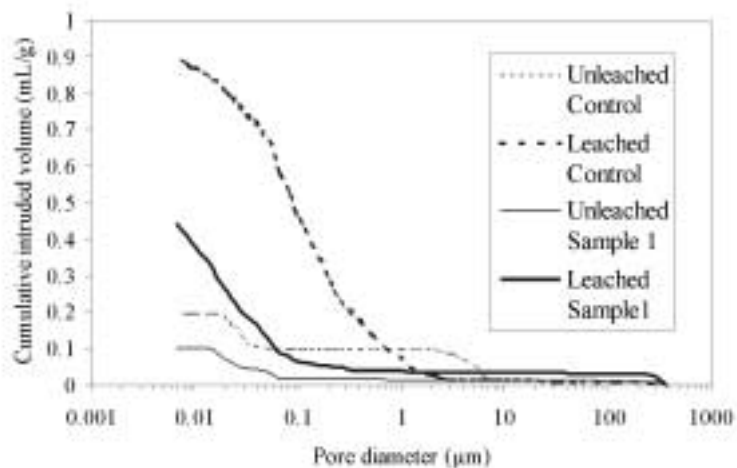
Typical MIP data for leached and unleached solidified samples are shown in Figure 2. Strength and permeability were governed by large pores while the small pores influenced the drying shrinkage and creep (Goto *et al.*, 1981). The control with 50% OPC had the higher intruded volume compared with Sample 1. The threshold capillaries ( $T_c$ ), defined as the diameter where significant mercury intrusion first occurred, were 7 and 0.06  $\mu\text{m}$  for control and Sample 1 paste, respectively. The total intruded volume of the control was much larger than that of Sample 1. The silica fume addition affected the pore distribution significantly. It caused the loss of void pores no matter that the mix was leached or not, and also decreased the pores in the capillary pore region (0.01  $\mu\text{m}$ –0.1  $\mu\text{m}$ ) as well as the void pore region ( $> 0.1 \mu\text{m}$ ). It had been proposed that pores larger than 0.05 to 0.1  $\mu\text{m}$  might be detrimental to strength and permeability (Goto *et al.*, 1981; Mehta, 1986). Rapid diffusion through cementitious matrices was associated with larger pores and their openness or connectivity (Glasser, 1993).

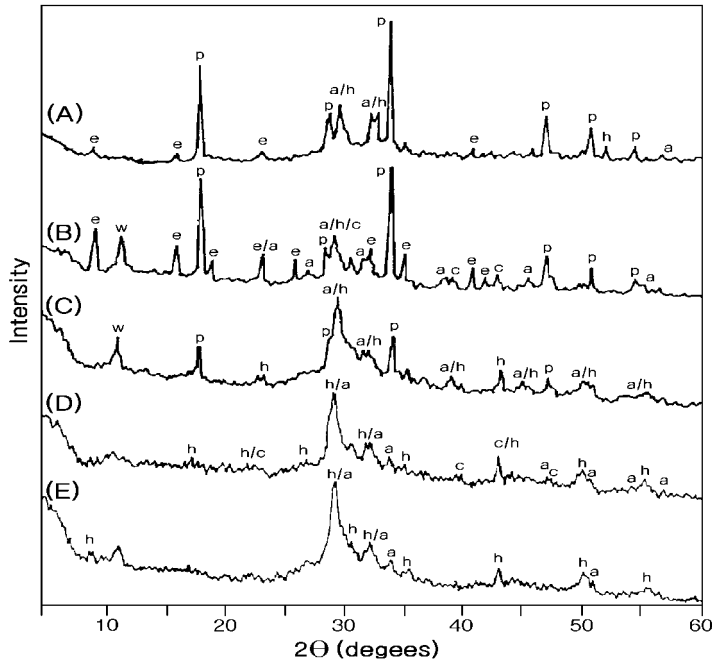
The addition of silica fume did not increase the void pores so much in spite of acidic leaching. The threshold capillaries ( $T_c$ ) became 2.5, and 0.1  $\mu\text{m}$  for control and silica fume paste, respectively. The results indicated that the control would contain larger pores than silica fume paste in acidic condition, therefore the physical and chemical properties of solidified sludge could be considerably worse. The addition of silica fume showed the least increase in capillary pores, however, the gel pores of each sample increased with a similar pattern in the acidic condition.

Considering the leachability of TOC and chromium in the leaching test, the interactions between OPC and silica fume decreased the total intruded volume, and provided hydration products within the fine porosity, ultimately shifting the distribution to finer sizes leading to a decrease in the permeability of the matrix, and making the paste persistent to leaching solution.

### X-ray diffraction analysis

XRD analysis shown in Figure 3 was carried out to determine the effect of silica fume on cement hydration, and to find which hydration products were most affected by its presence. The XRD analysis showed that the addition of organically contaminated heavy metal sludge to cement paste caused some changes in the formation of hydrates and had a detrimental effect on cement hydration as shown in Figure 3 (A) and (B).





**Figure 3** XRD Patterns of (A) Blank, (B) Control, (C) Sample 1, (D) leached Control, and (E) leached Sample 1, respectively. (a: unhydrated calcium silicates, h: calcium silicate hydrates, c: calcium carbonate, e: ettringite, p: calcium hydroxide, w: crystallized waste)

The prominence of the calcium hydroxide peaks and the presence of carbonate peaks in the control compared with Sample 1 (Figure 3(C)) indicated that calcium hydroxide (CH) reacted preferably with atmospheric  $\text{CO}_2$  to C-S-H according to the reaction,  $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ , as well as some remains, as proposed before (Reardon *et al.*, 1989; Jun *et al.*, 1997). This reaction should result in a volume expansion and structural problems, which could affect the solidification and stabilization of waste, if it occurred in the bulk rather than on the surface (Glasser, 1993). Also, the ettringite that appeared in the control sample did not contribute to setting, but coated the cement particles and retarded the setting reactions significantly.

The XRD spectrum of the sample with silica fume shown in Figure 3(C) suggested significant decreases in the ettringite, calcium hydroxide, and calcium carbonate peaks compared with the control, and increases in other weak reflections identified as some hydrated materials such as C-S-H gels including C-S-H(I), C-S-H(II) and other types (relatively weak intensities accompanying strong intensities in XRD patterns of calcium silicate hydrates). It also contained some calcium aluminate hydrates. The reduced relative intensities of calcium hydroxide peaks and the disappearance of calcium carbonate peaks indicated that the calcium hydroxide reacted preferentially with reactive silica fume to atmospheric  $\text{CO}_2$  to produce the binder C-S-H very fast, and it was not affected by the detrimental reactions of organic materials and heavy metal. No ettringite peak in Sample 1 gave an indication of hydration progress compared with the control. In a comparable fashion, the high pozzolanic reactivity of silica fume served to minimize formation of calcium hydroxide, a soluble hydration product, and to enhance the formation of C-S-H, a relatively stable hydration product of OPC. Also, it probably led  $\text{C}_3\text{A}$  to form  $\text{C}_3\text{A}$  hydrates contributing to the rapid setting rather than ettringite ( $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ ) and other types of calcium

sulphoaluminates.

The leached control paste exhibited very different XRD pattern compared with unleached specimen as shown in Figure 3(B) and (D). The calcium hydroxide completely dissolved in the leachant. The significant decrease in crystallized waste peak at 11.4 degrees ( $2\theta$ ) and the disappearance of the ettringite peaks suggested that lots of the contaminants had been leached, so that the hydration proceeded. The considerable increase in intensity of calcium silicate hydrate peaks and the relative decrease of unhydrated calcium silicate ( $C_3S$ ,  $C_2S$ ) peaks barely visible as small peaks were indicative of a higher degree of hydration reaction than unleached control paste.

When the XRD pattern of the leached sample with silica fume shown in Figure 3(E) was compared with the unleached Sample 1 (Figure 3(C)), there was no significant difference between the two spectra except that the peaks of calcium hydroxide disappeared similarly to the control. Also, the XRD spectrum of leached Sample 1 exhibited a little decrease in the crystallized waste peak and a little increase in calcium silicate hydrate peaks identified as C-S-H(I) type. The XRD spectra of samples with silica fume suggested that the addition of silica fume could make the hydration products not change in spite of long term leaching, and the contaminants incorporate with C-S-H, which were persistent to leaching solution, rather than precipitate on hydration products. In the author's work (Jun *et al.*, 1997), though not presented in this paper, this agreed with the result of FT-IR (Fourier Transform Infrared) analysis.

#### Scanning electron microscopy and energy-dispersive spectrometry

The SEM photomicrographs showing typical microstructures of mixes are shown in Figure 4. The microstructure of control was typified by anhydrous cement grains coated with a hydrated calcium silicated hydrate (C-S-H) gel layer with initial fibrous morphology as shown in Figure 4B. Ettringite crystals appeared needle-like and fine rod, and deposited in the voids or on the surface of hydration material. Calcium hydroxide crystals, not fully developed, existed as thin polygonal crystals or platelets. The larger pores were clearly visible; they tended to cluster between unhydrated relict clinker grains and at regions of poor fit between clinker grains and  $Ca(OH)_2$  plates. Chromium was detected virtually everywhere and scarcely exhibited any crystalline behavior in all the SEM and energy-dispersive analysis of x-rays.

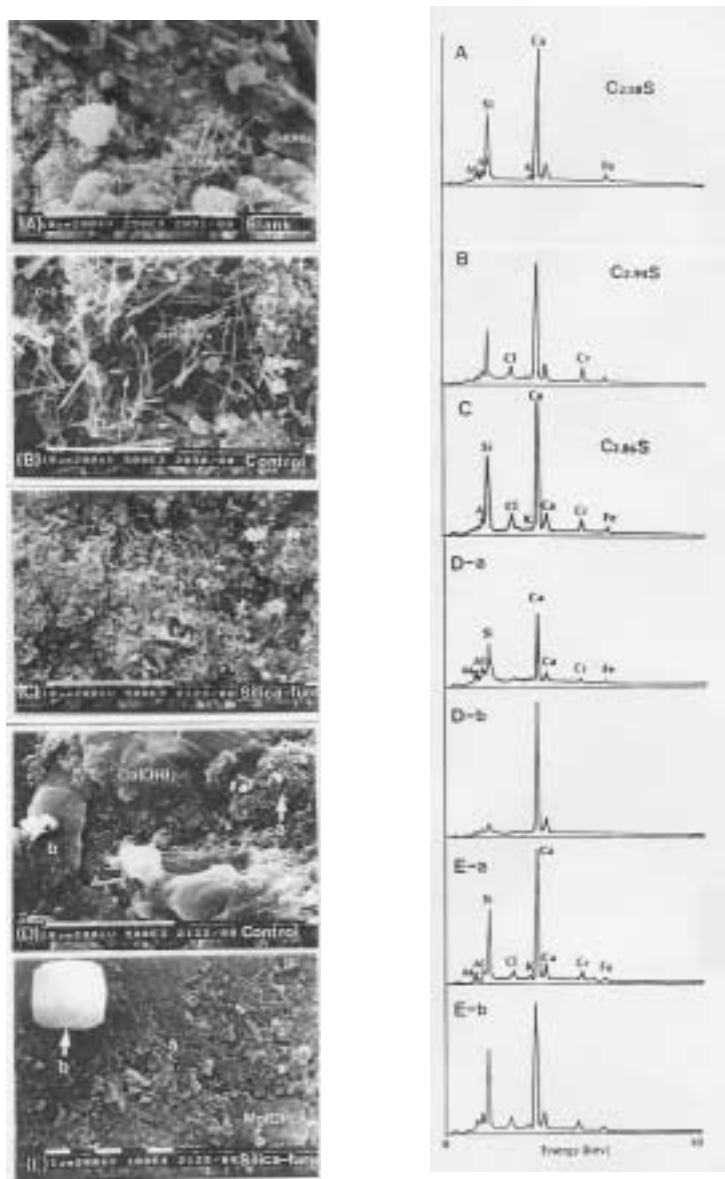
SEM analysis indicated differences in the gross microstructures between blank, control, and Sample 1 containing silica fume. The major difference between the three types of specimens was the significant decrease of calcium hydroxide and ettringite or any of the calcium sulfoaluminate related phases in the paste mixed with silica fume. The paste with silica fume mainly exhibited the hydrated calcium silicates C-S-H(II) with a fibrous structure and a  $CaO:SiO_2$  molar ratio (C/S) of 1.5 to 2, and neither ettringite-like phase nor calcium hydroxide. This morphology demonstrated the very high pozzolanic reactivity of silica fume in spite of organic compound presence. A decrease in hydroxide and chloride in pore water was reported when silica fume was added to Portland cement (Byfors *et al.*, 1986). It showed less void and visibly denser and more homogeneous material than blank and control pastes.

As shown in Figure 4D, gross morphology of the leached control paste having an irregular surface with products identified as calcium hydroxide suggested that contaminants as well as calcium had leached from solidified sludge through the pores. The considerable decrease in the ratio of  $CaO$  to  $SiO_2$  of the hydration products in the leached control paste from 2.8–3.7 to 1.5–1.71 was indicative of significant leaching of calcium components. The leaching of some contaminant was known to be very dependent on the loss of alkalinity in the cement (Cocke *et al.*, 1993). In the EDS spectrum of leached control, the disap-

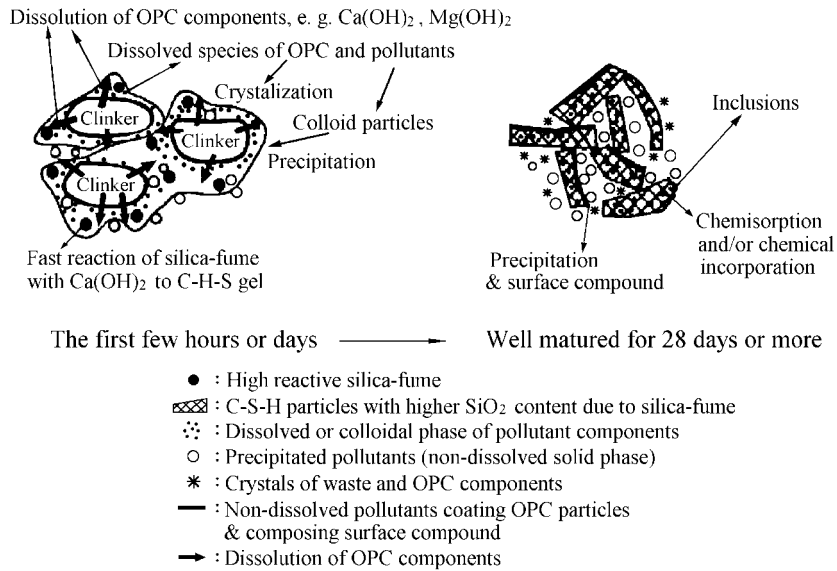
pearance of the chloride peak and the decrease of chromium peak were noted compared with the leached Sample 1 and unleached control. This suggested that the chromium had been incorporated with C-S-H and kept within the hydration products which were persistent to leaching solution, but the soluble ions such as chloride had existed as soluble salts and/or incompletely combined with hydration products which were yieldable to leaching solution.

The SEM and EDS results of the leached paste with silica fume were very different from the leached control. It showed a visibly denser and more homogeneous surface than the leached control paste, and it exhibited a nearly amorphous hydrated calcium silicate, not calcium hydroxide. The ratio of CaO to SiO<sub>2</sub> in overall surface hydration products ranged between 1.72–1.96, and most of the chromium and chloride remained in the leached paste.

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**Figure 4** SEM Pattern and X-ray Spectra of unleached Blank (A), Control (B), Sample 1 (C), leached Control (D), and leached Sample 1 (E), respectively



**Figure 5** Schematic view of hydration processes occurring in the stabilization/solidification of organic-containing heavy metal sludge with silica fume

These indicated that the high pozzolanic reactivity of silica fume made it very reactive with calcium hydroxide to produce more binder calcium-silicate-hydrates (C-S-H), so that more contaminants had been incorporated in C-S-H and resulted in low leaching in spite of long term extraction.

### Conclusions

Considerable progress has been made in the characterization of the binding states, the chemical and physical mechanisms of interaction and the leaching mechanisms of metal and organic pollutants solidified with cement and silica fume through the microstructural analyses for solidified pastes. Some of the processes involved in hydration with silica fume were formulated into models and summarized in Figure 5.

Solidification of wastewater residue with silica fume produced monolithic products with high strength and low leaching of organic compounds as well as heavy metal. The leaching of TOC and heavy metal was reduced by 55.6% and 87.2% compared with the control.

MIP results confirmed that the submicron particle size of silica fume tended to both maximize packing of particles and also to provide hydration products within the fine porosity, ultimately shifting the distribution to finer sizes, directly affecting (reducing) permeability and related diffusivity of ions.

XRD, SEM and EDS analyses indicated the formation of ettringite and needle-like crystals in the hydrating organic contaminated sludge/OPC mix. However, the presence of silica fume could diminish the detrimental effect of organics upon these phenomena. The high reactivity of silica fume served to minimize formation of  $\text{CaCO}_3$  and calcium hydroxide, a soluble hydration product, and to enhance the formation of C-S-H, a relatively stable one of OPC.

This study therefore indicated that the use of silica fume could reduce the adverse effects of organic compounds and heavy metal on cement hydration. This effect could ultimately be of considerable value in designing cement-based solidification for successful treatment of organically contaminated heavy metal sludge.



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