SOLIDIFICATION OF THE ELECTROPLATING SLUDGE USING BLENDED CEMENTS

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Abstract

This research work investigated the performance of solidified electroplating wastes using OPC blended with condensed silica fume (CSF) and furnace slag (FS) as solidification binder. CSF and FS were used to substitute for OPC at 0, 5, 10 and 0, 20, 30%(w/w), respectively. Electroplating sludge from a zinc-cyanide process was loaded to the blended cements at 0, 20, 35 and 50%(w/w). Strength development, leachability of heavy metals and durability to acid corrosion of the solidified waste forms were studied. Experimental results showed that compressive strength of cement blended with 5 and 10%(w/w) of CSF gave higher strength than that of cement paste after curing for 7 days, whereas cement with 5% (w/w) CSF and 20%(w/w) FS gave similar strength to that of the control after 28 days. A dramatic decrease in compressive strength of all solidified plating waste samples was observed, but the concentration of heavy metals in the TCLP leachates did not exceed the limit specified by the US.EPA. In addition, durability of the cement-based solidified waste matrices against sulfuric acid corrosion was greater compared to acetic and nitric acid solutions.

Introduction

Stabilization and solidification of hazardous wastes using ordinary Portland cement (OPC) is a potential treatment for wastes containing heavy metals. The chemical changes that take place as a result of the interaction between waste components and OPC play an important role in controlling the quality of the solidified waste products. The high and relatively stable pH produced when OPC hydrates results in resolubilization of some amphoteric heavy metal hydroxides. These metals therefore have the potential to interfere with the cement hydration and produce solidified wastes with reduced levels of structural integrity and increased leachability (Asavapisit *et al.*, 1997; Hanna *et al., 1995;* Hills *et al.*, 1992; Cartledge *et al.*, 1990; Tashiro *et al.*, 1979; Poon *et al.*, 1985)

The strength and durability of the cement-based solidified wastes are also influenced by calcium hydroxide and alkali produced during cement hydration. It is believed that the replacement of Portland cement by pozzolanic materials such as condensed silica fume and blast furnace slag results in the consumption of calcium hydroxide and alkali during pozzolanic reactions, thus increasing the strength and durability of the solidified waste forms (Asavapisit *et al.*, 1997; Toutanji and El-Korchi, 1995; Bagel, 1998; Pandey and Sharma, 2000; Singh and Garg, 1999).

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Accordingly, an ideal chemical composition of a cement-based solidified waste can be made by blending Portland cement with pozzolana to produce high performance solidified waste products.

In this work, condensed silica fume and cupola furnace slag were blended with OPC and the blended cements were used as solidification binders for the electroplating sludge. The unconfined compressive strength, leachability of heavy metals from the solidified wastes using the Toxicity Characteristic Leaching Procedure and durability to acid corrosion were analyzed to assess the performance of these solidified waste products.

Materials and Methods

Materials

Ordinary Portland Cement Type 1 was supplied by The Siam Cement Public Co. Ltd. (Thailand). Condensed silica fume (CSF) and cupola furnace slag (FS) were used as mineral additives for blended cements. Condensed silica fume was from the Microsilica JV Pty Ltd. (Australia). Cupola furnace slag was collected from a cast iron production facility in Bangkok, Thailand. The slag is produced from the fusion of limestone, pig iron and scrap iron in a cupola furnace during iron manufacturing. The cupola slag was then ground to a particle size of less than 45 μm using a Los Angeles Abrasion Machine.

The chemical composition of OPC, CSF and FS was given in Table 1. The chemical composition of the slag was analyzed using X-ray Fluorescence (XRF). The major components of the slag are SiO_2, CaO, and Al_2O_3 comprising 55.4, 27.8 and 8.4%(w/w), respectively. In addition, the hydraulic reactivity of the slag was evaluated by means of the strength activity indices with Portland cement (ASTM C 618-97). The 7 and 28 days strength activity indices with Portland cement were 76 and 84 percent of the control and complied with the minimum requirement for use as a mineral admixture in concrete.

Electroplating sludge was collected from the wastewater treatment plant of a zinc-cyanide process located in Bangkok, Thailand. The plating sludge was then oven dried overnight at 105°C and ground to a particle size of less than 0.5 mm. The ground sludge was digested using concentrated nitric acid and the concentration of heavy metals was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES) as shown in Table 2.

Sample Preparation

Condensed silica fume and cupola furnace slag were blended with OPC at 0, 5 and 10% (w/w) and 0, 20 and 30%(w/w), respectively. The mix designs are summarized in Table 3. The

Table 1. Chemical composition of OPC, CSF and cupola furnace slag (%,w/w).

Sample ID	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	SO_3	K_2O	LOI
OPC[#]	64.0	21.2	6.1	3.2	0.9	0.05	2.9	0.5	1.4
CSF[#`]	0.2	93.8	0.2	0.1	0.3	-	-	0.4	4.9
FS	27.8	55.4	8.4	3.4	2.6	-	-	0.8	-

Remark: [#]data was provided by the supplier

Table 2. Concentration of heavy metals in the plating sludge (mg/kg dry sludge).

Zn	Fe	Cr	Al	Pb	Cu	Cd
80,820	-23,472	13,302	2,200	67	20	5

optimum concentrations of CSF and FS were determined from the strength development of blended cement pastes prepared at water to solid ratio (w/s) ratio of 0.45. The plating sludge was then loaded to the optimum blended cements at 0, 20, 35 and 50%(w/w). A water to solid ratio of 0.6 was used to maintain good workability during transferring the sample into a cylindrical plastic mould. The slurry was mixed following the standard test method ASTM C 305-94 to achieve a uniform distribution of the solidification binders and the plating sludge before being transferred to the plastic mould. The mixes were allowed to solidify in the sealed plastic moulds to avoid carbonation prior to testing.

Unconfined Compressive Strength Test

The compressive strength of the solidified wastes was tested following ASTM D 1633-96 using molded cylinders as test specimens. The size of the cylindrical sample was modified using 50 mm in diameter and 100 mm in height. The compressive strength of the solidified wastes was tested after curing for 28 days. A set of five samples was used for the compression test and the arithmetic average was computed from the five observations.

Leaching Test

Metal leaching from the solidified wastes was assessed using the Toxicity Characteristic Leaching Procedure (TCLP) as defined by the U.S. EPA on the samples cured for 28 days. The leachates were filtered through a 0.45 μm membrane filter to remove suspended solids and were then divided into two portions. One was used for pH measurement and the other for determination of the metals present in the leachates by ICP-AES. Each leachate was analyzed in triplicate and the mean values were reported to ensure the reproducibility of the data.

Corrosion Tests

Acetic, nitric and sulfuric acid solutions were used as leachant in this work. Acetic acid solution was used to represent organic acid, which is normally generated during the decomposition of organic matter under anaerobic landfill conditions. Nitric and sulfuric acids are strong mineral acids, which were used to simulate acid rain. Each acid was used at a concentration of 0.2N to accelerate the corrosion processes. The initial pHs of acetic, nitric and sulfuric acid solutions were 2.8, 1.1 and 1.3, respectively.

The weight and dimension of the cylindrical samples were recorded prior to testing and a constant volume of acid solution to sample surface area of 20:1 was used to ensure that all surfaces of the samples were in contact with the solution. The solidified waste samples containing 20%(w/w) plating sludge were suspended in the geometric center of the solution in a closed

Table 3. Mix designs of the blended cement pastes.

OPC (%,w/w)	CSF (%,w/w)	FS (%,w/w)	w/s
100	0	0	0.45
95	5	0	0.45
90	10	0	0.45
80	0	20	0.45
70	0	30	0.45
75	5	20	0.45
65	5	30	0.45
70	10	20	0.45
60	10	30	0.45

system under static condition. Three sets of 5 samples with the same composition were suspended in five different bottles containing acetic, nitric and sulfuric acid solutions. Each set of samples was exposed to acetic, nitric and sulfuric acid solutions, for 1, 8, 15, 29 and 57 days, respectively. One bottle from each set was removed after each exposure time for analysis. The tests were completed in duplicate to confirm the reproducibility.

Results and Discussions

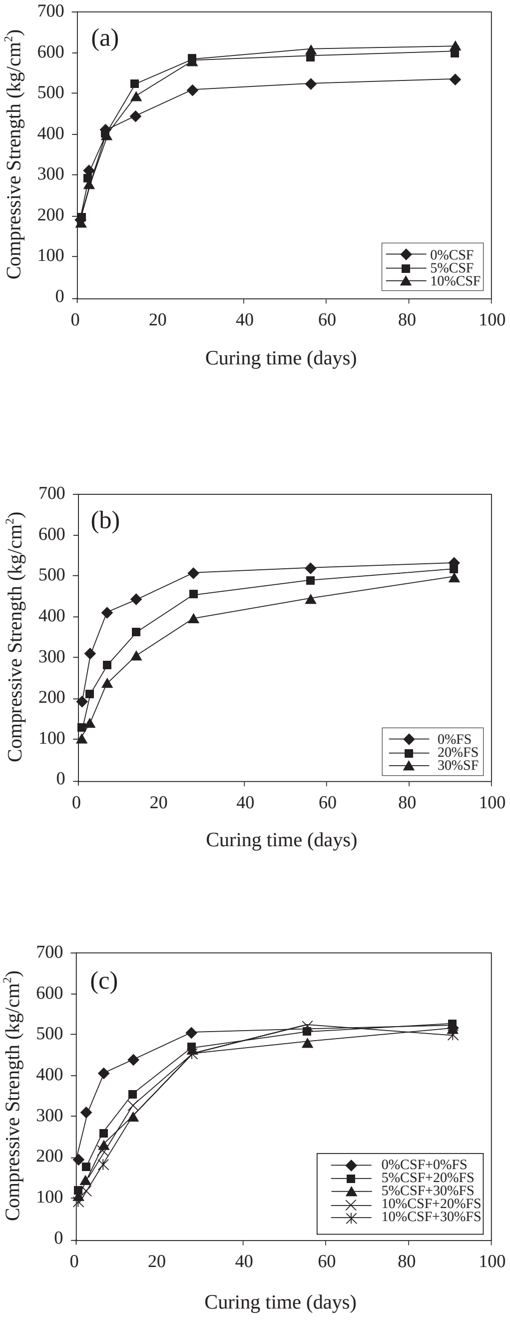
Strength Development of the Blended Cements

Figures 1 a-c show the strength development of the blended cement pastes containing CSF and FS. It was observed that the addition of 5 and 10%(w/w). CSF to OPC had no significant effect on the compressive strength of the blended cement pastes during 1 and 7 days of curing, but after these curing durations the rate of strength development in cements blended with CSF was higher than that of the control (Figure 1a). Generally, it is known that pozzolanic reactions occurreal at a lower rate than the hydration reactions of OPC and therefore would lower the early strength. But at later age, the pozzolanic reactions between calcium hydroxide obtained from the hydration of OPC and the added CSF resulted in the production of secondary cementitious material to fill the void space and contribute better to strength (Lam *et al.*, 2000).

The addition of 20 and 30%(w/w) FS to OPC reduced the rate of strength development of the blended cement pastes at every curing duration (Figure 1b). In addition, compressive strength of cements containing FS was lower than those containing CSF even after a long curing duration. This may be due to either the higher level of cement replacement by FS or the lower hydraulic reactivity of FS compared to CSF. Similar observations were found in blended cements containing both CSF and FS (Figure 1c).

Compressive Strength of the Solidified Wastes

Addition of the plating sludge to OPC and the blended cements resulted in a significant



Figuer 1. Compressive strength of the blended cement pastes at increasing curing time: (a) OPC + CSF; (b) OPC + FS; and (c) OPC + CSF + FS

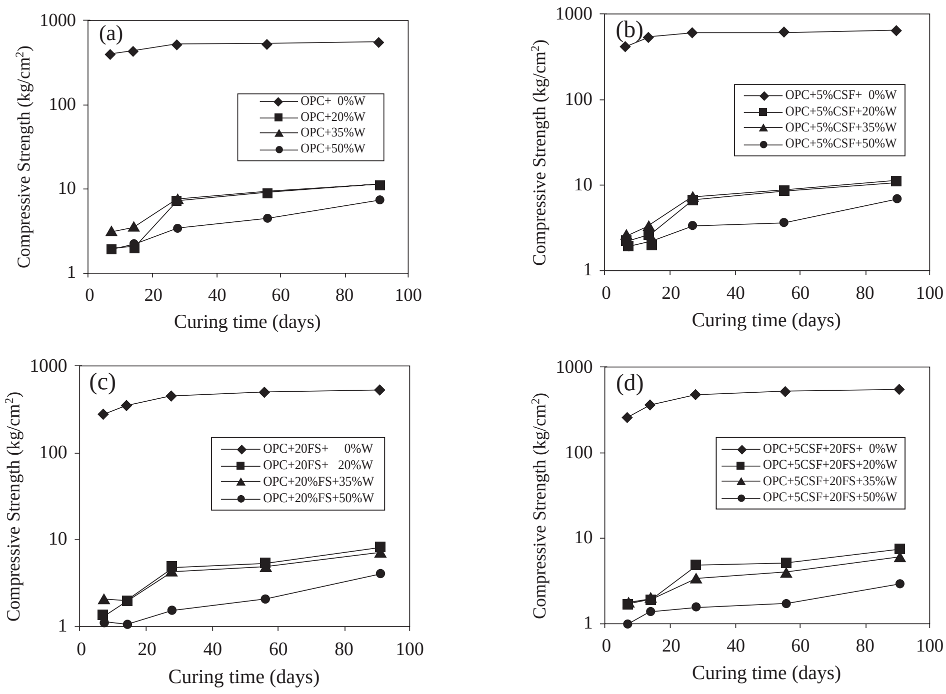
reduction in the rate of strength development of the solidified wastes (Figure 2 a-d). A further reduction in strength of the solidified wastes with increasing waste loading was also observed.

Several metals are known to be resolubilised under the highly alkaline environment of cement and therefore could retard or inhibit the hydration reactions of the hydraulic cements. These soluble metals block the normal hydration reactions by adsorption or formation of complex ions on the surface of the cement particles. In addition, zinc oxide and hydroxide are among the interfering metals that were reported to cause most severe hydration retardation or inhibition of OPC (Asavapisit *et al.,* 1997; Hanna *et al.,* 1995: Hills *et al.,* 1992). It could be possible that zinc, which was present at the highest concentration in the plating sludge, was rapidly resolubilised resulting in a severe hydration inhibition of the blended cementitious binders. Another possibility that the plating sludge caused severe hydration retardation could arise from the complexity of the sludge itself, which contained other metal hydroxides. The retardation effect of ZnO has been reported to be enhanced by the presence of other metal oxides (Olmo *et al.,* 2001).

Leachability of the Solidified Wastes

Metal concentrations and leachate pHs during TCLP leach testing are presented in Table 4. Leachate pHs of the solidified waste samples were in the range of 11.2 - 11.7 and gradually decreased at increasing waste loading. It could be possible that at increasing waste loading the proportions of cementitious materials in the mixes were reduced and resulted in a lower acid neutralization capacity of the solidified wastes.

Cement-based solidified wastes are porous materials. The pores are saturated with water, which is in equilibrium with the surrounding solid matrix. When it is exposed to acid leachant the chemical equilibrium of the pore water is disturbed and this may initiate the partial



Figuer 2. Compressive strength of the solidified wastes containing various waste loading concentrations; (a) OPC; (b) OPC + 5%CSF, (c) OPC = 20%FS; and (d) OPC + 5%CSF + 20%FS

dissolution of the cement-based matrix. As a result, resolubilization and desorption of several insoluble metals at the interface between solid and the leachate occurred. However, the certain amount of H^+ present in the leachant was rapidly buffered to an alkali leachate pH due to dissolution of $Ca(OH)_2$. This resulted in concentration of some amphoteric metal pollutants, especially Cr, Pb and Cd, seing in leachates from all solidified waste samples being lower than the regulatory limit of the U.S.EPA and is in good agreement with several researchers (Cheeseman *et al.*, 1998).

Durability of the Solidified Wastes due to Different Acid Attack

Weight change data of the solidified waste samples containing 20%(w/w). plating sludge exposed to various acid solutions for different exposure duration is shown in Figure 3 a-c. Experimental results showed that the sample weight loss gradually increased with increasing exposure duration in acetic and nitric acid solutions, but at a decreasing rate. Cement-based solidified waste materials are alkali in nature and therefore they start to deteriorate after exposure to acid solutions. Ingression of an aggressive acid solution into the pore water of the solidified wastes disturbs the chemical equilibrium formed with the surrounding solids. This may result in dissolution of the soluble products, especially $Ca(OH)_2$, from pore water and progressive decalcification of the cement matrix, and as a result a soft and porous corroded layer remained.

The percentage weight loss from the samples contacted with sulfuric acid solution was significantly lower than that observed in acetic and nitric acid solutions. This is because an insoluble calcium sulfate (gypsum) was formed by the reaction between sulfuric acid and calcium

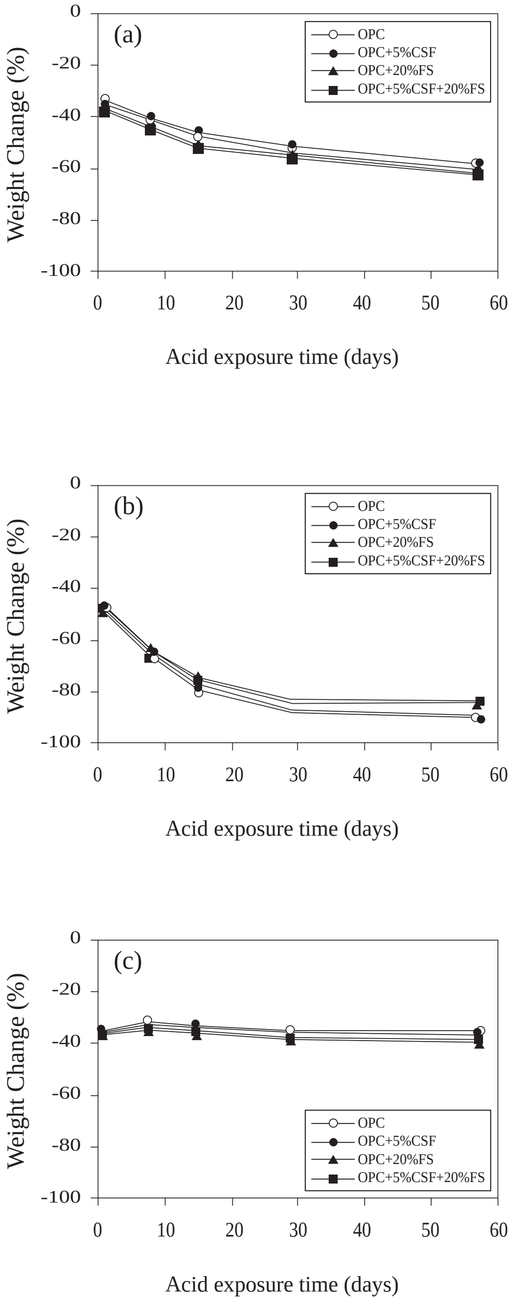
Table 4. Metal concentrations and leachate pHs during TCLP leach testing.

Sample ID	pH	Metal concentration in the leachate (mg/l)					
		Zn	Cr	Pb	Fe	Al	Cd
Regulatory level (mg/l)		**#**	**5**	**5**	**#**	**#**	**1**
OPC+20%W	11.7	3.7	0.1	0.1	0.5	0.2	b.d.
OPC+35%W	11.6	6.7	0.1	0.1	0.4	0.2	b.d.
OPC+50%W	11.5	13.7	0.1	0.1	0.8	0.2	b.d.
OPC+5%CSF+20%W	11.7	3.7	0.1	0.1	0.6	0.2	b.d.
OPC+5%CSF+35%W	11.6	7.7	0.1	0.1	0.7	0.2	b.d.
OPC+5%CSF+50%W	11.4	16.8	0.2	0.1	0.9	0.2	b.d.
OPC+20%FS+20%W	11.7	4.7	0.1	0.4	0.6	0.2	b.d.
OPC+20%FS+34%W	11.6	8.7	0.1	0.1	0.6	0.2	b.d.
OPC+20%FS+50%W	11.3	15.9	0.2	0.1	0.7	0.1	b.d.
OPC+5%CSF+20%FS+20%W	11.7	4.4	0.1	0.1	0.4	0.2	b.d.
OPC+5%CSF+20%FS+35%W	11.6	8.7	0.1	0.1	0.7	0.2	b.d.
OPC+5%CSF+20%FS+50%W	11.2	14.8	0.2	0.1	0.6	0.2	b.d.

no regulatory limit

b.d = below detection limit

hydroxide upon contact with sulfuric acid solution. This calcium sulfate was deposited on the surface of the solidified waste sample and the formation of a white protective layer was observed. However, this layer was loosely connected with the solidified waste and spalled off spontaneously allowing the solidified waste to be in direct contact with the sulfuric acid solution again.



Figuer 3. **Weight change of the solidified waste sample containing 20%(w/w) plating sludge after exposure to acid solutions: (a) acetic; (b) nitric; and (c) sulfuric**

Conclusions

The following conclusions can be drawn from this work:

Addition of 5 and 10%(w/w) CSF to OPC resulted in higher rate of strength development than cement paste after curing for 7 days whereas cement with 5%(w/w) CSF and 20%(w/w) FS gave similar strength to that of the control after 28 days. CSF and FS, an industrial by-product and waste, can be partially used as mineral additives to substitute for OPC in solidifying the electroplating sludge. The solidified plating waste made with blended cements gave similar quality to OPC in terms of compressive strength, leachability of heavy metals and durability to by various acids corrosion. The presence of several metal hydroxides in the plating sludge resulted in a severe hydration retardation of the solidification binders. More than 90% reduction in strength of the solidified wastes at each curing duration was obtained. Durability of the solidified wastes against different acid corrosion was in the following order: sulfuric > acetic > nitric acid solutions. The deposition of calcium salts on the surface of the solidified wastes upon contact with acid solutions affected the rate of cement matrix deterioration.

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References

Asavapisit, S., Fowler, G. and Cheeseman, C.R. (1997). Solution chemistry during cement hydration in the presence of metal hydroxide wastes. Cement and Concrete Research. 27:1249-1260.

Asavapisit, S., Nanthamontry, W. and Polprasert, C. (1997). Influence of condensed silica fume on the properties of cement-based solidified wastes. Cement and Concrete Research. 27:1249-1260.

Bagel, L. (1998). Strength and pore structure of ternary blended cement mortars containing blast furnace slag and silica fume. Cement and Concrete Research. 28:1011-1020.

Cartledge, F.K., Butler, L.G., Chalasani, D., Eaton, H.C., Frey, F.P., Herrera, E., Tittlebaum, M.E. and Yang, S.L. (1990). Immobilisation mechanisms in solidification/stabilisation of Cd and Pb salts using Portland cement fixing agents. Environ. Sci. Technol. 24:867-873.

Cheeseman, C.R., Asavapisit, S. and Knight, J. (1998). Effect of uniaxially pressing ordinary portland cement pastes containing metal hydroxides on porosity, density, and leaching. Cement and Concrete Research. 28: 1639-1653.

Hanna, R.A., Barrie, P.J., Cheeseman, C.R., Hills, C.D., Buchler, P.M. and Perry, R. (1995). Solid state ^{29}Si and ^{27}Al NMR and FTIR study of cement pastes containing industrial wastes and organics. Cement and Concrete Research. 25:1435-1444.

Hills, C.D., Koe, L., Sollars, C.J. and Perry, R. (1992). Early heat of hydration during the solidification of a metal plating sludge. Cement and Concrete Research. 22:822-832.

Lam, L., Wong, Y.L. and Poon, C.S. (2000). Degree of hydration and gel/space ratio of high-volume fly ash/cement systems. Cement and Concrete Research. 30:747-756.

Olmo, I.F., Chacon, E. and Irabien, E.C. (2001). Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of Portland cement. Cement and Concrete Research. 31:1213-1219.

Pandey, S.P. and Sharma, R.L. (2000). The influence of mineral additives on the strength and porosity of OPC mortar. Cement and Concrete Research. 30: 19-23.

Poon, C.S., Clark, A.I. and Perry, R. (1985). Investigation of the physical properties of cement-based fixation processes for the disposal of toxic wastes. Public Health Engineer. 13:108-110.

Singh, M. and Garg, M. (1999). Cementitious binder from fly ash and other industrial wastes. Cement and Concrete Research. 29:309-314.

Tashiro, C., Takahashi, H., Kanaya, M., Hirakida, I. and Yoshida, R. (1979). Hardening property of cement mortar adding heavy metal compound and solubility of heavy metal from hardened mortar. Cement and Concrete Research. 7:283-290.

Toutanji, H.A. and El-Korchi, T. (1995). The influence of silica fume on the compressive strength of cement paste and mortar. Cement and Concrete Research. 25:1591-1602.