

Solidification and stabilization of chromium laden wastes in cementitious binders

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Solidification/stabilization (S/S) technology was applied to a simulated sludge containing chromium. Leaching tests such as toxicity characteristic leaching procedure (TCLP), ANS 16.1 and multiple TCLP tests conducted on stabilized blocks showed that chromium was immobilized by the binder studied. A linear relationship was obtained between the cumulative fraction of chromium leached and time^{1/2} in the stabilized samples proving that chromium is leached by diffusion. The leachability indices obtained for the solidified materials satisfy the guidance value as per US Nuclear Regulatory Commission. Chromium concentrations in the TCLP leachates were well within the regulatory levels of the United States Environmental Protection Agency. Microchemistry and morphology of the stabilized samples were studied using Fourier transformation infrared (FTIR) technique and scanning electron microscopy (SEM). FTIR confirms the presence of ν_2 CO₃ band and O–H stretching of Ca(OH)₂ and SEM shows uniform dense crystalline morphologies in all the samples. X-ray diffraction indicates the presence of bentorite, which proves that Cr replaces Al in the ettringite.

Keywords: Bentorite, leachability index, sludge, solidification, stabilization, toxicity characteristic leaching procedure.

TOXIC heavy metal laden wastewater and solid/semisolid waste are discharged from metal finishing, plating, tanning, automotive, engineering, mining, battery and other industries. Unscientific management and indiscriminate disposal of solid wastes generated by these industries often lead to serious environmental problems.

Among the technologies developed to render waste non-toxic, solidification/stabilization (S/S) by cementitious binders has been most promising and has been designated as one of the best demonstrated available technologies for a variety of wastes¹. S/S is used as a pre-landfill waste treatment technology that aims to make hazardous industrial waste safe for disposal. This technology has been applied to many types of wastes and industrial effluents mainly those containing heavy metals. The technology is both cost-effective and safe, since the metals are converted (or retained as) into highly insoluble

salts, which do not leach into groundwater at appreciable rates. Several binder systems are currently available and widely used for S/S of many types of wastes and industrial effluents containing heavy metals^{1–4}.

This technology has been reported to be cost-effective and safe for sludges containing heavy metals^{5–8}. Assessment of different leaching procedures^{7,9} and different stabilization mechanisms have also been discussed^{5,8}. Palomo and Palacios¹⁰ studied the stabilization capacity of a cementing matrix, prepared using alkali-activated fly ash, in the presence of toxic elements chromium and lead and reported that chromium affects the activation mechanism of fly ash and, consequently, its hardening process due to the formation of sodium chromate. Rossetti *et al.*¹¹ summarized the optimization of S/S system for Cr, Pb, Zn and Li in aqueous solution. Halim *et al.*¹² observed that Pb and As were incorporated within the C–S–H matrix, whereas a greater portion of Cd located in the cement pores as discrete particles and Cr(VI) existed mostly as free CrO₄^{2–} ions.

Wang and Vipulandan¹³ studied the X-ray diffraction (XRD) pattern of solidified hexavalent chromium and observed that chromium inhibited cement hydration process. Rossetti and Medici¹⁴ studied XRD of cement-solidified Cd, Cr, Zn and Pb containing waste.

The present study aims to explore the mechanism of fixation of Cr using XRD, scanning electron microscopy (SEM), Fourier transformation infrared (FTIR) and to evaluate the stability of S/S system using standard and accelerated leaching tests.

Four different kinds of binder materials, Portland cement, Portland cement–fly ash, Portland cement–lime and Portland cement–gypsum were used for solidification of a synthetic metal containing waste. The cement used was of grade 43 and fly ash was obtained from a coal-based thermal power plant. Lime (Ca(OH)₂) and gypsum hemihydrate (CaSO₄·1/2H₂O) were purchased from the local market at Chennai, Tamil Nadu. The composition of the Portland cement, fly ash, lime and gypsum used is presented in Table 1. Heavy metal concentrations were found to be negligible in the binders.

Chromium chloride CrCl₃·6H₂O (10.26%) was the source of heavy metal. A water/solid (W/S) ratio of 0.36

Table 1. Chemical composition of binder materials

	Cement (%)	Fly ash (%)	Lime (%)	Gypsum (%)
SiO ₂	19.7	33.12	0.55	1.28
Al ₂ O ₃	7.1	17.3	0.4	0.30
Fe ₂ O ₃	2.7	4.6	0.17	0.46
CaO	61.24	26.6	53.47	32.5
MgO	3.24	4.87	1.02	BDL
Na ₂ O	0.19	2.65	0.02	0.03
K ₂ O	0.68	0.65	0.01	0.05
SO ₃	1.8	2.32	BDL	46.2

BDL, Below detectable limit.

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was maintained throughout the experiment. The sample preparation has been explained earlier¹⁵. The mix ratios prepared were: C (10.26% $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$; 89.74% cement), FC (10.26% $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$; 10% fly ash; 79.74% cement), LC (10.26% $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$; 10% lime; 79.74% cement) and GC (10.26% $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$; 10% gypsum; 79.74% cement). All the analyses were done in duplicate and the average results are presented.

Toxicity characteristic leaching procedure (TCLP) of unsolidified and solidified wastes was carried out by extracting at a liquid to solid ratio of 20:1 using TCLP leaching fluid as medium. The solidified samples after crushing to size $<9\ \mu\text{m}$ along with leaching fluid were placed in a rotary shaker for 18 h. The samples were filtered and analysed for metals. Other aggressive leaching tests, viz. multiple TCLP (MTCLP) and ANS 16.1 test were performed on two-month-old sample. Diffraction coefficient (D_e , $\text{cm}^2\ \text{s}^{-1}$) and leachability index (LI) were calculated from eqs (1) and (2).

$$\text{CFL} = \sum a_n/A_0 = 2(S/V)(D_e t/\pi)^{1/2}, \quad (1)$$

$$\text{LI} = -\log D_e, \quad (2)$$

where a_n is the total amount of substance released in all leaching periods of time t , A_0 the total amount of substance originally present, V the volume of waste, S the surface area of the waste. The details of the tests have been presented earlier¹⁶.

FTIR was carried out using a Bruker Vector 22 FTIR instrument. Well cured samples (two months old) were prepared for analysis by grinding a known mass of solid with dried KBr. The resulting powder was then pressed to produce a pellet for analysis. IR data were collected over the wave number range $700\text{--}4000\ \text{cm}^{-1}$.

SEM (Hitachi S-520) at an accelerating voltage of 10 kV with Hitachi HUS 5 GB vacuum evaporator for gold coating was used to analyse the microstructure of 2- and 9-month-old solidified samples.

Results of the TCLP test are presented in Table 2. The pH of the leachate ranges from 4.5 to 5.0. It is clearly seen that as the curing time increases the fixation of chromium also increases. Chromium levels in all the mix ratios on the 14th day of curing are less than the TCLP

Table 2. Concentration of chromium by TCLP

Sample	Curing time (days)			
	7	14	21	28
C	4.97	1.58	0.32	BDL
FC	5.05	1.59	0.31	BDL
LC	4.4	1.4	0.30	BDL
GC	9.98	2.88	1.68	0.15

BDL, Below detectable limit.

regulatory value ($5\ \text{mg}\ \text{l}^{-1}$), demonstrating that chromium is well fixed in all the systems studied. The order of metal retention is in the order cement–lime \geq cement = cement–fly ash \geq cement–gypsum. The cement–gypsum system has excess sulphate, which may be responsible for the impedance in the fixation of chromium. Fly ash acts both as a fine aggregate and as a cementitious component enhancing the binding. Lime increases the pH of the block and enables the formation of insoluble metal hydroxides¹⁷. Chang *et al.*¹⁸ reported that chromium level in plating sludge ($10.71\ \text{mg}\ \text{l}^{-1}$) was reduced to $\leq 0.3782\ \text{mg}\ \text{l}^{-1}$ after solidification using binders like slag, fly ash, shell lime and cement. Park¹⁹ has reported that a synthetic sludge of chromium, lead and cadmium made from $2500\ \text{mg}\ \text{l}^{-1}$ of the metal solutions leached out $<100\ \mu\text{g}\ \text{l}^{-1}$ of chromium after solidification using cement, clinker kiln dust and quick setting agent.

MTCLP test was carried out on all the systems and the results are shown in Figure 1. The cumulative leaching of chromium was found in the range $2.69\text{--}3.06\ \text{mg}\ \text{l}^{-1}$, which is considerably lower than the TCLP regulatory limits. Yang and Kao²⁰ have reported that solidification of electroplating sludge using cement and calcium carbonate sludge has reduced the cumulative leaching of zinc from 2.83 to 0.034 wt% and cumulative leaching of

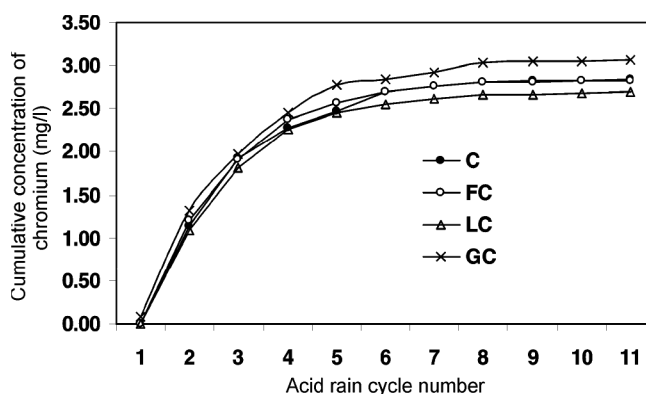


Figure 1. Concentration of chromium by multiple toxicity characteristic leaching procedure test.

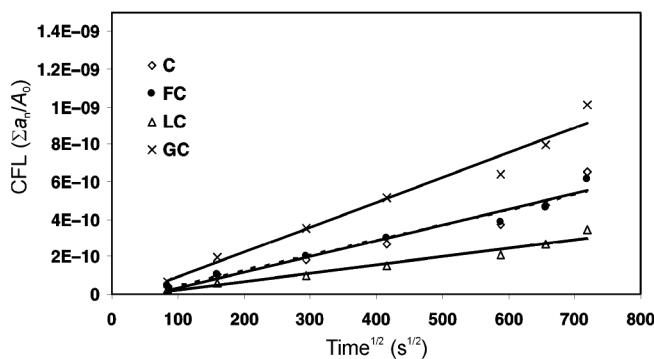


Figure 2. Cumulative fraction of chromium leached from stabilized system as a function of square root of time.

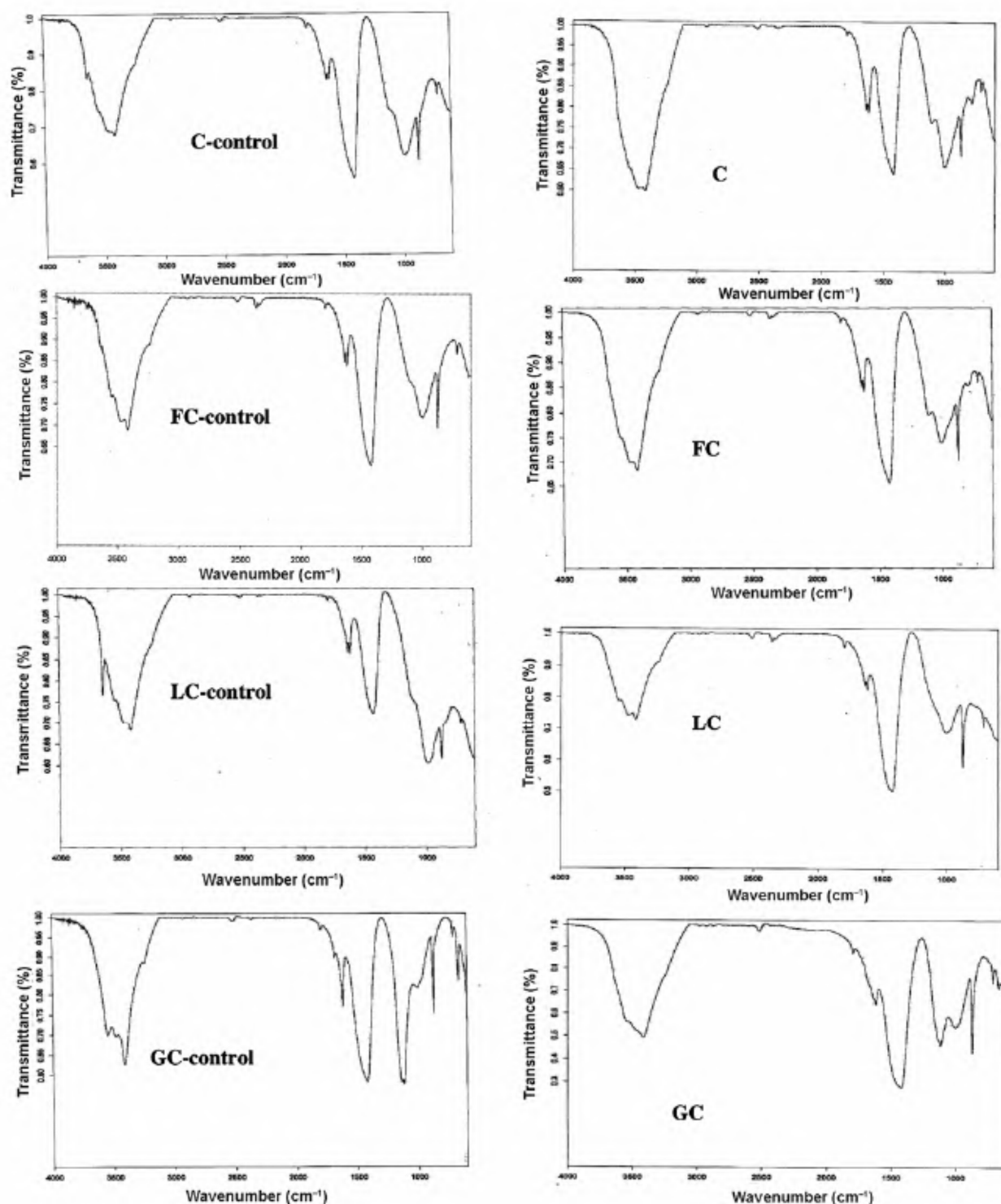


Figure 3. FTIR spectra of samples.

cadmium from 18.85 to 0.4 wt%. This indicates that even after subjecting the S/S blocks to rigorous leaching conditions, the stabilized systems exhibit good binding ability for chromium and can be considered chemically durable.

Solidified samples were tested according to the American Nuclear Society leaching test procedure, and the

results are presented in Figure 2. Cumulative fraction of chromium leached (CFL) versus $\text{time}^{1/2}$ over a selected range of leaching data shows linearity which proved that the transport mechanism of chromium from solidified sample by the leaching liquid is controlled by diffusion. The values of D_e and LI derived are presented in Table 3. The LI values obtained were > 15 for the systems studied,

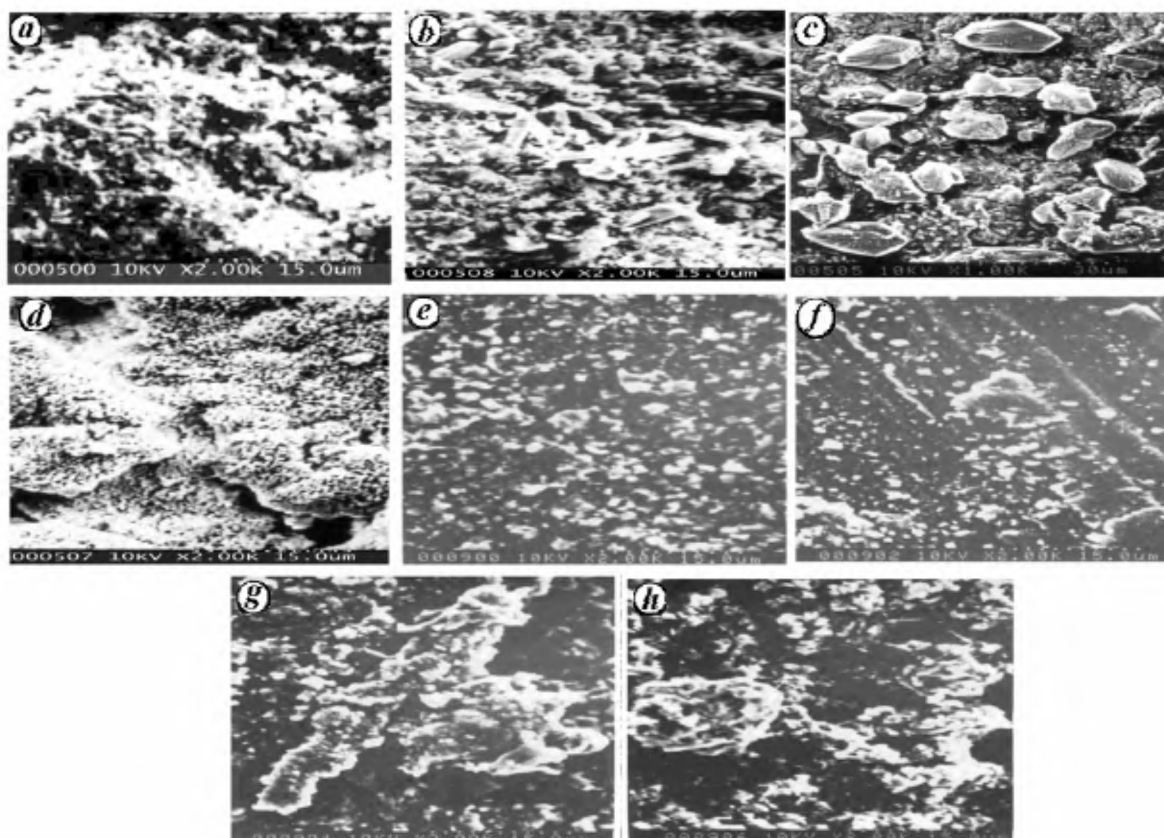


Figure 4. SEM micrograph of the solidified samples. *a*, C 2 months cured sample. *b*, FC 2 months cured sample. *c*, LC 2 months cured sample. *d*, GC 2 months cured sample. *e*, C 9 months cured sample. *f*, FC 9 months cured sample. *g*, LC 9 months cured sample. *h*, GC 9 months cured sample.

Table 3. Diffusion coefficient and leachability index of chromium by ANS test

Sample	Diffusion coefficient (D_e) (cm^2/s)	Leachability index (LI)
SC	$1.13\text{E}-17$	17.0
SFC	$9.7\text{E}-18$	17.0
SLC	$4.93\text{E}-18$	17.3
SGC	$2.64\text{E}-17$	16.6

indicating high chromium fixation by the binders investigated. Andres *et al.*⁹ reported that a value of $D_e = 10^{-5} \text{ cm}^2/\text{s}$ shows very high mobility or rapid diffusion and $D_e = 10^{-15} \text{ cm}^2/\text{s}$ indicates immobility or very slow diffusion. It could be seen from the table that the LI values range from 16.6 to 17.0 for the mix formulation studied, indicating high chromium fixation. Shon *et al.*²¹ have also reported that a LI value greater than 6 implies low contaminant diffusion. Chan *et al.*⁷ have reported LI values for heavy metals, viz. Zn, Cr, Pb, Cu and Fe ranging from 7.6 to 9.1 and from 8.3 to 9.5 in cement and cement-activated carbon matrix respectively.

FTIR results (Figure 3) confirm the presence of $\nu_2 \text{ CO}_3$ bands (874 cm^{-1}) in the control and samples containing chromium. CO_3 bands arise from the reaction between atmospheric CO_2 and $\text{Ca}(\text{OH})_2$ from the cement. The presence of CO_3 bands has been reported by Mollah *et al.*²²

and Rho *et al.*²³. A sharp band was observed at $3642, 3645, 3644$ and 3649 cm^{-1} , which is due to O–H stretching of $\text{Ca}(\text{OH})_2$. For the cement, cement–fly ash, cement–lime and cement–gypsum systems, it appears as a shoulder in the samples at $3642, 3645, 3644$ and 3645 cm^{-1} respectively. The water-stretching region, as the bending vibration band appears at 1638 cm^{-1} in cement, cement–fly ash, cement–lime control and samples, whereas in cement–gypsum control and sample it remains at 1620 cm^{-1} . The silicate phase in dry clinker exhibits a broad absorption band at 925 cm^{-1} ($\nu_3 \text{ SiO}_4^{4-}$ stretching band)²², which shifts to higher wave number (990 – 1010 cm^{-1}) on hydration. It could be seen from Figure 3 that the magnitude of shift is indicative of the degree of polymerization, which could be due to the formation of polymeric C–S–H gel and/or due to the incorporation of chromium in the place of silica or aluminium.

Scanning electron photomicrographs of all solidified samples show presence of ettringite in various forms (Figure 4). The cement stabilized sludge cured for two months showed presence of pseudocrystalline ettringite. Samples cured for nine months showed rods of chromium rich alite and chromium rich C–S–H. Belite (C_2S) phases were also seen in the sample.

The two-month-old cement–fly ash system showed prismatic crystals of ettringite. The nine months cured

specimens showed dense crystalline morphologies. Uniform distribution of fly ash particles was observed in the surface of the samples. Kula *et al.*²⁴ reported similar SEM micrograph for 5% tin ore sample solidified with 10% fly ash and 85% cement.

The two-month-old cement–lime system showed hexagonal crystals of ettringite on the surface. The nine-month cured sample showed dense morphology.

The SEM of cement–gypsum system was observed to have dense clusters of ettringite in two-month cured samples. Gypsum is one of the materials added for the formation of ettringite²⁵. The nine-month-old samples showed dense morphologies. Albino *et al.*²⁵ have reported needle-like and plate-like ettringite for systems containing Cu, Cr, Cd, Pb, Zn and Fe.

Four different kinds of binder materials, Portland cement, fly ash, lime and gypsum were tried for solidification of a synthetic metal containing waste. The stability of the solidified blocks was tested using different leaching tests such as TCLP, MTCLP and ANS 16.1. It was observed that the chromium leaching out was below the TCLP and US NRC limits. CFL versus time^{1/2} over a selected range of leaching data shows linearity, which proved that the transport mechanism of chromium from solidified sample by the leaching liquid is controlled by diffusion. The surface morphology was studied using SEM and the molecular studies were done using FTIR. There was shift in frequency due to the formation of polymeric C–S–H gel due to the incorporation of chromium in the place of silica or aluminium. Solidification can be effectively used for stabilization of chromium containing waste sludges.

1. Conner, J. R., *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, NY, 1990, p. 692.
2. Zhang, J. and Bishop, P. L., Stabilization/solidification (S/S) of mercury-containing wastes using reactivated carbon and Portland cement. *J. Hazard. Mater.*, 2002, **92**, 199–212.
3. Savvides, C., Papadopoulos, A., Haralambous, K. J. and Loizidou, M., Cement-based stabilization/solidification of metal plating industry sludge. *J. Environ. Sci. Health*, 2001, **A36**, 1129–1134.
4. Tommaseo, C. E. and Kersten, M., Aqueous solubility diagrams for cementitious waste stabilization systems. 3. Mechanism of zinc immobilization by calcium silicate hydrate. *Environ. Sci. Technol.*, 2002, **36**, 2919–2925.
5. Catalan, L. J. J., Merlière, E. and Chezick, C., Study of the physical and chemical mechanisms influencing the long-term environmental stability of natrojarosite waste treated by stabilization/solidification. *J. Hazard. Mater.*, 2002, **94**, 63–88.
6. Wang, Y. M., Chen, T. C., Yeh, K. J. and Shue, M. F., Stabilization of an elevated heavy metal contaminated site, *J. Hazard. Mater.*, 2001, **88**, 63–74.
7. Chan, Y. M., Agamuthu, P. and Mahalingam, R., Solidification and stabilization of asbestos waste from an automobile brake manufacturing facility-using cement. *J. Hazard. Mater.*, 2000, **B77**, 209–226.
8. Glasser, F. P., Fundamental aspects of cement solidification and stabilization. *J. Hazard. Mater.*, 1997, **52**, 151–170.
9. Andres, A., Velasco, F. M., Coz, A., Ruiz, C., Viguri, J. R. and Irabien, J. A., Treatment of foundry sludges by stabilization/

solidification with cement and siliceous binders. *Fresen. Environ. Bull.*, 2002, **11**, 849–853.

10. Palomo, A. and Palacios, M., Alkali-activated cementitious materials: alternative matrices for the immobilization of hazardous wastes. Part II. Stabilization of chromium and lead. *Cem. Concr. Res.*, 2003, **33**, 289–295.
11. Rossetti, A. V., Di Palma, L. and Medici, F., Assessment of the leaching of metallic elements in the technology of solidification in aqueous solution. *Waste Manage.*, 2002, **22**(6), 605–610.
12. Halim, C. E., Short, S. A., Scott, J. A., Amala, R. and Low, G., Modelling the leaching of Pb, Cd, As and Cr from cementitious waste using PHREEQC. *J. Hazard. Mater.*, 2005, **A125**, 45–61.
13. Wang, S. and Vipulanandan, C., Solidification/stabilization of Cr(VI) with cement leachability and XRD analyses. *Cem. Concr. Res.*, 2000, **30**, 385–389.
14. Rossetti, A. V. and Medici, F., Inertization of toxic metals in cement matrices: effects on hydration, setting and hardening. *Cem. Concr. Res.*, 1995, **25**(6), 1147–1152.
15. Sophia, A. C., Swaminathan, K. and Sandhya, S., Microbially influenced degradation of solidified/stabilized metal waste. *Biores. Technol.*, 2007, **98**, 2562–2567.
16. Sophia, A. C. and Swaminathan, K., Assessment of the mechanical stability and chemical leachability of immobilized electroplating wastes. *Chemosphere*, 2005, **58**, 75–82.
17. Sophia, A. C. and Swaminathan, K., Stabilization of heavy metal contaminated sludge using cement–lime system. *J. IAEM*, 2004, **31**(1), 81–86.
18. Chang, J. E., Lin, T. T., Ko, M. S. and Liaw, D. S., Stabilization/solidification of sludges containing heavy metals by using cement and waste pozzolans. *J. Environ. Sci. Health*, 1999, **A34**, 1143–1160.
19. Park, C. K., Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials. *Cem. Concr. Res.*, 2000, **30**, 429–435.
20. Yang, G. C. C. and Kao, K. L., Feasibility of using a mixture of an electroplating sludge and calcium carbonate sludge as a binder for sludge solidification. *J. Hazard. Mater.*, 1994, **36**, 81–88.
21. Shon, J. S., Lee, S. H., Lee, J. W., Kim, K. J. and Lee, J. H., Characteristics of the mechanical stability and leachability of waste form with plating sludge by reused polyethylene. *J. Environ. Sci. Health*, 2000, **A35**, 941–955.
22. Mollah, M. Y. A., Palta, P., Hess, T. R., Vempati, R. K. and Cocke, D. L., Chemical and physical effects of sodium lignosulfonate superplasticizer on the hydration of Portland cement and solidification/stabilization consequences. *Cem. Concr. Res.*, 1995, **25**(3), 671–682.
23. Rho, H., Arafat, H. A., Kountz, B., Buchanan, R. C., Pinto, N. G. and Bishop, P. L., Decomposition of hazardous organic materials in the solidification/stabilization process using catalytic-activated carbon. *Waste Manage.*, 2001, **21**, 343–356.
24. Kula, I., Olgun, A., Sevinc, V. and Erdogan, Y., An investigation on the use of ore waste, fly ash, and coal bottom ash as Portland cement replacement materials. *Cem. Concr. Res.*, 2002, **32**, 227–232.
25. Albino, V., Cioffi, R., Marroccoli, M. and Santoro, L., Potential application of ettringite generating systems for hazardous waste stabilization. *J. Hazard. Mater.*, 1996, **51**, 241–252.

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