Indian Geotechnical Journal, 38(1), 2008, 89-100

Stabilization of Heavy Metal Containing Waste using Flyash and Cement

S.S. Shah* **and Malik Shoeb Ahmad****

Introduction

Metal finishing and electroplating industries generate large quantities of toxic waste sludge containing Cr, Pb, Ni, Cd and Zn that are mainly disposed on landfill, causing real threat to the environment (Savvides et al., 2001). Solidification/Stabilization (S/S) is a promising technology that uses the addition of a binding agent to encapsulate and reduce the mobility of the hazardous waste elements (Lange et al. 1996). As the restrictions on landfilling become stronger and wastes are banned from land disposal, S/S could potentially play an important role in making wastes acceptable for land disposal. Lower permeability and lower contaminant leaching rates can make banned wastes acceptable for land disposal after S/S (Wiles, 1987).

Cement-based S/S uses portland cement as a binding agent. When portland cement is mixed with water, heat is evolved and the mixture becomes strongly alkaline. During the initial reaction period, the anhydrous clinker grains become coated with a nearly amorphous precipitate, which acts as a semiprotective film and slows reaction during the induction period. Towards the end of the induction period, breakdown of the film marks the onset of rapid strength gel network linking particles, resulting in physical stiffening of the cement matrix. As the gel continues to stiffen and densify, the cement gains strength. Typical modern portland cement achieves about two thirds of hydration in 28 days (Glasser, 1997). The main chemical that is considered in hydrated cement is colloidal calcium silicate hydrogel known as C-S-H and this gel product is formed at the cement particle surfaces (Cocke 1990). C-S-H has important implications for the mechanisms of fixation during solidification (Yousuf et. al. 1995; Hills et al. 1996) and is principally responsible for strength development (Cartledge et. al. 1990). Ghosh and Subbarao (1998) studied stabilization of fly ash containing heavy metals by using lime as a binder and gypsum as an additive. Fly ash was effectively stabilized with lime to reduce leaching of metals, such as copper, iron, nickel, and zinc. Moreover, lime and gypsum reduced the hydraulic conductivity of the unstabilised fly ash by approximately three orders of magnitude from 8×10^{-7} to 4.53×10^{-10} m/s. Chang et. al. (1999) studied the S/S of metal containing hazardous sludge using cement and waste pozzolanas. The solidification additives were chosen as 17% cement, 14% slag, 55% fly ash, and 14% shell lime. Tanning and electroplating waste sludge were used. The characteristics of the S/S product, including

---

* Professor, Dept. of Civil Engineering, Aligarh Muslim University, Aligarh 202002, Email sssced@yahoo.com

** Lecturer, Dept. of Civil Engineering, Aligarh Muslim University, Aligarh 202002

compressive strength and metal concentration in the leachate, were evaluated. Unconfined compressive strength values at the end of the 28 day-cure period were in the range of 1,200–5,700 kN/m^2 and 1,600–4,600 kN/m^2 for electroplating and tanning waste sludges, respectively. Although several studies on the solidification of metals in synthetic waste are reported, data on application of solidification to industrial waste sludge is very few. Asavapisit and Chotklang (2004) investigated the potential for utilization of alkali-activated pulverized fly ash (PFA) as solidification binder for the treatment of electroplating sludge. Carmalin et. al.(2005) have assessed the mechanical stability and chemical leachability of immobilized electroplating waste containing chromium. Sludge generated from electroplating industries is highly complex due to the presence of metal ions and other inorganics, which pose serious problem on disposal. Therefore, the prior treatment and precipitation of the waste sludge containing heavy metals is important before stabilization. In the past, lime was added to the sludge to dehydrate it and to raise the pH to 12 or higher but the use of lime as a stabilizing agent has only recently gained recognition (Metcalf and Eddy, 2003). Mendonca, et. al (2006) have studied the stabilization of arsenic-bearing sludge using lime. The study determines the shear strength characteristics of the sludge before and after lime stabilization and were obtained through unconsolidated undrained triaxial tests performed at lime content weight percentages of 0, 5, 10, and 20%. Leaching potential of metal ions after S/S was evaluated by TCLP leaching test. The study showed that the technique is promising in fixing the heavy metals.

About 3,881 million litres of effluents are being generated by different industries in India. The wastewater generated in Aligarh by lock industries, specially electroplating industries is around 250 million litres per day (Agarwal, 2001). The present study was carried out with an aim to stabilize the detoxified and precipitated electroplating waste sludge using portland cement and flyash as binder for solidification. In this study a modest but environmental friendly method has been proposed to solidify the waste to a solid having high structural integrity with prior destruction of cyanide and reduction of Cr (VI) to Cr (III) by effective precipitation.

Materials and Methodology

Materials

Electroplating waste sludge was collected from one of the electroplating industries in Aligarh City, India, in which Nickel, Chromium, Zinc and Cadmium plating is done, associated mostly of lock and other allied industries. The waste sludge was obtained by filtration process (waste sludge passing through screen) of the electroplating water. By oven drying method it was found that the filtrate consists of 30% wastewater and 70% solid waste. Heavy metal analysis was carried out using GBC-902 Atomic Absorption Spectrophotometer.

The flyash used in this study was obtained from Harduaganj Thermal Power Plant, Kasimpur, (India). An x-ray diffraction was carried out to identify the mineral phases present in the flyash. X-ray diffraction showed that the flyash contains substantial amount of alumina and silica but the potential clay minerals (e.g. illite, kaolinite, and montmorillonite) were absent in the Harduaganj flyash. This flyash is characterized by low specific gravity (1.85) due to presence of hollow particles (Kaushik et. al. 1998). The flyash is predominantly a silt sized material about 90% particles are silt sized (Gray & Lin, 1972). In the present study, flyash contains around 88% silt sized particles. The presence of unburnt carbon and silt sized particles results in lower dry density (9.3 kN/m^3). The physical and chemical properties of flyash and electroplating waste sludge are given in Table 1 to Table 3.

Table 1 Physical and Chemical Properties of Flyash

Constituent/Property	*Value*
Colour	Grey
Percent passing 75 micron sieve	70%
Size of the particle	0.002-0.10mm
Maximum dry density	9.3 kN/m^3
Specific gravity	1.85 at 27^o C
Surface Area	3060 cm^2/g
Unburnt Carbon	11.80%
SiO_2	46-62%
Al_2O_3	19-28%
Fe_2O_3	4 -20%
CaO	0.6-4%
MgO	0.2-2%
S_2O_3	Traces to 0.3%

Table 2 Physical Properties of Electroplating Waste Sludge

Constituent/Property	*Value*
Total Solids	128345mg/l
Total dissolved solids	6417.2mg/l
Total suspended solids	121927mg/l
Specific gravity	1.022
pH	1.2<2 (Hence hazardous)

Table 3 Heavy Metal Concentration in Electroplating Waste sludge

Metals	*Concentration (mg/l or ppm)*
Nickel	610
Chromium	630
Zinc	800
Cadmium	25
Copper	300
Lead	5.0

Methodology

The treated and precipitated electroplating waste sludge was dried, grinded and sieved through 425 µ IS sieve.

The Proctor compaction test was carried out to obtain Maximum Dry Density (MDD) and Optimum Moisture Content (OMC) of oven dried flyash. The OMC of the flyash was obtained as 25%, which also satisfies, the IS: 456 (2000) requirements (i.e. 25% water by weight of cement is to be added to cement mortar for chemical reactions).

The 100x100x100mm cubes were cast for various percentages by weight of flyash (FA) and sludge(S) without cement (95%FA+5%S, 90%FA+10%S, 85%FA+15%S, 80%FA+20%S, 75%FA+25%S, 70%FA+30%S, 65%FA+35%S, 60%FA+40%S).

To obtain good workability and better strength the cubes were cast by replacing a small part of flyash with cement(C) in different percentages 2% to 12%(with the variation of 2%) with flyash and sludge such as for 8% cement, 5% sludge and 87% FA the mix can be represented as 8% C + 87% FA + 5% S .

After 24 hours, the cubes were taken out from the moulds and cured in a temperature controlled curing tank. Each set of four cubes was cured for 7 days, 14 days, 21 days, 28 days and 90 days.

The cured cubes were tested for compressive strength determination by compression testing machine.

Finally Toxicity Characteristics Leaching Procedure (TCLP) tests were conducted to determine the leachates from different samples to establish the environmental acceptability of the mix.

TCLP is the Environmental Protection Agency’s (EPA) Procedure for assessing the potential for hazardous wastes to leach in the ground water from a landfill (EPA, 1992). As described in the TCLP procedure, the moulded cubes of 90 days curing were crushed to particles less than 1 mm in diameter and then blended with a weak acetic acid extraction liquid, in liquid to solid weight ratio of 20:1 and was agitated in a rotary extractor for a period of 18 hours of agitation. The extract was filtered through a certified TCLP 0.7µ borosilicate glass fibre filter, and the filtrate was analyzed for Ni, Cr, Cd, Pd and Zn by using GBC-902 Atomic Absorption Spectrophotometer.

Treatment and Precipitation of Waste Sludge

Cyanide may be present in electroplating waste in complex form. The waste was hence checked for the presence of cyanide using silver nitrate solution. Formation of white silver cyanide precipitate confirmed the presence of cyanide in the waste. Since metal in the form of cyanidic complex cannot be precipitated, pre-treatment of the waste was carried out using bleaching powder and sodium thiosulphate.

Calculated amount of lime was added for precipitation of other heavy metals present in the waste that increases the pH to 8.5 – 9.5, where solubility of heavy metals is the least (Metcalf & Eddy, 2003).

Results and Discussions

Compressive strengths for mix were determined at curing periods of 7, 14, 21, 28 and 90 days for specimen continuously cured in water.

Effect of Waste and Aging on Compressive Strength of Flyash-Waste mix

Figure 1 shows that the strength of mortar is affected by sludge percentages and curing periods.

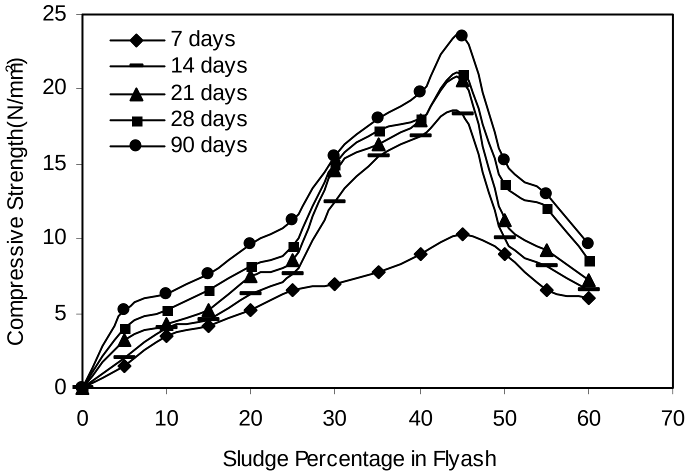

Fig. 1 Effect of Waste on Compressive Strength of Plain Flyash

It can be observed that as the sludge percentage increases the compressive strength also increases upto certain percentage of sludge thereafter strength starts decreasing. The increase in the strength upto certain extend might be due to use of lime for precipitation as well as presence of metal dust in sludge, which is acting as a reinforcing agent. The addition of lime to flyash-sludge mix causes two basic sets of reactions (Osinubi, 2006), one being a short-term reaction while the second is a longterm reaction. The immediate effect of introduction of lime to the flyash is to cause flocculation and agglomeration of the flyash particles caused by cation exchange at the surface of the flyash particles. The result of this short-term reaction is to enhance workability and provide an immediate reduction in swell, shrinkage. The long-term reactions which are accomplished over a period of time for completion of these reactions depending on the rate of chemical breakdown and hydration of the silicates and aluminates. This results in the formation of cementitious material, which binds the flyash particles together. However, owing to the flocculation which predominates at the initial stage as a result of the quicker short-term cation exchange reaction, the subsequent strength improvement is as a result of the long term pozzolanic reaction which is enhanced by the hydration of slag. Furthermore, additional bonding is provided by compaction as this enhances the close packing between particles mechanical bonding while soaking and curing provide hydraulic and thermal bonding effects, respectively.

However, on addition of sludge to flyash beyond 45% the decrease in compressive strength can be observed. On inspection it was observed that the cubes made of higher sludge percentage showing shrinkage and cracks, which might be due to presence of sulphate, chloride and boric acid etc. present in the mix. According to IS: 456 (2000) the sulphate is a strength retarder, it should be restricted to 0.02% in soil, which is in contact with concrete. However, the waste sludge used in this study contains 5% sulphate, which is reasonably high as compared to minimum limit. Sulfate attack will cause expansion, cracking or spalling or softening and disintegration.

It is evident from Figure 1 that the optimum sludge percentage is around 30% to 45%. The maximum compressive strength at 55% flyash and 45% sludge after 90 days curing is 23.50 N/mm^2. It is also observed from Figure1 that the compressive strength increases with increase of aging but the significant gain in strength can be observed for the above combination at 14 days curing with comparison to 7 days curing. The percent increase in strength at 14 days curing with respect to 7 days is 78%. The compressive strength at 7, 14, 21, 28 and 90 days are 10.25, 18.25, 20.56, 21.03 and 23.5N/mm^2 respectively. This indicates that the gain in the strength continues with aging but most of the strength is achieved at 14 days curing. According to IS: 3812 the average compressive strength of flyash stabilized with lime at 28 days should be 4 N/mm^2. However, in the present study when flyash is mixed with lime precipitated sludge nearly 487% increase in the compressive strength is observed as compared to flyash mixed with lime only.

Effect of Cement on Compressive Strength of Plain Flyash

Cement in various percentages (2%, 4%, 6%, 8%, 10%, 12%, 14%, 16%, 18% and 20%) was added as additive to the flyash without sludge. The results presented in Figure 2 shows that by increasing the cement percentage, compressive strength of flyash-cement mix also increases but the significant increase in strength was observed from 8.2 N/mm^2 at 6% cement to 14.5 N/mm^2 at 8% cement at 7 days curing, while at 20% cement the compressive strength was observed as 22.4 N/mm^2 for 7 days curing.

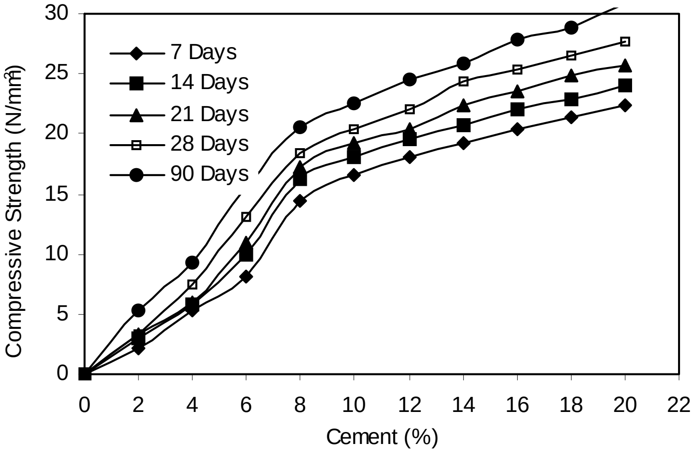

Fig. 2 Effect of Cement on Compressive Strength of Plain Flyash

Therefore, due to economical considerations the optimum percentages of cement may be considered as 8% for further study.

Effect of Waste and Cement on Compressive Strength of Flyash-Waste- Cement Mix

Asavapisit and Chotklang, (2004) reported that as the sludge ratio in the solidified blocks increases, the compressive strength decreases. However, in this study it is observed that the compressive strength increases upto certain percentage of lime precipitated sludge (30% to 45%) in cement flyash system as shown in Figures (3 to 6).

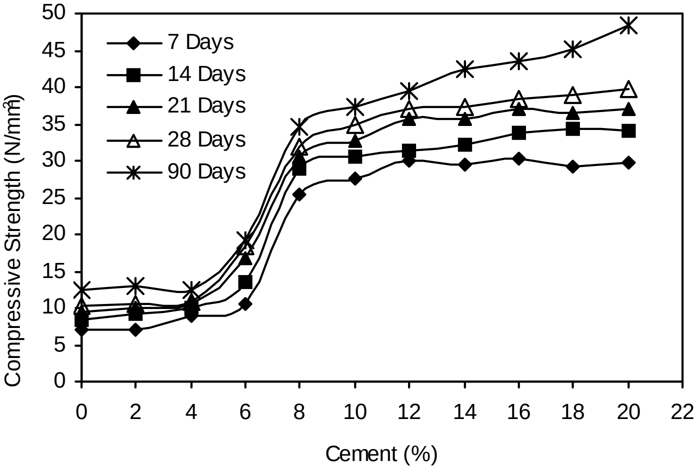

Fig. 3 Effect of Cement on Compressive Strength of Flyash-30% Waste Mix

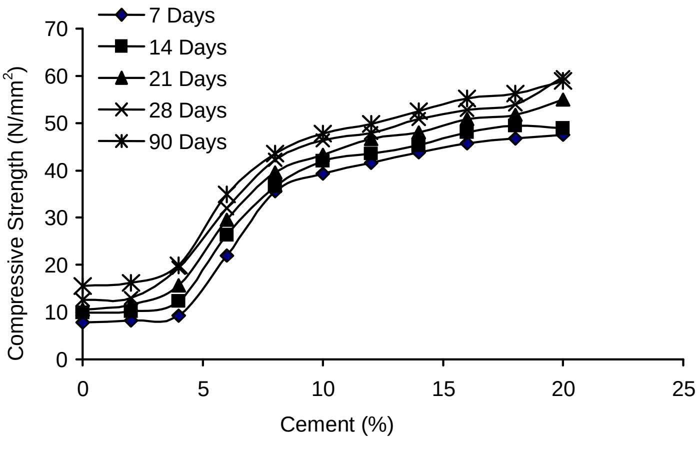

Fig. 4 Effect of Cement on Compressive Strength of Flyash-35% Waste Mix

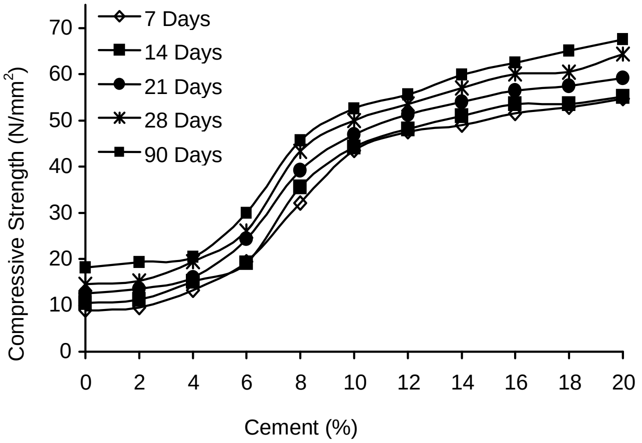

Fig. 5 **Effect of Cement on Compressive Strength of Flyash-40% Waste Mix**

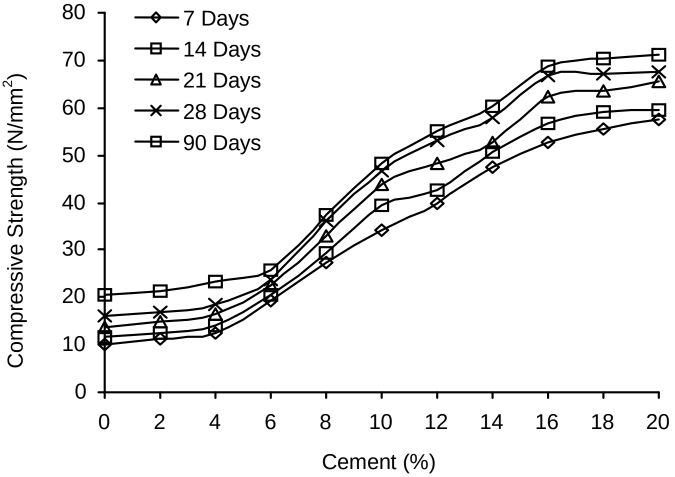

Fig. 6 **Effect of Cement on Compressive Strength of Flyash-45% Waste Mix**

The initial gain in the strength is due to presence of excess lime in sludge. Rehsi, (1998) have suggested that the mechanism of pozzolonic reaction between siliceous and aluminous constituents of flyash- lime mixture leading to strength development. However, the excessive quantity of lime in flyash causes decrease in strength of the mix due to carbonation reaction, while the excessive presence of sulfate in the mix retards the process (Kaushik and Kumar, 1998, Perera, 2005). On analyzing these figures it can be observed that the significant strength has been observed for waste range between 30% to 45%. For further increase in sludge percentages up to 60% in the mix, the strength is decreasing. The percentage increase in 28days compressive strength from 30% to 40% at 8% cement is 36% while from 30% to 45% is 13%, therefore the optimum percentage may be adopted between 30% to 40% in general and 40% in particular. From Figures 3 to 6 it can also be observed that the strength is remarkably increasing with increase in curing cycle. For 30% sludge and 8% cement the percentage increase in the strength for 7 days curing to 90 days curing is 28%. For 40% sludge the increase is 42% and for 45% sludge it is around 36%. Therefore, it may be concluded that the optimum sludge percentage may be in the range of 30% to 40%.

Leachability

The results of TCLP test are presented in Figure 7. The heavy metals (Ni, Cr, Cd, Pb and Zn) limits in the mix C_4S_9 (Flyash = 47%, Waste = 45%, Cement =8%) on 90 days of curing were less than the TCLP regulatory value (3, 5, 1, 5 and 5.0) demonstrating that that the heavy metals in sludge is well fixed by cement-flyash system.

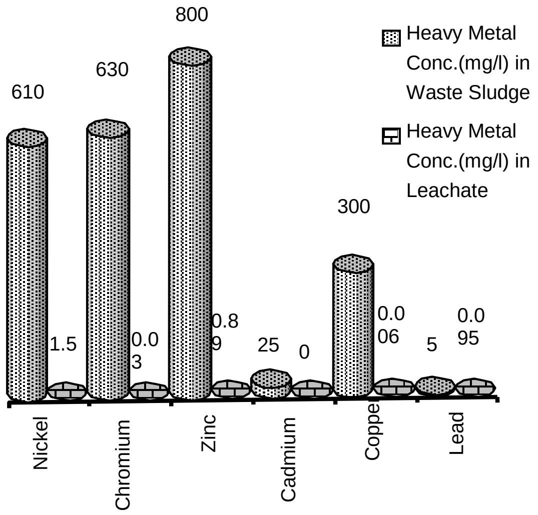

Fig. 7 Leaching of Heavy Metals from Cement Flyash Stabilized Cubes after 90 days of Curing

The order of metal retention was greater in cement-flyash mix than the cement system as the addition of flyash in mix enhanced heavy metal binding. The reason could be that, the flyash acts both as a fine aggregate and as a cementitous component enhancing the binding process. Chang et. al. (1999), Pinero et. al (1998) and (Carmalin et. al. 2004) have reported similar results. Therefore, from present study it can be concluded that the higher percentages of flyash in the mix restricts the mobilization of heavy metals.

Conclusions

The laboratory investigations lead to the conclusion that the electroplating waste and flyash (the waste product of Thermal Power Plants), which creates enormous problems of dumping and disposal can be well utilized as construction materials. On the basis of the present study, the following conclusions were drawn:

1. The stabilization process is very effective in controlling the environmental pollution because the heavy toxic metals are completely recycled without any adverse impact on the environment.
2. The maximum compressive strength was obtained for 60% to 55% flyash, 30% to 45% waste and 8% cement composition. The average compressive strength for the above range of mix is 38.4 N/mm^2 at 28 days curing cycle.
3. To achieve better economy and moderate strength the 55% flyash – 45% waste gives the best composition to have 21.03 N/mm^2 & 23.5 N/mm^2 compressive strengths at 28 & 90 days curing cycles respectively. Therefore, the optimum percentages of flyash and waste are 55% & 45% respectively.
4. As curing time increases, the compressive strength also increases, which shows that the mix is durable and long lasting. The significant increase in compressive strength is observed between 14 to 28 days curing cycles. However, on increasing curing cycle for further upto 90 days, the mix not only maintains its strength but the increase in its strength can be observed.
5. On studying the leaching effect of different mixes it is found that the pH is between 8.0-11.0. On analyzing the mix by Atomic Absorption Technique, it is observed that the concentration of heavy metals in the leachates is drastically reduced. This process is so effective that it reduces around 97% to 100% heavy metal in the leachates when compared with TCLP limit into land surface water.
6. It is also concluded that the quantity of waste could be added maximum upto 45% because the further addition of waste in flyash increases the strength but shrinkage cracks occurs after certain passage of curing time.

References

Agarwal, A. (2001). *“Water pollution from small scale industries.”* Centre for Science and Environment, New Delhi.

Asavapisit, S. and Chotklang, D. (2004). *“Solidification of electroplating sludge using alkali-activated pulverized fuel ash as cementitious binder.”* Cem. Concr. Res. 34, 349–353.

Carmalin, A. and Swaminathan, K. (2005). *“Assessment of the mechanical stability and chemical leachability of immobilized electroplating waste.”* Chemosphere, 58, pp.75-82.

Cartledge, F. K., Butler, L. G., Chalasani, D., Eaton, H. C., Frey, F. P., Herrera, E., Tittlebaum, M. E., and Yang, S. (1990). *‘‘Immobilization mechanisms in solidification/stabilization of Cd and Pb salts using portland cement fixing agents.’’* Environ. Sci. Technol., 24 (6), 867– 873.

Chang, J., Lin, T., Ko, M., and Liaw, D. (1999). *‘‘Stabilization/solidification of sludges containing heavy metals by using cement and waste pozzolans.’’* J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng., 34 (5), 1143–1160.

Cocke, D. L. (1990). *‘‘The binding chemistry and leaching mechanism of hazardous substances in cementitious solidification/stabilization systems.’’* J. Haz. Mat., 24(2/3), 231–253.

Environmental Protection Agency (1992). *“Test methods for evaluating solid waste.”* Vol. 1C, method 1311, Washington, DC.

Ghosh, A., and Subbarao, C. (1998). *‘‘Hydraulic conductivity and leachate characteristics of stabilized fly ash.’’* J. Environ. Eng. (Reston,Va.), 124(9), 812–820.

Glasser, F. P. (1997). *‘‘Fundamental aspects of cement solidification and stabilization.’’* J. Haz. Mat., 52(2/3) 151–170.

Gray & Lin (1972). *“Engineering properties of compacted flyash.”* ASCE Soil Mechanics and Foundation Engineering Division, Vol. 101, No. 3, pp. 239-255.

Hills, C. D., Lange, L. C., Mole, C. F., Schrapel, K., and Poole, A. B. (1996). *‘‘The effect of alite content on portland cement solidified waste forms.’’* Environ. Technol., 17(6), 575–585.

IS: 3812 (1999). *“Specification for Flyash For Use as Pozzolana and Admixture.”* BIS, New Delhi.

IS: 456 (2000). *“Plain and Reinforced Concrete- Code of Practice.”* BIS, New Delhi.

Kaushik, N.P. and Ramaswamy, G. (1998). *“Bulk Untilization Possibilities of Ash.”* Proceeding of workshop on Utilization of Flyash. ICI, Roorkee pp. 20-29.

Kaushik, N.P. and Ramaswamy, G. (2000). *“Performance of compacted ash and sand fills under load.”* Ph.D. Thesis, Department of Civil Engineering, University of Roorkee, Roorkee.

Kaushik, S.K. and Kumar, A. (1998). *“Flyash – Silica fume high performance concrete – A state of the art.”* Proceeding of workshop on Utilization of Flyash. ICI, Roorkee, pp. 15-47.

Lange, L., Hills, C., and Poole, A. (1996). *‘‘Preliminary investigation into the effects of carbonation on cement-solidified hazardous wastes.’’* Environ. Sci. Technol., 30(1), 25–30.

A. Mendonça; T. C. Brito Galvão; D. C. Lima and Soares E. P. (2006). *“Stabilization of Arsenic Bearing Sludge using lime.”* Journal of materials in Civil Engineering, ASCE, Vol. 18, No. 2, pp. 135-139.

Metcalf and Eddy Inc. (2003). *“Waste Water Engineering. Treatment, Disposal, Reuse.”* Fourth Ed. Tata McGraw Hills New Delhi.

Osiubi, K.J. (2006). *"Influence of compactive efforts on lime slag treated black cotton clay."* J. of Materials in Civil Engineering. Vol. 18, No. 2, pp. 174-181.

Perera, A.S.R. (2005). *"Accelerated carbonation of stabilised/solidified contaminated soils."* PhD, Thesis University of Cambridge, UK.

Pin˜ero, R.M., Pereira, F.C., Francoy, R.E.C., Parapar, V.J.F. (1998). *"Stabilization of a chromium-containing solid waste immobilization of hexavalent chromium."* Journal of Air Waste Management Association 48, 1093–1099.

Rehsi, S.S. (1998). *"Characteisation of Flyashes."* Proceeding of Workshop on Utilization of Flyash. ICI, Roorkee pp.48-54.

Savvides, C., Papadopoulos, A., Haralambous, K.J., Loizidou, M. (2001). *"Cement-based stabilization/solidification of metal plating industry sludge."* J. Environ. Sci. Health A 36, 1129– 1134.

Wiles, C. C. (1987). *''A review of solidification/stabilization technology.''* J. Haz. Mat*.,* 14(1), 5–21.

Yousuf, M., Mollah, A., Vempati, R. K., Lin, C., and Cocke, D. L. (1995). '*'The interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems.''* Waste Management. 15(2), 137–148.