Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 153 (2008) 1103–1109
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Influence of pH, curing time and environmental stress on the immobilization of hazardous waste using activated fly ash

Shefali Srivastava, Rubina Chaudhary *, Divya Khale

School of Energy and Environmental Studies, Devi Ahilya University, Takshila Campus, Khandwa Road, Indore 17, M.P., India

Received 18 November 2006; received in revised form 18 September 2007; accepted 18 September 2007
Available online 25 September 2007

Abstract

The current work is related to inorganic species in sludge generated from Common Effluent Treatment Plant contaminated with hazardous wastes at relatively high concentration. The environmental sensitive metals studied in the sludge are Pb, Fe, Ni, Zn and Mn. The solidification/stabilization (S/S) of heavy metals within fly ash-cement-based matrix was conducted for low cost treatment and reuse of sludge. The study examines the strength of the S/S product by predicting the effect of supplementary cementing material from efficiency factor (k) at 60 °C curing temperature. The leaching test was performed at two different pH 7 and 4 to determine the efficiency of heavy metal immobilization. It was observed that replacing 76% OPC by 56% fly ash and 20% sludge for 28 days curing period shows increase in strength as well as rate of stabilization for zinc, iron and manganese at pH 7, lead and nickel were stabilized by 79 and 82%, respectively. Environmental stress test was performed to evaluate the tolerance of extreme adverse environmental condition.

Keywords: Activated fly ash; Compressive strength; Leaching; Environmental stress

1. Introduction

The present scenario is the disposal of the waste generated from the industry like sludge and fly ash. Being bulky in nature, both the sludge and fly ash face disposal problem. Presently, landfill is not the only desirable option as it causes huge financial burden to the industries. At the same time increasing load of toxic metals causes the potential threat to contaminate soil as well as ground water [1,2].

The solidification/stabilization (S/S) of hazardous wastes by pozzolan-based binders is a most familiar technology that has been applied to many types of industrial wastes, mainly those containing heavy metals [3,4]. S/S technology does not remove heavy metals from the polluted waste but has the purpose to physically as well as chemically fix them in the solid matrix in order to reduce their mobility, to minimize the threat to the environment, and to ensure compliance with existing regulatory standards [5,6]. Earlier studies were conducted for the immobilization of heavy metals by ordinary Portland cement but for the generation of 1 t of Portland cement about 1 t of green house gas CO_2 released to the atmosphere as a result of de-carbonation of lime in the kiln during manufacturing of cement and cause major problem of global warming [2,7]. To reduce this CO_2 emission a major portion of Portland cement is replaced by fly ash which itself has pozzolanic properties. This pozzolanic character of fly ash immobilizes the heavy metal by the formation of well bonded and low porosity network of calcium silicate and aluminate hydrates that acts as a binding agent [8–10]. The mechanical and durable property of the final S/S of the pozzolan increases by alkali activation and curing at elevated temperature [10–16]. The objective of the present work is to utilize fly ash for the immobilization of heavy metal bearing CETP sludges and to study its treatability by the solidification/stabilization process at different pH, and effect of environmental stress conditions.

2. Materials

The sludge samples were collected by grab-composite method from the sludge drying bed of the Common Effluent Treatment Plant of electroplating units, drying units, and pickling units. The physico-chemical and heavy metals (Mn, Zn, Pb, Cu, Fe and Ni) analysis of the sludge are given in the

* Corresponding author. Tel.: +91 731 2460309; fax: +91 731 2467378.
E-mail address: rubina_chaudhary@yahoo.com (R. Chaudhary).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.09.065

Table 1
Physico-chemical analysis of raw sludge

pH	EC (μS)	Bulk density	Moisture content (%)	Alkalinity (mg/l)	Chloride (mg/l)	Sulphate (mg/l)
6.5	3.8	0.55	12.70	119.0	209.9	2080

Table 2
Heavy metal analysis of raw sludge and available content at pH 7 and 4

Serial no.	Heavy metals	Conc. (mg/kg) (total)	Available conc. (mg/kg) (pH 7)	Available conc. (mg/kg) (pH 4)
1	Mn	3019.8	2743.1	2986.2
2	Pb	381.4	362.3	375.3
3	Zn	395.3	349.4	371.5
4	Ni	960.8	882.0	926.2
5	Fe	5683.6	5228.9	5513.0

(Tables 1 and 2). Low calcium fly ash and commercially available 53 grade Portland cement was used as a binder for fixation of the heavy metals. For alkali activation of fly ash, 5 M sodium hydroxide and 5% of total weight sodium silicate was used. The percentage of waste and binders is given in Table 3.

2.1. Procedure

2.1.1. Unconfined compressive strength

In order to simplify the sample screening process, the compressive strength was selected as the benchmark parameter. This is not unusual because compressive strength has an intrinsic importance in the structural design of concrete structures [17].

For UCS testing, cubes of 5 cm × 5 cm × 5 cm were prepared using different waste-binder ratios. The mixture was inserted in a cubic mold, compacted and vibrated to remove all the entrapped air. The cubes were unmolded after 24 h. The test was performed on a Universal Testing Machine (Model—TUN 400).

2.1.2. Efficiency factor

To predict the effect of fly ash on the compressive strength of cement as a binder, the concept of the efficiency factor (*k*-value) was described by Papadakis and Tsimas [18].

The efficiency factor is defined as the part of fly ash that can be considered as equivalent to Portland cement having same properties without fly ash. The *k*-value is equal to 1 for Portland cement. In this work, the efficiency factor was determined in order to draw conclusions regarding the effectiveness of fly ash and other activating solutions.

For estimating the *k*-values, the expression for the compressive strength (f_c) measured for the constructed systems:

$$f_c = K\left\{\frac{1}{W/(C+kP)}\right\} \quad (1)$$

where K is a parameter depending on the cement type (here, 30 MPa), C and P are the cement and fly ash contents, respectively, in the mix (kg/m^3), and W is the water content (kg/m^3).

2.1.3. Total available leaching test

The leaching test involves testing the material in the worst conditions to stimulate the effects of handling and other environmental conditions. The rapid attainment of equilibrium was facilitated by agitation, which prevented stratification. The Dutch total available leaching test NEN 7431[19] was used to quantify the elemental mass fraction available for leaching. The extraction solubilized all readily soluble and marginally soluble minerals. Three grams of material (size < 125 μm) were leached in distilled water in two serial steps: first at pH 7 with liquid/solid ratio (L/S) of 100 for 3 h and then at pH 4 for 18 h. The pH was controlled by using 1 M HNO_3. These two leachate fractions were kept separately for chemical analysis and heavy metals analysis. The instruments used for above analysis were Nephalometer, pH meter, conductivity meter (systronics), and atomic absorption spectrophotometer (Shimadzu AA-6300) [20].

Table 3
Percentage composition of the samples used during investigation

Sample no.	Sludge (%)	Cement (%)	Fly ash (%)
1	0	30	70
2	10	27	63
3	14.2	25.7	60
4	20	24	56
5	25	22.5	52.5
6	33	20	46.6
7	50	15	35

2.1.4. Environmental stress test

Durability relates to the long-term stability of the S/S product. Durability testing evaluates resistance of a solidified/stabilized product to degradation, due to external environmental stresses. The tests are designed to mimic natural condition by stressing the specimen through (a) freezing and thawing and (b) heating and thawing. The solidified/stabilized specimen undergoes repeated cycling during the testing. Each of the test specimens was subjected for freezing at $-8 \pm 2\,^{\circ}$C and heating at $60 \pm 2\,^{\circ}$C for 12 cycles [21,22].

In this study, environmental stress test was performed on the screened ratios. Criteria of 30% weight loss were used as a rejection ground for the durability test based on the study of Stegemann and Cote [23]. The effect of varying temperatures on the matrix was monitored. The importance of waste resistance to freeze thaw and heat thaw is strongly dependent on the geographical location of the disposal site.

3. Results and discussions

The samples were studied for UCS, leachability and environmental stress test. The results are discussed on the immobilization of heavy metals at pH 4 and 7, for different waste-binder ratios cured for 7 and 28 days.

3.1. Unconfined compressive strength

Strength test data often used to provide a baseline comparison between unstabilized and stabilized wastes. Prepared samples of different waste-binder ratio were cured for 7 and 28 days at 60 °C and were subjected to unconfined compressive strength test. Unstabilized waste materials generally do not exhibit good compressive strength; however, if the waste is stabilized into cement-like form the strength characteristics can increase significantly [5].

Table 4
Comparison of compressive strength and efficiency factor for 7 and 28 days curing period

Sample no.	Sludge (%)	UCS		*k*-value	
		7 Days	28 Days	7 Days	28 Days
1	0	20	21.4	0.9	0.87
2	10	18.5	18.6	0.8	0.84
3	14.2	16.5	17.4	0.7	0.73
4	20	17	17.8	0.68	0.7
5	25	13.5	15.4	0.41	0.5
6	33	11	13.4	0.18	0.3
7	50	10.5	12.2	0.02	0.09

Table 4 shows the sludge percentage and strength of the sample. It was observed that, for 7 and 28 days of curing period, strength for reference sample increased whereas strength decreased with increase in sludge from 0 to 50% for 7 days curing. For 28 days curing, strength of the sample increased with increase in sludge from 10 to 20% and then decreases on further addition of sludge. For 25–50% sludge, the strength was almost same for both 7 and 28 days curing period (Table 4). Initial curing temperature of 60 °C, accelerates pozzolanic reaction and hence decreases setting days. Strength for all W/B ratios was lower as compared to reference sample. Low strength may be due to waste addition that affects the C–S–H hydration. Metal ions form precipitates on cement clinker grain are believed to be responsible for the retardation of cement hydration reaction (CSH) [24]. Another reason for the low strength may be increased L/S ratio. With the increase in W/B ratio the water demand of the sample increases resulting in lower compressive strength [25,26].

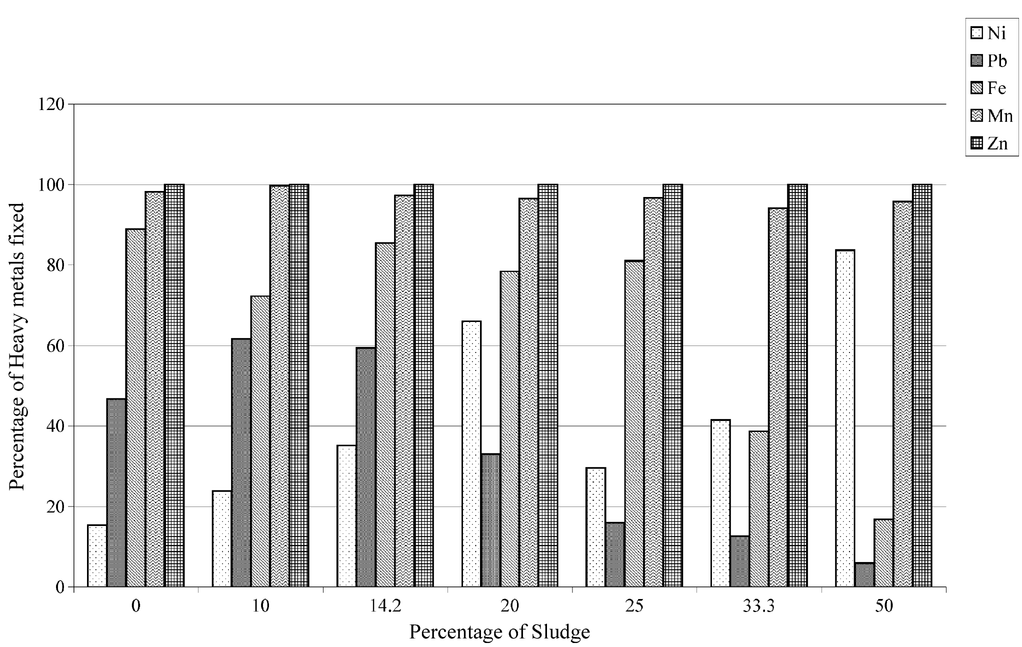

Fig. 1. Effect of pH 7 on metal fixation at 7 days of curing.

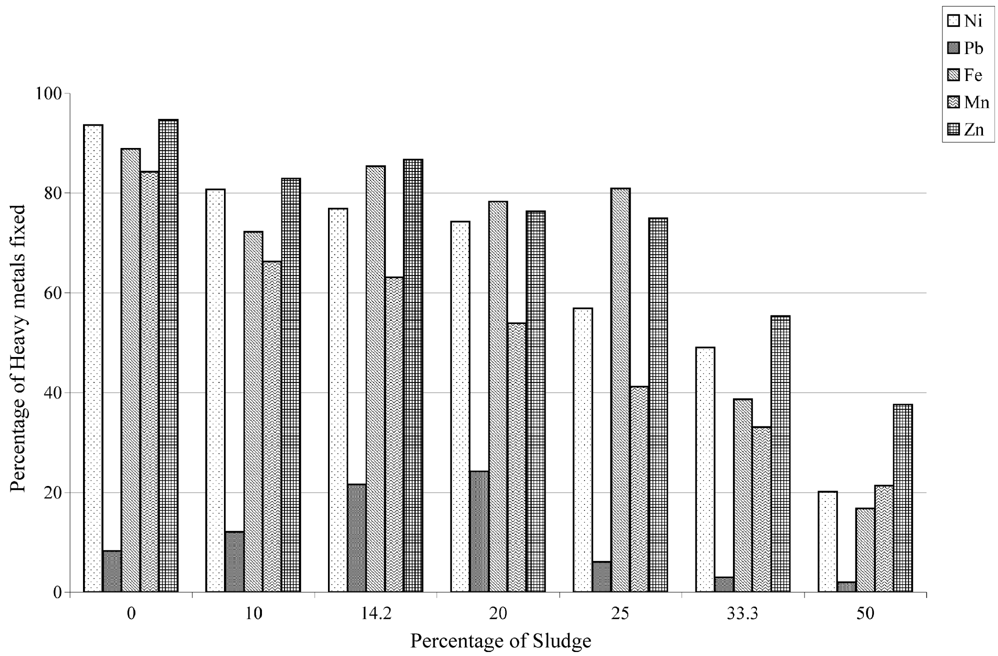

Fig. 2. Effect of pH 4 on metal fixation at 7 days of curing.

In the frame of this study, where a small replacement of fly ash by alkali took place, *P* was considered as the sum of fly ash and alkali in each blend. Applying in the Eq. (1), the measured values of the compressive strength, the *k*-values, for the activated systems were calculated and presented in Table 4.

For the pure binder specimen, the efficiency factor increases with increase of curing days as the hydration procedure evolved. Table 4 shows that on increasing sludge from 10 to 25% the *k*-value was nearer to unity which indicates that compressive strength is comparable to cement and can be further studied for environmental stress test.

3.2. *Heavy metal leaching*

Leaching test is probably the single most important measure of the effectiveness of heavy metals immobilization within fly ash-based matrix. Table 2 presents maximum leachable portion of the heavy metals from raw sludge, available under aggressive leaching condition. The S/S products showed a high retention of heavy metal. The predominant metals in the sludge are iron, manganese and nickel accomplished by lesser amount of lead and zinc (Table 2). In terms of total amount of metals these species were more abundant in sludge. Figs. 1 and 2 present percentage of heavy metals fixed in the alkali-activated matrix

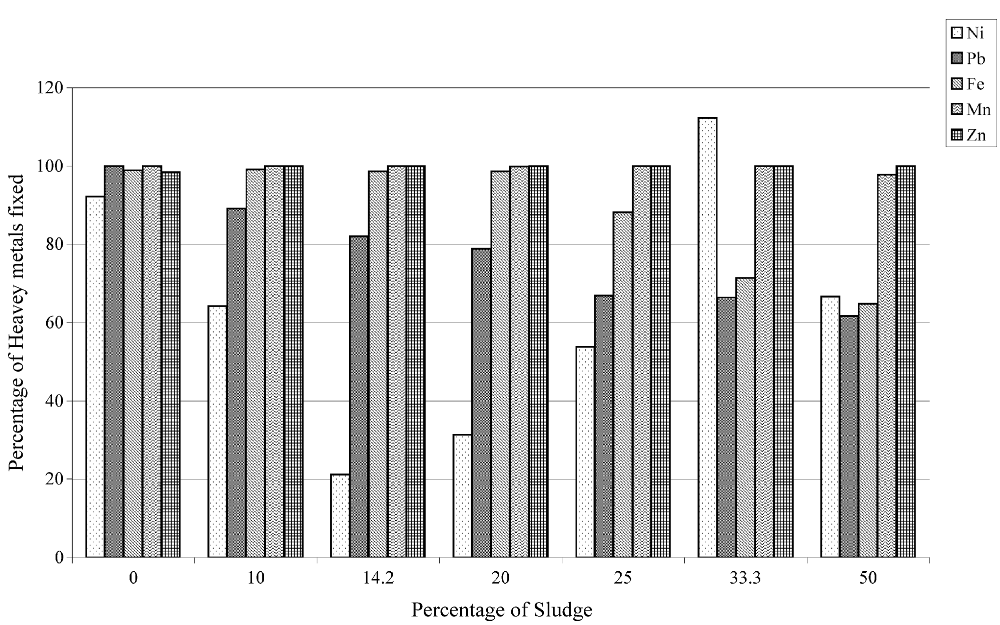

Fig. 3. Effect of pH 7 on metal fixation at 28 days of curing.

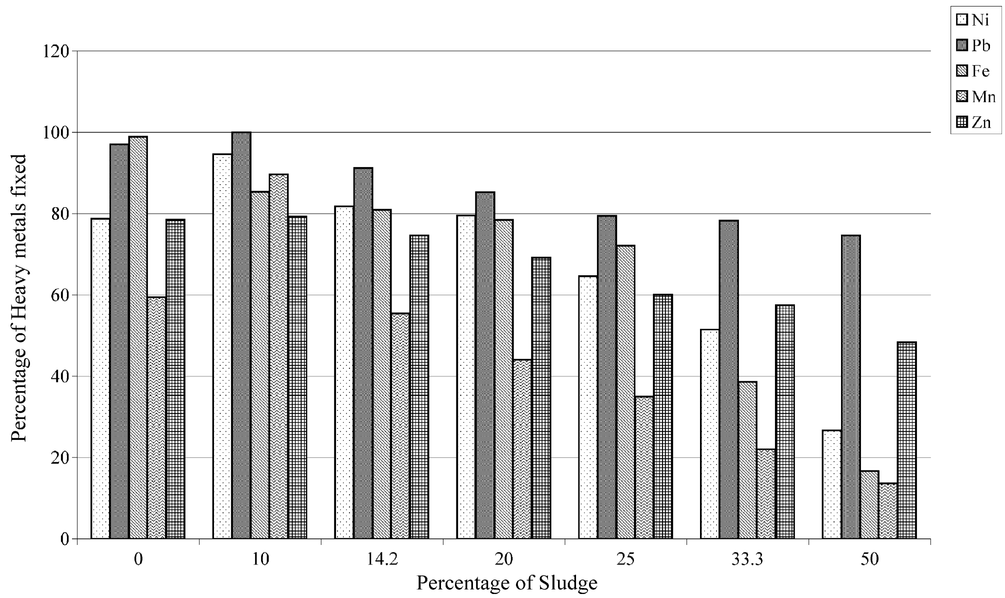

Fig. 4. Effect of pH 4 on metal fixation at 28 days of curing.

at 7 days and Figs. 3 and 4 at 28 days of curing under aggressive leaching conditions.

Zinc possesses amphoteric properties and its stability is lowest at pH range 9–11. In neutral environmental condition (pH 7) zinc was completely stabilized for all the waste-binder ratios after 7 days curing period. Bhatty [27] also showed excellent fixation of zinc by the tricalcium silicate component of OPC. In drastic environmental conditions (pH 4) the zinc was completely immobilized with increase of W/B ratios after 7 or 28 days curing periods (Figs. 1 and 2). Complete stabilization was observed for manganese after 28 days curing period at pH 7. Mn precipitation as $Mn(OH)_2$ is expected at pH 8–13 [3]. At pH 4 the leaching of Mn increased for all the W/B ratios in optimized curing period (Figs. 2 and 4).

The investigation showed that some of the studied components could be considerably demobilized by alkali activated fly ash. Concentration of some metals like Mn and Zn were below or not quit above the determination and were considered as completely locked. At pH 7, for 7 and 28 days curing period the leaching of lead increases steadily with increase in sludge content. Fixation of lead was 79–89% for 10–50% sludge content for 28 days of curing.

At pH 4, specimens cured for 28 days showed comparatively less leaching than 7 days.

Even when exposed to most drastic condition the lead was found stable from 91.2 to 79.4%, i.e., insignificant with increasing sludge from 14.2 to 25% in 28 days curing period (Figs. 3 and 4) and for 7 days curing period leaching was very

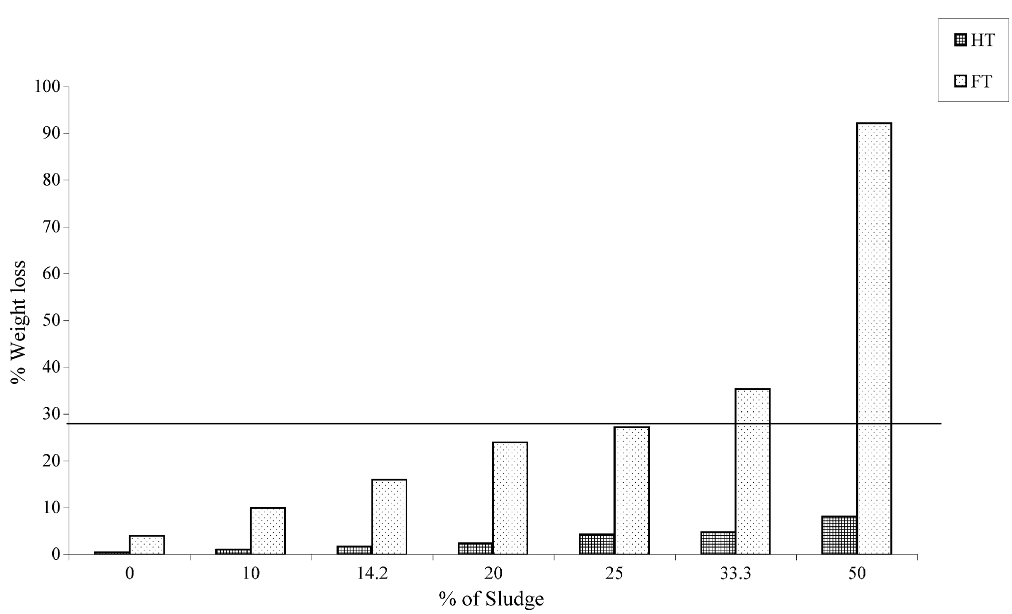

Fig. 5. Weight loss during durability test.

high. It was up to 94% for the same sludge percentage. Lead leaching is significantly elevated as pH falls below 4.8. In pH range 8–9 lead leaching is lowest, addition of fly ash results in the wider pH range (7–11) of Pb immobilization [25]. Leaching rate increases as the pH decreases or increases beyond this pH range [28].

At 7 days curing period with increase of sludge from 14.2 to 25% nickel stabilization decreases by 77–57%. Result shows that after 28 days curing period Ni stabilization was improved by 65–80% (Figs. 3 and 4). At pH 4, Ni shows almost same fixation in 7 and 28 days curing period for all the samples. On addition of sludge content the leaching of Ni increases.

AT pH 7, maximum fixation of iron was observed at curing period of 28 days. With the increase of sludge content the leaching of iron increases. With increasing sludge content from 14 to 25%, iron stabilization decreases by 8581 and 98–88% for 7 and 28 days of curing period, respectively (Figs. 1–4). With the increase of sludge content from 10 to 50%, the rate of fixation decreases from 85.4 to 16.7%, respectively, for 28 days curing.

3.3. Environmental stress test

The ratios for environmental stress test were screened on the basis of higher strength achieved in curing days. As per EPA guidelines [29], for the S/S product 0.35 MPa is the minimum strength required for the landfill. The strength obtained was five times higher for the screened ratios in both the curing days.

Durability relate to the long-term stability of the S/S product. The solidified samples when subjected to freezing thawing cycle and heating thawing cycle process withstand all 12 cycles. The average cumulated, corrected mass loss for 14–50% sludge was 16, 24, 27, 35 and 98% for freezing thawing cycle and 1, 2, 4, 6 and 8% for heating thawing cycle (Fig. 5).

4. Conclusions

Results indicate that, with the increase of sludge from 14.2 to 25% the UCS was almost same for both the curing days. The replacement of 76% OPC by 56% fly ash and 20% sludge for 28 days curing period shows increase in strength as well as rate of stabilization within range of 95–99% for zinc, iron and manganese at pH 7. Leaching of heavy metals in the S/S matrix can be considered as pH-dependent and corresponding metal hydroxide solubility controlled process. The pH-dependent leach test allows a good characterization of the environmental properties of stabilized product. The order of fixation of toxic metals in the alkali activated fly ash matrix was Zn > Mn > Fe > Ni > Pb. In environmental stress conditions, freeze thaw was found to be more deteriorating than heating thaw. It also withstands conditions with higher threshold limit.

Hence, alkali activation of fly ash for solidification/stabilization can be an alternative technology for the ultimate disposal of heavy metal sludge wastes. In condition of sanitary landfill environment, numerous interacting factors can simultaneously affect desorption of heavy metal in the binder.

Acknowledgements

Authors are thankful to School of Energy and Environment Studies. Authors also extend sincere thanks to Institute of Engineering Technology, Indore for providing strength testing facility during course of this study.

References

[1] S. Antiohos, S. Tsimas, Activation of fly ash cementitious systems in the presence of quicklime. Part 1. Compressive strength and pozzolanic reaction rate, Cem. Concr. Res. 4 (2004) 769–779.
[2] D. Hardijito, S.E. Wallah, D.M.J. Sumajouw, B.V. Rangan, On the development of fly ash-based geopolymer concrete, ACI Mater. J. 101 (2004) 1–15.
[3] J.R. Conner, Chemical Fixation and Solidification of Hazardous Waste, Van Nostrand Reinhold, New York, 1990.
[4] J. Means, L. Smith, K. Nehring, S. Brauning, A. Gavaskar, B. Sass, C. Wiles, C. Mashni, The Application of Solidification/Stabilization to Waste Materials, Lewis Publishers, CRC Press, Inc., Boca Raton, FL, 1995.
[5] R. Malviya, R. Chaudhary, Evaluation of leaching characteristics and environmental compatibility of solidified/stabilized industrial waste, J. Mater. Cycles Waste Manag. 8 (2006) 78–87.
[6] J. Parsa, S.H. Munson-McGee, R. Steiner, Stabilization/solidification of hazardous waste using fly ash, J. Env. Eng. 122 (1996) 935–940.
[7] D. Khale, R. Chaudhary, Mechanism of geopolymerization and factors influencing its development: a review, J. Mater. Sci. 42 (2006) 729–746.
[8] A. Buchwald, M. Schulz, Alkali-activated binders by use of industrial byproducts, Cem. Concr. Res. 35 (2005) 968–973.
[9] A. Palomo, S. Alonso, A. Fernandez-Jimenez, Alkaline activation of fly ashes: NMR study of the reaction products, J. ACS 87 (2004) 1141–1145.
[10] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes; A cement for the future, Cem. Concr. Res. 29 (1999) 1323–1329.
[11] Z. Xie, Y. Xi, Hardening mechanism of an alkaline-activated class F fly ash, Cem. Concr. Res. 31 (2001) 1245–1249.
[12] C. Shi, R.L. Day, Acceleration of the reactivity of fly ash by chemical activation, Cem. Concr. Res. 25 (1995) 15–21.
[13] C. Shi, R.L. Day, Pozzolanic reaction in the presence of chemical activators: Part 1. Reaction kinetics, Cem. Concr. Res. 30 (2000) 51–58.
[14] J.C. Swanepoel, C.A. Syrtdom, Utilization of fly ash in a geopolymeric material, Appl. Geochem. 17 (2002) 1143–1148.
[15] C. Shi, R.L. Day, Acceleration of strength gain of lime-natural pozzolan cements by thermal activation, Cem. Concr. Res. 23 (1993) 824–832.
[16] V.M. Malhotra, Role of supplementary cementing materials and superplasticizers in reducing greenhouse gas emissions. In Fiber composites, high-performance concrete, and smart materials; *Proc. ICFRC intern. conf., Chennai, India, January 2004*: 489–499.
[17] A.M. Neville, Properties of Concrete, Wiley, New York, 1996.
[18] V.G. Papadakis, S. Tsimas, Supplementary cementing materials for sustainable building sector growth, European Commission DGXII, Marie Curie Fellowship, Final Scientific Report, Project No. HPMF-CT-1999-00370, National Technical University Of Athens, Greece (2001).
[19] NEN 7341, Leaching characteristics of building material and solid waste material-leaching test-determination of leaching characteristics of inorganic components from granular and building materials NNI Delft, The Netherlands, 1992.
[20] APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Waste-Water, 20th ed., United Book Press Inc., Baltimore, MD, 1998.
[21] ASTM D: 4843-88, Standard Test Method for Determining the Wetting and Drying Test of Solid Wastes, 1988.
[22] ASTM D: 4842-90, Standard Test Method for Determining the Resistance of Solid Wastes to Freeze and Thawing, 1990.
[23] J.A. Stegemann, P.L. Cote, Summary of an investigation of test methods for solidified waste evaluation, Waste Manag. 10 (1990) 41–52.
[24] C.D. Hills, The hydration of OPC during cement based solidification of toxic waste, Ph.D. Thesis, University of London, 1993.

[25] D. Dermatas, N. Menounou, X.G. Meng, Mechanism of lead immobilization in treated soils, Land Contam. Reclam. 14 (2006) 43–56.
[26] Peter C. Hawlette (Ed.), Lea's Chemistry of Cement and Concrete, Fourth ed., Butterworth Heinmann, New Delhi, 1998.
[27] M.S.Y. Bhatty, Fixation of metallic ions in Portland Cement Superfund'87, 1987, pp. 140–147.
[28] A. Jirka, M. Shannon, J. Morris, P. Parikh, Factors effecting EP toxicity metals results, in: In Proceedings of Third Annual Symposium Solid Waste Testing and Quality Assurance, 1987, 115-47-5-52.
[29] M.J. Cullinane, L.W. Jones, Stabilization of hazardous waste, Cincinnati: U.S. Environmental Protection Agency (U.S.EPA) Hazardous Waste Engineering Research Laboratory (HWERL), EPA/600/D-86/028, 1986.