Characterization of heavy metals from a contaminated industrial site

Vemula A. Reddy*[1], Deepak Haritwal[1], Chandresh H. Solanki[1], Shailendra Kumar[1], Krishna R. Reddy[2]

[1]Applied Mechanics Department, Sardar Vallabhbhai National Institute of Technology (SVNIT), Surat, Gujarat, India. E-mail: vemulaanandreddy@gmail.com, chandresh1968@yhoo.co.in, skumar1863@gmail.com
[2]Department of Civil and Materials Engineering, University of Illinois, Chicago, IL 60607, USA. E-mail: kreddy@uic.edu

Abstract: Soil contamination due to heavy metals has become a global problem. The knowledge of heavy metal speciation in soils must be understood for the rational investigation of risk and remediation of contaminated soils. This study presents a systematic investigation of an industrial site soil, known as Jarosite, which is obtained from a zinc smelter. The soil was found to be clayey soil with low to medium consistency, with organic content of 2.13 % and pH of 5.59. The total heavy metals in the soil were determined using acid digestion procedure, and TCLP (toxicity characteristic leaching procedure) tests were also conducted for understanding the leachable metals from the soil. The total concentrations of heavy metals were found to be: zinc (Zn) = 13653 mg/kg, lead (Pb) = 6871 mg/kg, cadmium (Cd) = 1371 mg/kg, copper (Cu) = 128 mg/kg, nickel (Ni) = 37 mg/kg, arsenic (As) = 19 mg/kg, and cobalt (Co) = 13 mg/kg. TCLP concentrations were found to be: Zn = 1263 mg/kg, Pb = 503 mg/kg, and Cd = 251 mg/kg. The total heavy metals and TCLP metals are found to exceed the allowable limits, hence remediation action is required. Stabilization/solidification is considered to be promising technology to use for the site conditions.

Keywords: Heavy metals, soil, leaching, remediation, stabilization

1 Introduction

During the last few decades rapid industrialization has led to manifold decline in the quality of environment (Agrawal et al. 2004, Sharma and Reddy 2004)). Particularly, the waste generated from the smelting activities all over the world (Li et al. 2008). Several studies indicated that people living near to the smelter have been affected significantly with the most toxic elements such as lead (Pb) and cadmium (Cd) (Carvalho et al. 1986). Surveys showed that high (Pb) levels in blood were observed in the children who lived near the smelter (Beiyuan et al. 2017, Li et al. 2015). The increase in the production of various non-ferrous metals leads to solid waste generation in large quantities. Some of the non-ferrous metals include aluminum, lead, zinc, and copper (Agarwal et al. 2004). Red mud which is generated during the production of 1 ton alumina has about 1.0-1.5 ton of waste generated (Borra et al. 2015, Kumar et al. 2006, Liu and Li 2015), likewise natrojarosite residue is the waste generated during the production of zinc and lead (Catalan et al. 2002). Currently, about 960 million tonnes of waste is generated during mining and industrial activities of these about 4.5 million tonnes are hazardous in nature Mehra et al. (2016). The disposal/dumping of such type of solid waste and resulting contamination of soils is a matter of concern to the geotechnical/geoenvironmental engineers. In this study, the characterization of Zn-Pb smelter waste was evaluated for potentially toxic heavy metals and leaching concentrations under weak acid environment. The goal of the study is to evaluate the most suitable remediation process for the successful application as an engineered and sustainable material.

2 Materials and Methods

2.1 Industrial contaminated site soil

The soil contaminated with heavy metals was collected from Pb-Zn smelter (Latitude 24.60289^{O}, Longitude 73.814657^{O}), Hindustan zinc limited, Debari district, Rajasthan, India. The annual production of zinc is about 435,666 MT and lead 51, 759 MT (Agrawal et al. 2004, Asokan et al. 2010). About 500 kg of sample was collected from the dumping site in sealed containers. The soil is air dried, homogenized and sieved through a 10 mesh (2 mm) sieve. The basic properties and oxide composition of heavy metal contaminated soil is given in Table 1 and Table 2.

Table1 Basic properties of heavy metal contaminated soil

Property	Value
Specific gravity	2.78
pH	5.59
Color	Light Yellow
Organic content (%)	2.13
Natural water content (%)	14.20

Table 2 Oxide chemistry of field contaminated soil

Oxide	Value (%)
Aluminum oxide (Al_2O_3)	16.63
Calcium oxide (CaO)	11.18
Ferric oxide (Fe_2O_3)	36.21
Magnesium oxide (MgO)	2.89
Sulfate oxide (SO_4)	23.57
Phosphorus oxide (P_2O_5)	1.13
Potassium oxide (K_2O)	0.31
Loss of ignition	7.93

2.2 Determination of total heavy metals

Several methods are available to evaluate the heavy metal concentrations in the contaminated soils. The most common method adopted is decomposition by Aqua Regia

(3)

method ISO 11466:1995 (1995) where 3:1 concentrated hydrochloric acid (HCL) and nitric acid (HNO_3) is used for the determination of total heavy metals. The strong oxidizing power chemically decompose the organic substances and dissolve the most insoluble metals available in the soil. About 3 grams of oven dried soil is taken and mixed with 21 ml of HCL and 7 ml of (HNO_3) in the digestion vessel and the sample is heated to $95^{O}C \pm 5^{O}C$ and refluxed for 15 minutes. Later 5 ml of (HNO_3) is added and refluxed for 30 min, the procedure is repeated till the brown fumes are unseen in the sample. Further the sample is made up to 100 ml using distilled water and subjected to heavy metal concentrations analysis using atomic absorption spectrophotometer (AAS).

2.3 Toxicity characteristic leaching procedure test

During landfilling of any toxic materials, it is essential to fulfil TCLP limits given by Hazardous Waste Management Rules (HWM 2016) in India. In this study leaching test was carried using toxicity characteristic leaching procedure test TCLP 1311 (USEPA 1992), which represents landfilling conditions in the field. The same TCLP procedure is used to characterize hazardous characteristics of contaminated soils and assess the need for remediation (Sharma and Reddy 2004). Approximately 10 grams of soil is mixed in TCLP extraction solution 200 ml with pH 4.93±0.05 (glacial acetic acid CH3COOH and NaOH diluted in deionized double distilled water) is used. The mixture is tumbled in a 500 ml high density polyethylene bottle for 18±2 hours in a TCLP extractor. Later the soil-solution mixture is subjected to centrifugation of 5 min at 3000 rpm, then leachant is acidified with nitric acid at pH 2 and subjected to heavy metal concentration analysis by AAS. All the samples in the study were tested in triplicates for reproducibility of results.

3 Results

3.1 Total heavy metals concentrations

Table 3 shows the distribution of heavy metal concentrations present in the contaminated soil sample. The lowest concentrations are for Cobalt (Co), Arsenic (As), Nickel (Ni) and Copper (Cu) and the highest for Zinc (Zn), Lead (Pb) and Cadmium (Cd). The order of heavy metal content are as follows: Zn >Pb > Cd >Cu >Ni >As >Co. The order of distribution of heavy metals are similar for many Zn-Pb smelters in the world (Lima and Bernardez 2011, Xia et al. 2018, Voglar and lestan 2010). The contaminated soil revealed high concentrations of Zn, Pb and Cd which are attached to various metallic and complex phases.

(4)

Table 3: Total heavy metal concentrations of contaminated soil

Metal	**Concentrations (mg/kg)**
Lead (Pb)	6871
Zinc (Zn)	13653
Cadmium (Cd)	1371
Copper (Cu)	128
Nickel (Ni)	37
Arsenic (As)	19
Cobalt (Co)	13

3.2 Leaching of heavy metals

Based on the TCLP results, Table 4 shows the extremely high toxicity levels for Zn, Pb and Cd, indicating 100 times for Pb, 5.05 times for Zn and 251 times for Cd as compared allowable limits. The acceptable limits for Zn is 250 mg/kg, Pb 5 mg/kg and Cd 1 mg/kg according to Hazardous Waste Management rules (HWM, 2016). The results are pertaining to weak acidic environment and are extracted from the acid soluble phases of the contaminated soil particles which are easily available for leaching.

Table 4: TCLP concentrations of heavy metal contaminated soil

Heavy metal	Concentration (mg/kg)
Lead	503
Zinc	1263
Cadmium	251

4 Conclusions

An industrial Zn-Pb smelter soil was characterized for total heavy metal concentrations and leachable heavy metal concentrations. The following conclusions were drawn from this study:

1. High concentrations of Pb, Zn and Cd are due to pyro-metallurgical process involved in the removal of Zn and Pb.
2. Leachability study indicated that the heavy metals are mobile in weak acidic environments.
3. Remediation of the soil is necessary to convert hazardous soil into non-hazardous form. Our ongoing studies show that solidification/stabilization can be one the most appropriate methods in treating the contaminants in such soils.

(5)

References

Agrawal, A., Sahu, K. K., & Pandey, B. D. (2004). Solid waste management in non-ferrous industries in India. Resources, conservation and recycling, 42(2), 99-120.

Asokan, P., Saxena, M., & Asolekar, S. R. (2010). Recycling hazardous jarosite waste using coal combustion residues. Materials Characterization, 61(12), 1342-1355.

Beiyuan, J., Tsang, D. C., Valix, M., Zhang, W., Yang, X., Ok, Y. S., & Li, X. D. (2017). Selective dissolution followed by EDDS washing of an e-waste contaminated soil: extraction efficiency, fate of residual metals, and impact on soil environment. Chemosphere, 166, 489-496.

Borra, C. R., Pontikes, Y., Binnemans, K., & Van Gerven, T. (2015). Leaching of rare earths from bauxite residue (red mud). Minerals Engineering, 76, 20-27.

Catalan, L. J., Merlière, E., & Chezick, C. (2002). Study of the physical and chemical mechanisms influencing the long-term environmental stability of natrojarosite waste treated by stabilization/solidification. Journal of hazardous materials, 94(1), 63-88.

Carvalho, F. M., Tavares, T. M., Silvany-Neto, A. M., Lima, M. E. C., & Alt, F. (1986). Cadmium concentrations in blood of children living near a lead smelter in Bahia, Brazil. Environmental research, 40(2), 437-449.

De Andrade Lima, L. R. P., & Bernardez, L. A. (2011). Characterization of the lead smelter slag in Santo Amaro, Bahia, Brazil. *Journal of hazardous materials*, *189*(3), 692-699.

Government of India. (2016). Waste management rules, 1981, 1-68.

Li, P., Lin, C., Cheng, H., Duan, X., & Lei, K. (2015). Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China. Ecotoxicology and Environmental Safety, 113, 391-399.

Li, Y., Perederiy, I., & Papangelakis, V. G. (2008). Cleaning of waste smelter slags and recovery of valuable metals by pressure oxidative leaching. Journal of Hazardous Materials, 152(2), 607-615.

Liu, Z., & Li, H. (2015). Metallurgical process for valuable elements recovery from red mud—A review. Hydrometallurgy, 155, 29-43.

Mehra, P., Gupta, R. C., & Thomas, B. S. (2016). Assessment of durability character istics of cement concrete containing jarosite. Journal of cleaner production, 119, 59-65.

International Organization for Standardization. (1995). Soil quality-Extraction of trace elements soluble in aqua regia. ISO.

Sharma, HD., & Reddy, K.R. (2004). Geoenvironmental Engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies, John Wiley & Sons, Hoboken, NJ, USA.

Voglar, G. E., & Leštan, D. (2010). Solidification/stabilisation of metals contaminated industrial soil from former Zn smelter in Celje, Slovenia, using cement as a hydraulic binder. Journal of Hazardous Materials, 178(1-3), 926-933.

USEPA Method 1311. (1992), Toxicity Characteristic Leaching Procedure (TCLP), United States Environmental Protection Agency, (USEPA), Washington, DC.

Xia, W. Y., Feng, Y. S., Du, Y. J., Reddy, K. R., & Wei, M. L. (2018). Solidification and stabilization of heavy metal–contaminated industrial site soil using KMP binder. Journal of Materials in Civil Engineering, 30(6), 04018080.