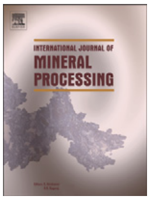
International Journal of Mineral Processing 123 (2013) 165–171

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro



Assessment of leaching characteristics of heavy metals from industrial leach waste☆

Semra Çoruh [a],*, Sermin Elevli [b], Osman Nuri Ergun [a], Gönül Demir [a]

[a] Department of Environmental Engineering, Ondokuz Mayıs University, 55139 Samsun, Turkey
[b] Department of Industrial Engineering, Ondokuz Mayıs University, 55139 Samsun, Turkey

ARTICLE INFO

Article history:
Received 13 September 2012
Received in revised form 14 June 2013
Accepted 22 June 2013
Available online 29 June 2013

Keywords:
Zinc leach waste
Leachability
Immobilization
Thermal treatment
Regression analysis with dummy variable

ABSTRACT

Leaching of valuable metals from residues generated by pyrometallurgical or hydrometallurgical process usually results in a large amount of wastes. In the present study, the leaching behavior of the zinc leach waste was investigated by utilizing a regression model with dummy variables. The results of different leaching methods indicate that addition of fly ash and blast furnace slag to the zinc leach waste reduces the heavy metal content in the effluent and that fly ash performs better than blast furnace slag. The results of thermal treatment showed that the zinc leach waste cannot be disposed of in the present form. The metal release from the zinc leach waste decreased in relation to increasing treatment temperature. Metal releases for residues treated at 1000–1200 °C decreased because of heat-induced formation of a glassy matrix. The levels of Zn, Pb and Mn released for 1200 °C treatment temperature were 1.05, 0.08, 0.07 mg/l, respectively. Therefore an immobilization treatment is necessary prior to disposal.

1. Introduction

Large amounts of industrial wastes are produced every year by various industries. Metallurgical industries generate vast quantities of solid wastes such as slag, ash, sludge, dross and tailings. Environmental pollution by heavy metals from industrial activities can become a very important source of contamination both in soil and water (Margui et al., 2004; Al-Jabri et al., 2006). The presence of heavy metals produced during metal extraction in the aquatic environment is of major concern due to their toxicity to many life forms (Gupta et al., 2000; Montanaro et al., 2001; Rashchi et al., 2005; Moors and Dijkema, 2006).

It is known that hydrometallurgical and pyrometallurgical wastes of the zinc production industry pose major environmental problems and are considered hazardous and toxic due to the presence of heavy metals like Zn, Pb, Cd, Mn and Co (ILZSG, 1985; Baba and El-Sayed, 1995; Porcu et al., 2004; Alizadeh et al., 2011). The zinc residues are stockpiled until the recovery of valuable metals in the residues becomes economic and/or the grade of zinc ores decreases. The stockpiled residues may cause heavy metal pollution problems (Gönül, 2007; Ruşen et al., 2008). Therefore, disposing of these heavy metals is not allowed at landfills without treatment. Stabilization/solidification (S/S) and thermal treatment technologies are widely applied for immobilization of hazardous wastes such as sludges, slags and ashes containing heavy metals. The main aims in the S/S processes are to reduce the hazard of a waste by converting the contaminants into less soluble, mobile or toxic forms by using some stabilization additives and binding materials such as cement, clay, zeolite, red mud, fly ash. Among the other methods thermal treatment has been an increasingly attractive approach to the remediation of improperly discarded hazardous and toxic materials. One of the aims of thermal treatment is the immobilization of heavy metals by the formation of a glass matrix in which the metals may be stabilized; this is known as vitrification. Therefore, the vitrification process has the potential to reduce leachability of hazardous constituents from waste (Marsh, 1997; Rincon et al., 1999; Pelino et al., 2004).

Although there is already a considerable amount of research applied to different industrial residues, there are only a few studies on zinc leach waste (Rashchi et al., 2005; Al-Abed et al., 2006; Çoruh and Ergun, 2010; Vahidi et al., 2009). The aim of this study is to investigate the possibility of safe disposal of the zinc leach waste according to leaching tests, immobilizing agents, treatment temperature, particle size, immobilizing agent amount and time. In order to construct a regression model for prediction of Zn releases, dummy variables for leaching tests, immobilizing agent types and temperature of treatment were used.

2. Materials and methods

2.1. Materials

The zinc leach waste sample used in this study was obtained from a zinc plant of Kayseri, Turkey. This is the only plant in Turkey that

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* Corresponding author. Tel.: +90 362 312 19 19/1328.
E-mail address: semcoruh@omu.edu.tr (S. Çoruh).

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http://dx.doi.org/10.1016/j.minpro.2013.06.005

produces zinc from a primary ore containing zinc carbonate. The chemical composition of the sample is presented in Table 1. The XRD characterization was performed by using X-ray diffraction (Rigaku D/max) with Cu Kα radiation at room temperature. X-ray diffraction pattern shows that the zinc leach waste was composed mainly of anglesite ($PbSO_4$), gypsum ($CaSO_4.2H_2O$), and zinc sulfate hydrate ($ZnSO_4 \cdot 2H_2O$). Details of the mineralogical composition of the zinc leach waste have been given in the previous paper (Gönül, 2007).

The fly ash sample used for this study was collected using electrostatic precipitators from the Soma thermal power plant in Turkey. The fuel type of the power plant is lignite. Fly ash is in the size range of less than 0.074 mm. The chemical composition of the fly ash was evaluated by using X-ray fluorescence techniques (Rigaku ZSX Primus) and the results are presented in Table 1. The total immobilizing agent amount of SiO_2, Al_2O_3, Fe_2O_3 and CaO content is about 90%. Details of the mineralogical composition of the fly ash have been given in the previous paper (Çoruh and Ergun, 2010).

Blast furnace slag used in the study was collected from Kardemir, Turkey. Blast furnace slag was grounded below 0.150 mm before leaching tests. The chemical composition of the blast furnace slag was evaluated by using X-ray fluorescence techniques (Rigaku ZSX Primus).

2.2. Experimental

2.2.1. Leaching tests

In this study, the following leaching tests were used:

- TCLP is widely used in the US and Australia to determine whether waste products require disposal in landfills characterized as "hazardous". Prior to extraction, the solid material was passed through a 9.5 mm standard sieve. A 20:1 liquid to solid (L/S) ratio (mass/mass, m/m) is employed, and the mixture is mixed for 18 h at 30 rpm using a rotary agitation apparatus. The mixture is filtered using a glass fiber filter and stored at 4 °C for metal analysis (USEPA, 1989; Kim, 2003; Cohen and Petrie, 2005).
- For the ASTM leaching procedure, the liquid–solid ratio was set as 4:1, the pH of the solution was the same with distilled water and the ASTM extractions were performed with a 25 g sample placed in 100 ml of distilled water for 48 h.
- Synthetic precipitation leaching procedure (SPLP) (US EPA Method 1312) is a method to evaluate a worst-case scenario of the waste during the practice of disposal. The extraction fluid consists of slightly acidified de-ionized water that is formulated to simulate natural precipitation. A mixture of 60/40 H_2SO_4/HNO_3 (by weight) is used to achieve the appropriate pH for extraction. The samples are extracted at a liquid to solid ratio (L/S) of 20 at 30 rpm for 18 h at room temperature on a shaker (USEPA, 1994).
- The field leach test has been used to predict, assess, and characterize the geochemical interactions between water and a broad variety of geologic and environmental matrices. Examples of some of the samples leached include metal mine wastes, various

Table 1
Chemical composition (wt.%) of the used zinc leach waste, fly ash and blast furnace slag.

	Zinc leach waste	Fly ash	Blast furnace slag
SiO_2	22.49	22.8	39.90
TiO_2	0.27	0.55	–
Al_2O_3	6.16	9.3	9.34
Fe_2O_3[a]	11.03	4.9	1.15
Cr_2O_3	0.08	0.09	0.04
CaO	6.73	40.6	34.89
MgO	0.48	2.6	7.95
CuO	0.10	–	0.84
ZnO	13.20	–	–
PbO	21.40	–	–
BaO	0.46	–	–
SrO	–	–	0.06
MnO	0.78	0.08	2.76
CO_2	–	1.6	–
K_2O	0.82	0.5	1.38
Na_2O	–	0.2	0.20
SO_3	15.39	13.4	1.42
LOI[b]	0.61	3.38	0.07

[a] Iron oxides are presented as Fe_2O_3.
[b] Loss on ignition.

Table 2
Dummy variables.

Method	D1	D2	D3	D4
TCLP	0	0	0	0
ASTM	1	0	0	0
SPLP	0	1	0	0
LEP	0	0	1	0
FLT	0	0	0	1

Table 3
Estimated coefficients and ANOVA results.

Zn	**Predictor**		**Coef**	**SE Coef**	**t**	**p**
	Constant		466.342	9.680	48.17	0.000
	D1		93.86	12.65	7.42	0.000
	D2		−356.67	12.65	−28.20	0.000
	D3		−332.02	12.65	−26.25	0.000
	D4		−382.90	12.65	−30.28	0.000
	Size		−10.100	1.363	−7.41	0.000
	Source	**DF**	**SS**	**MS**	**f**	**p**
	Regression	5	2,060,704	412,141	515.41	0.000
	Residual error	44	35,184	800		
	Total	49	2,095,888			
	$S = 28.2778\ R^2 = 98.3\%\ R^2\ (\mathrm{adj}) = 98.1\%$					
	$Zn_{Release} = 466.342 + 93.86 \cdot D1 - 356.67 \cdot D2 - 332.02 \cdot D3 - 382.90 \cdot D4 - 10.10 \cdot Size$					
Pb	**Predictor**		**Coef**	**SE Coef**	**t**	**p**
	Constant		18.0406	0.5063	35.63	0.000
	D1		−11.3400	0.6614	−17.15	0.000
	D2		−12.6160	0.6614	−19.08	0.000
	D3		−11.8820	0.6614	−17.97	0.000
	D4		−12.1810	0.6614	−18.42	0.000
	Size		−0.3072	0.0713	−4.31	0.000
	Source	**DF**	**SS**	**MS**	**f**	**p**
	Regression	5	1202.15	240.43	109.93	0.000
	Residual error	44	96.23	2.19		
	Total	49	1298.38			
	$S = 1.47889\ R^2 = 92.6\%\ R^2\ (\mathrm{adj}) = 91.7\%$					
	$Pb_{Release} = 18.0406 - 11.3400 \cdot D1 - 12.6160 \cdot D2 - 11.8820 \cdot D3 - 12.1810 \cdot D4 - 0.3072 \cdot Size$					
Mn	**Predictor**		**Coef**	**SE Coef**	**t**	**p**
	Constant		6.3113	0.0886	71.20	0.000
	D1		3.1410	0.1158	27.13	0.000
	D2		0.6100	0.1158	5.27	0.000
	D3		0.9420	0.1158	8.13	0.000
	D4		1.3990	0.1158	12.08	0.000
	Size		−0.1538	0.0124	−12.32	0.000
	Source	**DF**	**SS**	**MS**	**f**	**p**
	Regression	5	66.778	13.356	199.21	0.000
	Residual error	44	2.950	0.067		
	Total	49	69.728			
	$S = 0.258930\ R^2 = 95.8\%\ R^2\ (\mathrm{adj}) = 95.3\%$					
	$Zn_{Release} = 6.3113 + 3.1410 \cdot D1 + 0.6100 \cdot D2 + 0.9420 \cdot D3 + 1.3990 \cdot D4 - 0.1538 \cdot Size$					

Coef: coefficient, SE Coef: standard error for the estimated coefficient, t: t-value, p: p-value, DF: degrees of freedom, SS: sum of squares, MS: mean squares, f: f-value, S: estimate of standard deviation.