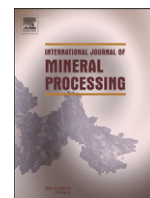


Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

## International Journal of Mineral Processing

journal homepage: [www.elsevier.com/locate/ijminpro](http://www.elsevier.com/locate/ijminpro)

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



Semra Çoruh <sup>a,\*</sup>, Sermin Eevli <sup>b</sup>, Osman Nuri Ergun <sup>a</sup>, Gönül Demir <sup>a</sup>

<sup>a</sup> Department of Environmental Engineering, Ondokuz Mayıs University, 55139 Samsun, Turkey

<sup>b</sup> 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.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY license](http://creativecommons.org/licenses/by/3.0/).

## 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

\* Corresponding author. Tel.: +90 362 312 19 19/1328.

E-mail address: [semcoruh@omu.edu.tr](mailto:semcoruh@omu.edu.tr) (S. Çoruh).

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 K $\alpha$  radiation at room temperature. X-ray diffraction pattern shows that the zinc leach waste was composed mainly of anglesite (PbSO<sub>4</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), and zinc sulfate hydrate (ZnSO<sub>4</sub>·2H<sub>2</sub>O). 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<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> 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

**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 <sub>2</sub>	22.49	22.8	39.90
TiO <sub>2</sub>	0.27	0.55	–
Al <sub>2</sub> O <sub>3</sub>	6.16	9.3	9.34
Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	11.03	4.9	1.15
Cr <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub>	–	1.6	–
K <sub>2</sub> O	0.82	0.5	1.38
Na <sub>2</sub> O	–	0.2	0.20
SO <sub>3</sub>	15.39	13.4	1.42
LOI <sup>b</sup>	0.61	3.38	0.07

<sup>a</sup> Iron oxides are presented as Fe<sub>2</sub>O<sub>3</sub>.

<sup>b</sup> 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

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<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (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 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 <sup>2</sup> = 98.3% R <sup>2</sup> (adj) = 98.1%					
	Zn <sub>Release</sub> = 466.342 + 93.86 · D1 – 356.67 · D2 – 332.02 · D3 – 382.90 · D4 – 10.10 · 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 <sup>2</sup> = 92.6% R <sup>2</sup> (adj) = 91.7%					
	Pb <sub>Release</sub> = 18.0406 – 11.3400 · D1 – 12.6160 · D2 – 11.8820 · D3 – 12.1810 · D4 – 0.3072 · 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 <sup>2</sup> = 95.8% R <sup>2</sup> (adj) = 95.3%					
	Mn <sub>Release</sub> = 6.3113 + 3.1410 · D1 + 0.6100 · D2 + 0.9420 · D3 + 1.3990 · D4 – 0.1538 · 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.

types of dust, biosolids, flood and wetland sediments, volcanic ash, and many other diverse matrices. The field leach test (FLT) determines the potential for the release of metals and acid from materials exposed to natural waters (El-Kamash et al., 2005; Hageman, 2007). This test uses a mass basis and a 20:1 (20 parts extractant to 1 part solid) leaching ratio. For this procedure, 50 g of <10 mesh (<2 mm) mine waste composite sample is weighed into a one-liter plastic bottle. Approximately 1 l deionized water is added slowly so that no dust is lost. The bottle is capped and vigorously hand shaken for 5 min (U.S. Geological Survey, 2005).

- Leaching extraction procedure (LEP) was used to investigate the leaching potential of toxic components to the environment by extraction with an acidic medium. A 50 g dry sample was tumbled continuously for 24 h in 1 l of deionized water. A pH of  $5 \pm 0.2$  was maintained throughout the extraction by adding 0.5 N acetic acid (USEPA, 1989; Peralta, 1997; Chang et al., 2001; Kim, 2003; Cohen and Petrie, 2005).

The pH of the recovered extracts was measured and recorded, after which they were acidified with  $\text{HNO}_3$  to a pH < 2. The preserved samples were stored at 4 °C until processed. All experiments were performed in duplicate and mean values were taken into account.

### 2.2.2. Metal leaching test and thermal treatment on zinc leach waste with or without immobilizing agent

Metal leaching tests were performed in leaching test conditions using samples of as received zinc leach waste before and after thermal treatment (1000 °C) and the same samples (25 g) were mixed with fly ash and blast furnace slag at different ratios (2.5, 5, 10, 15, 20 and 25 g, respectively) as immobilizing agents. These mixtures were subjected to ASTM leaching test. The leachate derived from the tests was filtered and acidified with concentrated nitric acid to pH < 2. The

metal concentration in the filtrate was determined using AAS (atomic absorption spectrophotometry).

### 2.2.3. Thermal treatment of zinc leach waste

Thermal treatment was applied to the zinc leach waste in order to determine the effects on Zn, Pb and Mn releases. Zinc leach waste was heated for 45 min at several temperatures from 100 to 1200 °C. The heating rates of zinc leach waste samples were controlled to about 18 °C/min. Treatment times were between 5 and 300 min on zinc leach waste. Metals released from the thermal treated waste were examined according to TCLP and ASTM test methods.

### 2.3. Linear regression model with dummy variables

An equation or a set of equations which represents the behavior of a system is called a mathematical model. A linear model is one of the mathematical models in which all parameters/variables appear linearly.

Regression analysis is a statistical tool for the investigation of relationships between variables. The linear regression model assumes that there is a linear, or “straight line”, relationship between the dependent variable and each predictor (independent variable). A linear regression model that contains more than one predictor/independent variable is called a multiple linear regression model. The following model is a multiple linear regression model with two predictor variables ( $x_1$  and  $x_2$ ).

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \quad (1)$$

where  $\beta_0$  is the intercept, the predicted value of the dependent variable when the value of every predictor is equal to zero, parameters  $\beta_1$

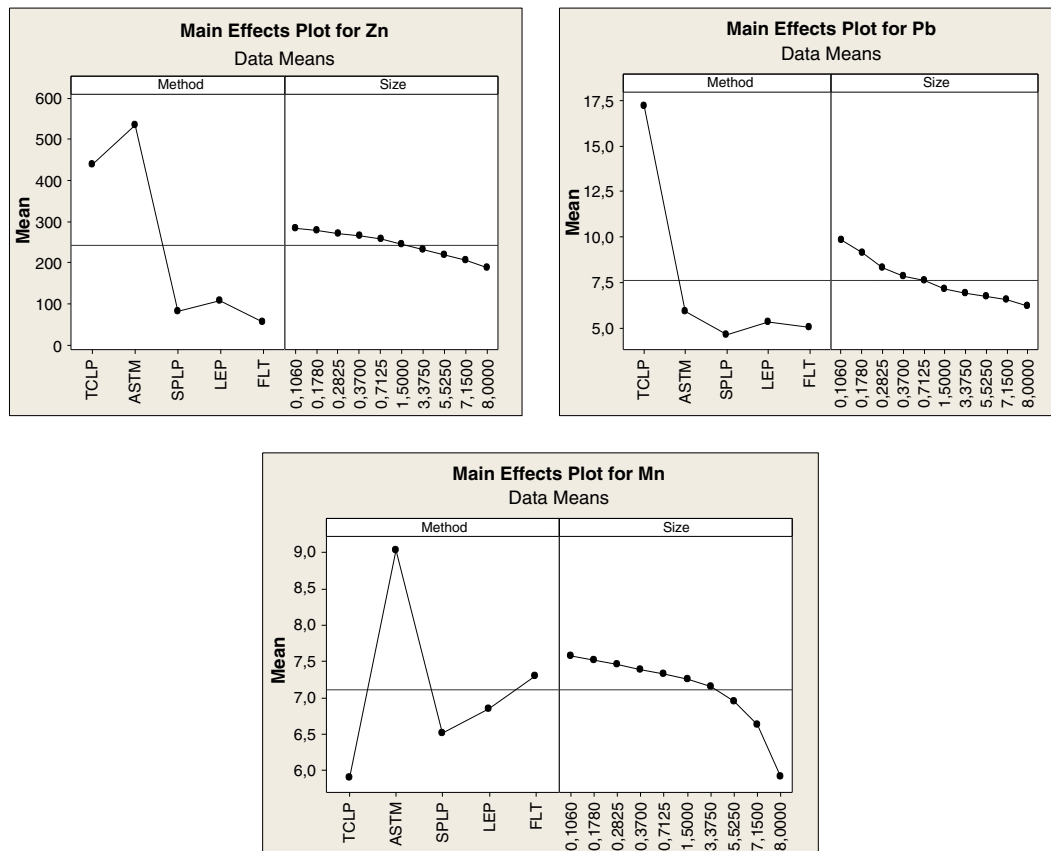


Fig. 1. Main effect plots for Zn, Pb and Mn releases.

and  $\beta_2$  are referred to as partial regression coefficients and  $\varepsilon$  is random or unexplained error. Since the maximum power of the variables in the model is one, the regression model in Eq. (1) is a first order multiple linear regression model.

The statistical methods used to develop the multiple linear regression models include analysis of variance (ANOVA). ANOVA provides an indication of the statistical significance of the regression by partitioning the variation into two components: a) variability accounted for by regression line: regression sum of squares and b) variability not accounted for by regression line: error sum of squares. ANOVA uses the f statistic to compare the variability accounted for by the regression model with the remaining variation due to error.

The most common measure of how well a regression model fits the data is  $R^2$ . This statistic represents how much of the variance in the response is explained by the weighted combination of predictors. The closer  $R^2$  is to 1, the better the model fits.

In order to include categorical variables as independent variables in a regression model, dummy variables are often used. The use of dummy variables allows the researcher to include categorical independent variables as part of the regression model. If a given categorical independent variable has m categories, then (m-1) dummy variables are introduced to the model. For example, for a categorical variable with six levels, five dichotomous variables are constructed that would contain the same information as the single categorical variable.

Dummy variables only take the value of either 0 or 1. In a regression model, a dummy variable with a value of 0 will cause its coefficient to disappear from the equation. Conversely, the value of 1 causes the coefficient to function as a supplemental intercept, because of the identity property of multiplication by 1. This type of specification in a linear regression model is useful to define subsets of observations that have different intercepts and/or slopes without the creation of separate models.

### 3. Result and discussion

#### 3.1. Effects of particle size and leaching tests

The particle size change of zinc leach waste was obtained between 0.106 and 8.0 mm. About 80% of the particle size distribution of zinc leach waste is between  $-4.750 + 0.425$  mm particle sizes. Thus, the particle size was chosen as  $-4.750 + 0.425$  mm.

Systematic differences among metal releases of the five leaching tests were controlled with dummy variables (Table 2). For example, D1 is one for ASTM, and zero for all methods.

The coefficients in Table 3 list the estimated coefficients for the predictors (dummy variables and size). The interpretations of the regression equations are as follows:

- Since the p-values are smaller than the 0.01, the relationship between the response variable (metal release) and the independent variables (dummy variables and size) is statistically significant at 1% level.
- From the coefficients in Table 3, as the size increases by one unit, the release of Zn, Pb and Mn decreases by 10.10, 0.3072 and 0.1538 units respectively.
- Dummy variables were found as significantly different from zero, which suggests that the leaching method is one of the key predictors of metal releases. From the magnitude of the coefficients, it can be concluded that while ASTM method increases the release of Zn and Mn, TCLP method increases the release of Pb.

**Table 4**  
Dummy variables.

Agent type	D1	Temperature	T1
Fly ash	0	0 °C	0
Blast furnace slag	1	1000 °C	1

- The values of the adjusted determination coefficients (adj.  $R^2$ ) indicate that 98.1% for Zn, 91.7% for Pb and 95.3% for Mn of the total variations are explained by the regression models.
- The regression p-values of 0.000 indicate that at least one of the regression coefficients is significantly different from zero for all the regression models.

According to Fig. 1, each level of the methods and particle size affects the release differently. For example, ASTM method results in higher mean response (Zn release) compared to other methods. Additionally, it is observed that metal releases decrease as the particle size increases.

#### 3.2. The effect of immobilizing agent type and amount, and treatment temperature

Metal releases according to ASTM test method were investigated. Zn releases without immobilizing agent are 580.12 mg/l and 13.88 mg/l for 0 °C and 1000 °C treatment temperatures, respectively. In order to include the categorical variable concerning the agent type and temperature, dummy variables were defined as shown in Table 4.

Table 5 shows the estimated coefficients and corresponding statistics for all independent variables. The results are interpreted as follows:

- The coefficients for D1 dummy variable mean that blast furnace slag increases the releases of Zn, Pb and Mn. It can be concluded that fly ash is an effective immobilizing agent for the stabilization of Zn, Pb and Mn ions from zinc leach waste.
- The coefficients for T1 dummy variable mean that releases of Zn, Pb and Mn for 1000 °C are less than that for 0 °C. That is, thermal treatment is necessary to reduce metal releases.

**Table 5**  
Estimated coefficients and ANOVA results.

Zn	Predictor	Coef	SE Coef	t	p	
	Constant	122.03	29.50	4.14	0.001	
	D1	97.72	26.21	3.73	0.002	
	T1	-138.15	26.21	-5.27	0.000	
	Dosage	-2.496	1.638	-1.52	0.147	
	Source	DF	SS	MS	f	p
	Regression	3	151150	50383	14.67	0.000
	Residual error	16	54967	3435		
	Total	19	206117			
	$Zn_{\text{Release}} = 122 + 97.7 \cdot D1 - 138 \cdot T1 - 2.50 \cdot \text{Dosage}$					
	$S = 58.6126 R^2 = 73.3\% R^2 (\text{adj}) = 68.3\%$					
Pb	Predictor	Coef	SE Coef	t	p	
	Constant	3.2015	0.08137	39.34	0.000	
	D1	1.1510	0.07230	15.92	0.000	
	T1	-0.2710	0.07230	-3.75	0.002	
	Dosage	-0.0518	0.00451	-11.47	0.000	
	Source	DF	SS	MS	f	p
	Regression	3	10.4295	3.4765	133.01	0.000
	Residual error	16	0.4182	0.0261		
	Total	19	10.8477			
	$Pb_{\text{Release}} = 3.20 + 1.15 \cdot D1 - 0.271 \cdot T1 - 0.0518 \cdot \text{Dosage}$					
	$S = 0.161672 R^2 = 96.1\% R^2 (\text{adj}) = 95.4\%$					
Mn	Predictor	Coef	SE Coef	t	p	
	Constant	6.4476	0.3017	21.37	0.000	
	D1	0.6030	0.2680	2.25	0.039	
	T1	-5.2710	0.2680	-19.67	0.000	
	Dosage	-0.0645	0.0167	-3.85	0.001	
	Source	DF	SS	MS	f	p
	Regression	3	146.065	48.688	135.54	0.000
	Residual error	16	5.748	0.359		
	Total	19	151.812			
	$Mn_{\text{Release}} = 6.45 + 0.603 \cdot D1 - 5.27 \cdot T1 - 0.0645 \cdot \text{Dosage}$					
	$7S = 0.599352 R^2 = 96.2\% R^2 (\text{adj}) = 95.5\%$					

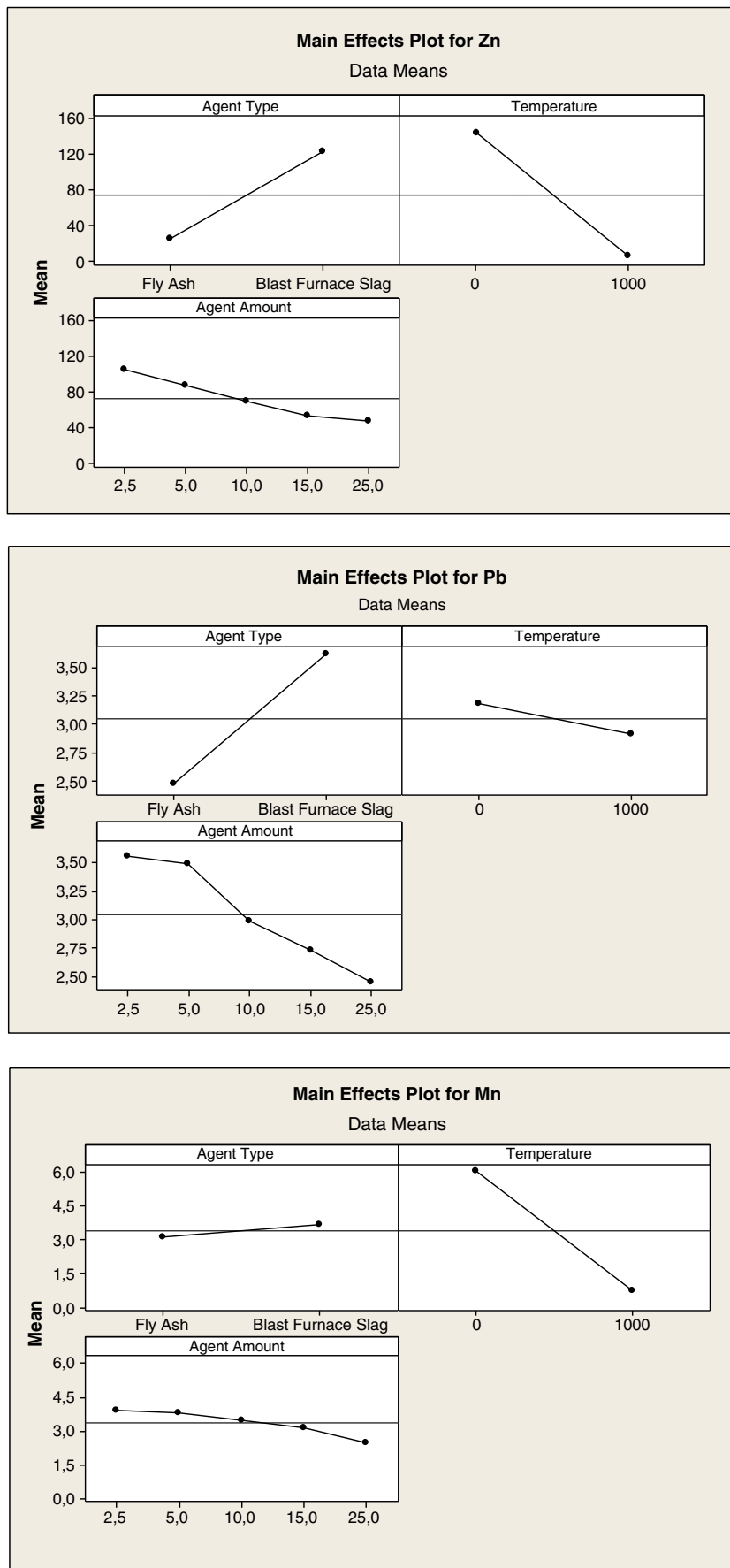


Fig. 2. Main effect plots for Zn, Pb and Mn releases (for ASTM test method).

- An increase in temperature and agent amount reversely affects the releases of Zn, Pb and Mn.
- Holding constant the effects of agent type and temperature, for each increase in the agent amount, the releases of Zn, Pb and Mn are estimated to decrease by 2.496, 0.0518 and 0.0645 respectively.
- Except for the variable of agent amount for Zn, all of the variables make a significant contribution to the model at a level of 5% significance.
- The regression p-values of 0.000 imply that at least one coefficient in the model is not zero.
- The coefficients of determination indicate that over 95% for Pb and Mn, and 68.3% for Zn of the variation in releases are explained by variation in the independent variables.
- Fly ash is an effective adsorbent for the removal of Zn, Pb and Mn ions from zinc leach waste. The Al, Fe oxides and hydroxides of fly ash were the other active components in heavy metal adsorption.

According to the main effect plots given in Fig. 2, metal releases from zinc leach waste decrease with the increase in treatment temperature and agent amount. Additionally, fly ash results in lower metal releases especially for Zn and Mn compared to that for blast furnace slag.

### 3.3. The effects of thermal treatment temperature, time and leaching tests

In order to see the effects of temperature, leaching method (TCLP and ASTM) and time on release of Zn, Pb and Mn simultaneously, two types of dummy variables were used which are temperature and leaching method (Table 6). 800 °C and TCLP method are base levels and are represented in the regression model by observations with values of 0 for all others.

The coefficients reflecting the change in metal releases as a result of a “unit change” in temperature, leaching method and time are shown in Table 7.

The main findings of Table 7 are given as follows:

- Coefficients of D1 for Zn and Pb mean that metal release for TCLP is higher than metal release for ASTM.
- The coefficient of D1 for Mn reflects that the mean release for the ASTM is 2.9073 higher than the mean for the reference group (ASTM).
- As time and temperature increase, releases of the Zn, Pb and Mn decrease.
- According to  $R^2$  values, approximately 65%, 64.3% and 73.3% of the variance in releases of Zn, Pb and Mn are explained by time, temperature and leaching method.
- Since the regression p-values are less than 0.01, the null hypothesis stating that the coefficients are zero was rejected. That is, at least one of the regression coefficients is significantly different from zero.
- The p-values for the estimated coefficients of the independent variables except for leaching method for Zn indicate that they are significantly related to releases of Zn, Pb and Mn.

From the main effect plots given in Fig. 3, it is clearly shown that as the temperature and time increase, metal releases decrease. The effect of the leaching test on Zn release is rather small since the slope is close to zero.

**Table 6**  
Dummy variables.

Leaching method	D1	Temperature	T1	T2	T3	T4
TCLP	0	800 °C	0	0	0	0
ASTM	1	900 °C	1	0	0	0
		1000 °C	0	1	0	0
		1100 °C	0	0	1	0
		1200 °C	0	0	0	1

**Table 7**  
Estimated coefficients and ANOVA results.

Zn	Predictor	Coef	SE Coef	t	p	
	Constant	359.02	29.47	12.18	0.000	
	D1	−35.70	22.54	−1.58	0.119	
	T1	−134.25	35.64	−3.77	0.000	
	T2	−252.00	35.64	−7.07	0.000	
	T3	−279.70	35.64	−7.85	0.000	
	T4	−300.70	35.64	−8.44	0.000	
	Time	−0.3814	0.1050	−3.63	0.001	
	Source	DF	SS	MS	f	p
	Regression	6	879,266	146,544	19.23	0.000
	Residual error	53	403,917	7621		
	Total	59	1,283,184			
	Zn = 359 − 35.7 · D1 − 134 · T1 − 252 · T2 − 280 · T3 − 301 · T4 − 0.381 · Time					
	S = 87.2988 R <sup>2</sup> = 68.5% R <sup>2</sup> (adj) = 65.0%					
Pb	Predictor	Coef	SE Coef	t	p	
	Constant	21.209	1.477	14.36	0.000	
	D1	−6.800	1.130	−6.02	0.000	
	T1	−3.708	1.786	−2.08	0.043	
	T2	−7.925	1.786	−4.44	0.000	
	T3	−9.075	1.786	−5.08	0.000	
	T4	−9.908	1.786	−5.55	0.000	
	Time	−0.0299	0.0053	−5.69	0.000	
	Source	DF	SS	MS	f	p
	Regression	6	2148.04	358.01	18.70	0.000
	Residual error	53	1014.83	19.15		
	Total	59	3162.87			
	Pb = 21.2 − 6.80 · D1 − 3.71 · T1 − 7.93 · T2 − 9.08 · T3 − 9.91 · T4 − 0.0299 · Time					
	S = 4.37581 R <sup>2</sup> = 67.9% R <sup>2</sup> (adj) = 64.3%					
Mn	Predictor	Coef	SE Coef	t	p	
	Constant	10.3745	0.7895	13.14	0.000	
	D1	2.9073	0.6038	4.82	0.000	
	T1	−4.2583	0.9547	−4.46	0.000	
	T2	−6.2167	0.9547	−6.51	0.000	
	T3	−7.5750	0.9547	−7.93	0.000	
	T4	−8.6433	0.9547	−9.05	0.000	
	Time	−0.0185	0.0028	−6.58	0.000	
	Source	DF	SS	MS	f	p
	Regression	6	919.91	153.32	28.04	0.000
	Residual error	53	289.83	5.47		
	Total	59	1209.75			
	Mn = 10.4 + 2.91 · D1 − 4.26 · T1 − 6.22 · T2 − 7.58 · T3 − 8.64 · T4 − 0.0185 · Time					
	S = 2.33850 R <sup>2</sup> = 76.0% R <sup>2</sup> (adj) = 73.3%					

## 4. Conclusion

A dummy variable is often used in regression models to distinguish different treatment groups. In this study, the dummy variables have enabled us to use a single regression equation to represent differences in leaching test, temperature, particle size and agent types. The TCLP, ASTM, SPLP, LEP and FLT test results show that decrease in particle size leads to an increase in Zn, Pb and Mn releases. The immobilizing agent amounts of Zn and Mn leached (except for Pb) by ASTM were greater than the other test methods. The results of laboratory leaching tests demonstrate that addition of fly ash and blast furnace slag to the zinc leach waste before and after thermal treatment drastically reduces the heavy metal content in the leachate and the fly ash performs better than blast furnace slag. Fly ash is an effective immobilizing agent for the stabilization of Zn, Pb and Mn ions from zinc leach waste. Thermal treatment studies at different temperatures between 800 and 1200 °C for Zn, Pb and Mn showed that the metal release from the zinc leach waste decreased with increasing temperature. Metal releases for residues treated at 1200 °C decreased because of the heat-induced formation of a glassy matrix.

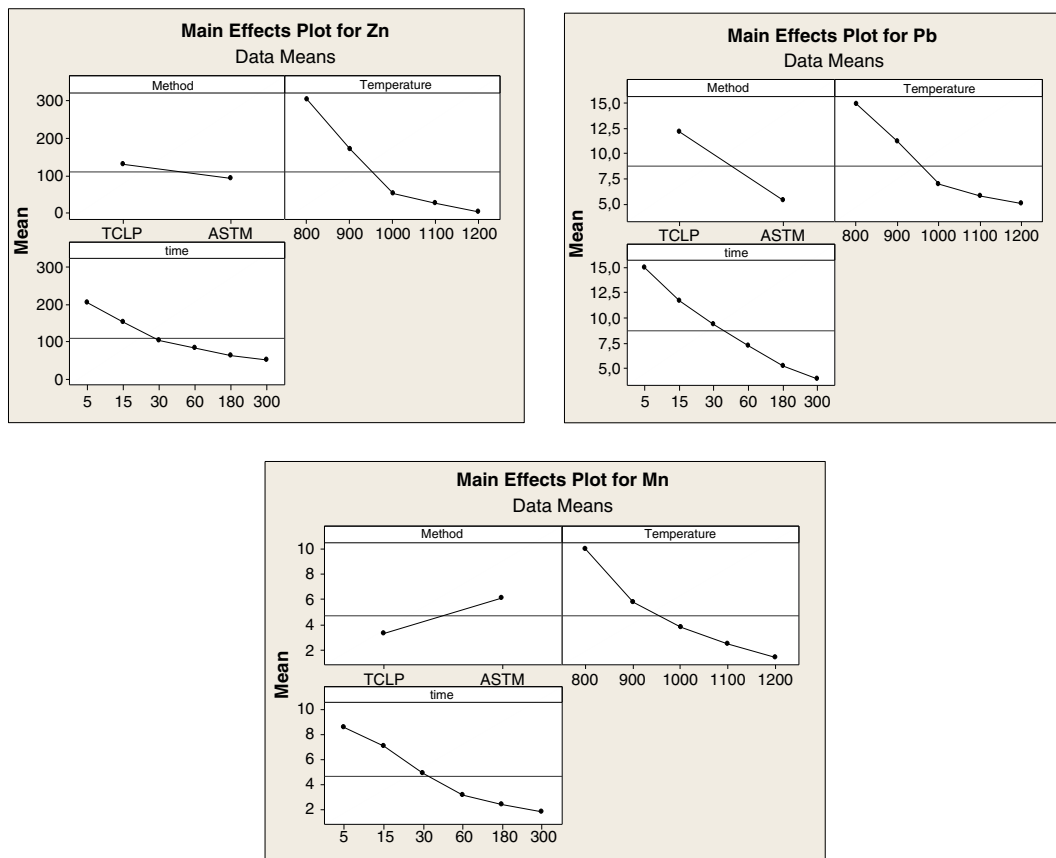


Fig. 3. Main effect plots for Zn, Pb and Mn releases.

The results have shown clearly that zinc leach waste can be safely immobilized with the use of the thermal treatment process. In addition, the leachability of Zn, Pb and Mn ions after thermal treatment up to 1000 °C is lower than the regulatory limits.

## References

- Al-Abed, S.R., Hagemen, P.L., Jegadeesan, G.N., Allen, M.D., 2006. Comparative evaluation of short-term leach tests for heavy metal release from mineral processing waste. *Sci. Total. Environ.* 3, 14–23.
- Alizadeh, R., Rashchi, F., Vahidi, E., 2011. Recovery of zinc from leach residues with minimum iron dissolution using oxidative leaching. *Waste Manag. Res.* 29 (2), 167–171.
- Al-Jabri, K.S., Taha, R.A., Al-Hasmi, A., Al-Harty, A.S., 2006. Effect of copper slag and cement by-pass dust addition on mechanical properties of concrete. *Constr. Build. Mater.* 20, 322–331.
- Babah, M.A., El-sayed, A.S., 1995. Recovery of zinc and some of its valuable salts from secondary resources and wastes. *Hydrometallurgy* 37, 23–32.
- Chang, E.E., Chiang, P.C., Lu, P.H., Ko, Y.W., 2001. Comparisons of metal leachability for various wastes by extraction and leaching methods. *Chemosphere* 45, 91–99.
- Cohen, B., Petrie, J.G., 2005. The application of batch extraction tests for the characterisation of solidified ferro alloy waste products. *J. Environ. Manage.* 76, 221–229.
- Çoruh, S., Ergun, O.N., 2010. Use of fly ash, phosphogypsum and red mud as a liner material for the disposal of hazardous zinc leach residue waste. *J. Hazard. Mater.* 173, 468–473.
- El-Kamash, A.M., Zaki, A.A., Abed El Geleel, M., 2005. Modelling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. *J. Hazard. Mater.* 127, 211–220.
- Gönül, D., 2007. Thermal Treatment of Zinc Industry Waste. MSc thesis Department of Environmental Engineering, Ondokuz Mayıs University, Samsun, Turkey.
- Gupta, V.K., Gupta, M., Sharma, S., 2000. Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste. *Water Res.* 35, 1125–1134.
- Hagama, P.L., 2007. U.S. Geological survey field leach test for assessing water reactivity and leaching potential of mine wastes, soils, and other geologic and environmental materials. Techniques and Methods 5-D3. U.S. Geological Survey, Reston, Virginia.
- ILZSG, 1985. *World Directory: Secondary Lead Plants*, International Lead and Zinc Study Group Report, London.
- Kim, A.G., 2003. Leaching methods applied to CUB: standard, regulation and other. 15th International Symposium on Management and Use of Coal Combustion Products, January 27–30, St. Petersburg.
- Margui, E., Salvado, V., Queral, I., Hidalgo, M., 2004. Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes. *Anal. Chem. Acta* 524, 151–159.
- Marsh, H.A.F., 1997. Investigation of the Behaviour of Thermally Treated Municipal Solid Waste Flyash. MSc. thesis Department of Chemical Engineering and Applied Chemistry University of Toronto.
- Montanaro, L., Bianchini, N., Rincon, J.Ma., Romero, M., 2001. Sintering behaviour of pressed red mud wastes from zinc hydrometallurgy. *Ceram. Int.* 27, 29–37.
- Moors, E.H.M., Dijkema, G.P.J., 2006. Embedded industrial production systems lessons from waste management in zinc production. *Technol. Forecast. Soc. Change* 73, 250–265.
- Pelino, M., Karamanov, A., Aloisi, M., Taglieri, G., Ergun, O.N., Çoruh, S., 2004. Vitrification of copper flotation waste. 2004 Global Symposium on Recycling, Waste Treatment and Clean Technology, Madrid, Spain, 26–29th September.
- Peralta, G.L., 1997. Characterization, Leachability and Acid Mine Drainage Potential of Geothermal Solid Residues. PhD thesis Department of Chemical Engineering and Applied Chemistry, University of Toronto.
- Porcu, M., Orru, R., Cao, G., 2004. On the use of industrial scraps for the treatment of zinc hydrometallurgical wastes by self-propagating reactions. *Chem. Eng. J.* 99, 247–256.
- Rashchi, F., Dashti, A., Arabpour-Yazdi, M., Abdizadeh, A., 2005. Anglesite flotation: a study for lead recovery from zinc leach residue. *Miner. Eng.* 18, 205–212.
- Rincon, J.M.A., Romero, M., Boccacini, A.R., 1999. Microstructural characterisation of a glass and a glass-ceramic obtained from municipal incinerator fly ash. *J. Mater. Sci.* 34, 4413–4423.
- Ruşen, A., Sunkar, A.S., Topkaya, Y.A., 2008. Zinc and lead extraction from Çinkur leach residues by using hydrometallurgical method. *Hydrometallurgy* 93, 45–50.
- U.S. Environmental Protection Agency, 1989. Stabilization/Solidification of CERCLA and RCRA Wastes, EPA/625/6-89/022.
- U.S. Geological Survey, 2005. A Simple Field Leach Test to Assess Potential Leaching of Soluble Constituents From Mine Wastes, Soil and Other Geological Materials: U.S. Geological Survey Fact Sheet.
- USEPA, 1994. Synthetic precipitation leaching procedure (SPLP). EPA Method 1312, Washington, USA.
- Vahidi, E., Raschi, F., Moradkhani, D., 2009. Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA. *Miner. Eng.* 22, 204–206.