Chemical Engineering Journal 162 (2010) 718–722

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Optimization of dissolution of metals from Waelz sintering waste (WSW) by hydrochloric acid solutions

Ayşe Vildan Beşe*, Nurcan Borulu, Mehmet Çopur, Sabri Çolak, Osman Nuri Ata

Department of Chemical Engineering, Atatürk University, 25240 Erzurum, Turkey

ARTICLE INFO

Article history:
Received 29 March 2010
Received in revised form 24 June 2010
Accepted 25 June 2010

Keywords:
Waelz process
Optimization
Taguchi method
Leaching
Zinc waste

ABSTRACT

In this study Taguchi method was applied to determine the optimum conditions of dissolution of metals in Waelz sintering waste (WSW) in HCl solutions. The effects of solid-to-liquid ratio, reaction temperature, stirring speed, acid concentration, and reaction time on extraction efficiency were investigated. The optimum conditions were determined as follows: solid-to-liquid ratio, 0.1; reaction temperature, 65 °C; stirring speed, 700 rpm; acid concentration, 3 M and the reaction time, 48 min. Under these conditions, extraction efficiencies of zinc, cadmium and lead from waste were 97%, 91% and 0.052%, respectively.

1. Introduction

Zinc is an important base metal required for various applications in metallurgical, chemical and textile industries. It is mainly recovered from primary sulphide concentrates. A part of zinc is also recovered from different secondary resources.

Various secondaries and wastes containing zinc are generated in metallurgical industries via galvanizing, casting, smelting, scrap recycling, etc. These are mainly zinc dross, flue dusts of electric arc furnace and smelting operation, automobile scrap, and sludge. Zinc present in the secondaries is in the form of metal, oxides and/or alloy and associated with different level of impurities depending on their source. The material can be used to recover the metallic values or it may be disposed off. However, the disposal of such materials is now becoming expensive because of increasingly stringent environmental protection regulations. Furthermore, the chemical nature of these dust particles is classified as hazardous waste. The toxicity is mainly due to the presence of different metals such as lead, cadmium, arsenic, and chromium.

Pyrometallurgical and hydrometallurgical processes are usually used for treating such secondaries. A major drawback of the pyrometallurgical method is the high-energy requirement and need of dust collecting and gas cleaning systems. The presence of chloride and fluoride salts in the dust causes severe corrosion problems which results in the use of expensive alloys as construction materials. The hydrometallurgical processes are more environmentally convenient and more economical to treat even low zinc containing materials on small scale [1].

Turan et al. [2] investigated the recovery of zinc and lead from zinc plant residue by H_2SO_4 and NaCl. Çopur et al. [3] investigated high purity recovery of metals from Waelz sintering waste by aqueous SO_2 solutions. Ruşen et al. [4] studied the extraction of zinc and lead from Çinkur leach residues by H_2SO_4 and brine leaching. Liaon and Deng [5] extracted zinc and lead by the combination of sequential bio-oxidation and acidic brine leaching from raw complex sulphide ores containing sphalarite, pyrite, and galena. Gouvea and Morais [6] investigated the recovery of zinc and cadmium from the industrial waste leaching with H_2SO_4 and cementation. Ata et al. [7] determined the optimum conditions for zinc extraction from sphalerite by hydrochloric acid. The optimum conditions of residues of zinc plant were determined by using the hydrometallurgical methods [8–10]. Besides the alkaline and acid extraction techniques mentioned above, chloride leaching process were employed using either NaCl [11] or $FeCl_3$ [12].

Waelz process is a well-known metallurgical process in which zinc ore or concentrate is heated with fuel oil, coke or powdered coal in a reducing rotary kiln, known as the Waelz Furnace at 1100–1200 °C. The zinc and other volatile non-ferrous metals in the feed are vaporized in the furnace and then carried to an external collection system comprised of a cyclone, and are baghoused. The collected dust, called as Waelz oxide, is a crude zinc bearing product. The Waelz oxide is further refined by a second kiln step where the material is further heated and sintered to form a zinc clinker material. At the sintering stage in the production of zinc, cadmium and lead, where harmful components for the electrolysis such as

* Corresponding author. Tel.: +90 0442 2314574; fax: +90 0442 2314544.
E-mail address: vbese@atauni.edu.tr (A.V. Beşe).

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doi:10.1016/j.cej.2010.06.035

Table 1
Chemical composition of Waelz sintering waste used in the study.

Constituent	Zn	Cd	Pb	Cu	Mg	Ni	Sb	Co	Mn	Fe_2O_3	CaO	Cl^-	$SO4_4^{2-}$
wt%	18.4	6.22	42.32	0.017	0.016	0.01	0.04	0.009	0.03	0.13	0.015	5.44	2.28

Table 2
Parameters and their values corresponding to their levels to be studied in experiments.

Parameters		Levels				
		1	2	3	4	5
A	Solid/liquid ratio (g/mL)	0.50	0.25	0.166	0.125	0.10
B	Reaction temperature (°C)	25	35	45	55	65
C	Reaction time (min)	12	24	36	48	60
D	Stirring speed (rpm)	300	400	500	600	700
E	Acid concentration (M)	1	1.5	2	2.5	3

F and Cl are removed, a powdered waste product is obtained from the condensation of metal vapors. This waste material named as "Waelz sintering waste" (WSW) contains mainly (up to 70%) ZnO, CdO, and PbO [3].

Although there are many study on zinc plant residues, there is not any study on optimization of Waelz sintering waste in HCl solutions in literature up to now. The present study proposes to determine the optimum dissolution conditions of metals in WSW by HCl solutions. The Taguchi method was used to determine the optimum conditions.

2. Materials and methods

2.1. Material

The waste sample used in this study was obtained from Çinkur in Kayseri, Turkey. The waste was already in powder form, so no further treatment was done including crushing, grinding and shifting. Waste, collected from the production site in different bags, was first blended thoroughly before dividing and re-packing it into 20–25 kg sample bags. The particle size was found to be below 74 μm by using the ASTM standard sieve analysis. The chemical composition of waste was analyzed by standard volumetric methods and atomic absorption spectrophotometer. The average composition is given in Table 1. Mineralogical characterization of WSW was performed using a Siemens D-5000 model X-ray diffractometer. The X-ray diffraction pattern obtained indicated the presence of $ZnCl_2$, ZnO, $ZnSO_4$, PbO, $PbCl_2$, $PbSO_4$, CdO and $CdSO_4$.

2.2. Experimental procedure

The leaching experiments were carried out in a 500 ml glass reactor equipped with a mechanical stirrer, a back cooler and a thermostat. The temperature of the reaction medium was controlled within ±1 °C. Firstly, 250 ml of HCl solution at predetermined concentration was put into the reactor. After the desired reaction temperature was reached, the predetermined amount of the waste was added to the solution while stirring the content of the vessel at a certain speed. After the leaching process, the reaction mixture was filtered and leach liquor was analyzed for zinc, cadmium and lead by using an atomic absorption spectrophotometer (Shimadzu AA-670).

Experimental parameters and their levels, determined in the light of preliminary tests, are given in Table 2. The orthogonal array (OA) experimental design was chosen as the most suitable method

Table 3
Responses and SNL values for zinc and cadmium.

Experiment no.	Parameters and their levels					Responses (Zn)			Responses (Cd)		
	A	B	C	D	E	1	2	SNL	1	2	SNL
1	1	1	1	1	1	49.45	48.88	33.766	45.16	43.54	32.933
2	1	2	2	2	2	57.71	56.91	35.101	53.78	52.60	34.515
3	1	3	3	3	3	60.26	59.89	35.573	58.12	56.71	35.178
4	1	4	4	4	4	61.05	62.17	35.791	59.43	57.11	35.303
5	1	5	5	5	5	71.14	70.12	36.979	68.43	65.73	36.529
6	2	1	2	3	4	63.43	62.17	35.957	56.55	56.98	35.081
7	2	2	3	4	5	73.09	72.11	37.218	67.32	66.73	36.524
8	2	3	4	5	1	65.12	64.17	36.210	55.98	57.93	35.106
9	2	4	5	1	2	60.00	60.72	35.614	51.87	54.00	34.469
10	2	5	1	2	3	70.16	69.33	36.869	62.53	63.00	35.954
11	3	1	3	4	2	71.89	72.99	37.198	64.15	67.71	36.372
12	3	2	4	5	3	68.93	69.71	36.816	60.43	65.00	35.930
13	3	3	5	1	4	62.26	60.13	35.730	56.33	55.88	34.979
14	3	4	1	2	5	67.13	66.18	36.475	61.00	62.19	35.789
15	3	5	2	3	1	74.32	73.44	37.370	68.73	69.15	36.769
16	4	1	4	5	5	85.43	83.47	38.530	79.01	79.81	37.996
17	4	2	5	1	1	64.78	68.65	36.473	60.22	65.73	35.958
18	4	3	1	2	2	70.01	65.66	36.615	65.66	62.14	36.100
19	4	4	2	3	3	71.12	70.16	36.980	67.41	66.71	36.528
20	4	5	3	4	4	73.19	74.78	37.381	70.03	68.15	36.784
21	5	1	5	1	3	69.43	70.16	36.876	66.78	65.05	36.377
22	5	2	1	2	4	74.60	73.47	37.387	70.71	67.73	36.798
23	5	3	2	3	5	84.62	82.92	38.460	79.43	78.76	37.962
24	5	4	3	4	1	74.56	75.13	37.483	70.03	71.41	36.989
25	5	5	4	5	2	90.19	89.16	39.053	86.19	85.21	38.659

to determine the experimental plan, L_{25} (5^5) (Table 3), five parameters, each with five values. In order to observe the effect of noise sources on the dissolution process, each experiment was repeated twice under the same conditions at different times.

2.3. Data analysis

The use of the quantity design in the Taguchi method to optimize a process with multiple performance characteristics includes the following steps: (a) to identify the performance characteristics and select process parameters to be evaluated; (b) to determine the number of parameter levels for the process and possible interaction between the process quantities; (c) to select the appropriate orthogonal array and the assignment of process parameters to the orthogonal array; (d) to conduct the experiments based on the arrangement of the orthogonal array; (e) to calculate the performance characteristics; (f) to analyze the experimental results using the performance characteristic and ANOVA; (h) to select the optimal levels of process parameters; (i) to verify the optimal process parameters through the confirmation experiments [13].

In order to observe the effects of noise sources on the dissolution process, each experiment was repeated twice under the same conditions at different times. The performance characteristics were chosen as the optimization criteria. There are three categories of performance characteristics, the larger-the-better, the smaller-the-better and the nominal-the-better. The performance characteristics were evaluated by using Eqs. (1) and (2):

$$\text{larger-the-better}\ \ \text{SNL} = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \tag{1}$$

$$\text{smaller-the-better}\ \ \text{SNS} = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}Y_i^2\right) \tag{2}$$

where SNL and SNS are the performance characteristics, n is the number of repetitions performed for an experimental combination, and Y_i performance value of ith experiment. In the Taguchi method, the experiment corresponding to optimum working conditions may not be carried out during the whole period of the experimental stage. In such cases, the performance value corresponding to the optimum working conditions can be predicted by utilizing the balanced characteristic of OA. For this aim the following additive model may be used

$$Y_i = \mu + X_i + e_i \tag{3}$$

where μ is the overall mean of performance value, X_i the fixed effect of the quantity level combination used in ith experiment, and e_i is the random error in ith experiment.

If the experimental results are given in percentages (%), before evaluating Eq. (3), the omega transformation of percentage values should be applied first using Eq. (4):

$$\Omega = -10\ \log\left(\frac{1}{X} - 1\right) \tag{4}$$

Here Ω (db) is the decibel value of percentage value subject to omega transformation and $0 < X < 1$ percentage of the product obtained experimentally. Once the statistical analysis is done, the percentage values can be recovered by inverting the omega transformation [14].

Because Eq. (3) is a point estimation, which is calculated by using experimental data in order to determine whether the additive model is adequate or not, the confidence limits for the prediction error must be evaluated [13]. The prediction error is the difference between the observed Y_i and the predicted Y_i. The confidence limits for the prediction error, S_e is given as;

$$S_e = \pm 2\sqrt{\left[\frac{1}{n_0}\right]\sigma_e^2 + \left[\frac{1}{n_r}\right]\sigma_e^2} \tag{5}$$

$$\sigma^2 = \frac{\text{sum of squares due to error}}{\text{degreees of fredom for error}} \tag{6}$$

$$\frac{1}{n_0} = \frac{1}{n} + \left[\frac{1}{n_{Ai}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Bi}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Ci}} - \frac{1}{n}\right] + \cdots \tag{7}$$

where S_e is the two-standard-deviation confidence limit, n the number of rows in the matrix experiment, n_r the number of repetition in confirmation experiment and n_{Ai}, n_{Bi}, n_{Ci}, ..., are the replication number for variables quantity level A_i, B_i, C_i, ... If the prediction error is out of these limits, it indicates that the possibility of inadequacy of the additive model. Otherwise, the additive model can be considered as adequate.

A verification experiment is a powerful tool for detecting the presence of interactions among the control quantities. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then it implies that the interactions are probably not important and that the additive model is a good approximation.

3. Results and discussion

3.1. Dissolution reactions

The following reactions probably occur during the solution of WSW in hydrochloric acid solutions:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \tag{8}$$

$$CdO + 2HCl \rightarrow CdCl_2 + H_2O \tag{9}$$

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O \tag{10}$$

Whilst zinc chloride is very soluble in water, solutions do not include simply solvated Zn^{2+} ions and Cl^- ions, $ZnCl_xH_2O_{(4-x)}$ species are also present [15–18]. The presence of $Zn(H_2O)_6{}^{2+}$, $ZnCl_{(aq)}{}^+$, linear $ZnCl_{2(aq)}$, and $ZnCl_4(H_2O)^{2-}$ is expressed in aqueous solutions of zinc chloride less concentrated than 10 M. Ion concentrations are reported as the functions of zinc chloride molarities. The tetrachloro complex dominates stoichiometric zinc chloride concentrations between ~0.5 and ~10 M with significant concentrations of $ZnCl^+$ below ~4 M zincs chloride and $ZnCl_2$ above ~4 M. For stoichiometric solutions greater than 10 M, the evidence suggests a polymeric species or aggregate with structural characteristics similar to those found in the crystal.

Aqueous solutions of $ZnCl_2$ are acidic: a 6 M aqueous solution has a pH of 1 [19]. The acidity of aqueous $ZnCl_2$ solutions relative to solutions of other Zn^{2+} salts is due to the formation of the tetrahedral chloro aqua complexes where reduction in coordination number from 6 to 4 further reduces the strength of the O–H bonds in the solvated water molecules.

Cadmium chloride has a high solubility in water, and it dissociates into ions. A certain amount of hydrolysis to species such as $[CdOH(H_2O)_x]^+$ may occur. The high solubility may be due to some part of formation of complex ions such as $[CdCl_4]^{2-}$ (*i.e.*, $CdCl_2$ is a Lewis acid). With excess chloride ions in water or acetonitrile it forms mainly $[CdCl_3]^-$ and the tetrahedral anion, $[CdCl_4]^{2-}$:

$$CdCl_2(aq) + 2Cl^-(aq) \rightarrow [CdCl_4]^{2-}(aq) \tag{11}$$

The solubility of $PbCl_2$ in water is low (9.9 g/L at 20 °C) and for practical purposes it is considered insoluble. Its solubility product constant (K_{sp}) at 25 °C (298 K) is 1.6×10^{-5} [20].

Table 4
Analysis of variance for zinc.

Effect	SS	df	MS	*F*
A (solid/liquid ratio)	999.0953	4	249.7738	21.91713
B (reaction temperature)	266.2491	4	66.5623	5.84070
C (reaction time)	257.0559	4	64.2640	5.63903
[a]D (stirring speed)	27.2483	4		
E (acid concentration)	303.6445	4	75.9111	6.66104
Residual	91.1703	8	11.3963	

[a] Effect pooled into error term.

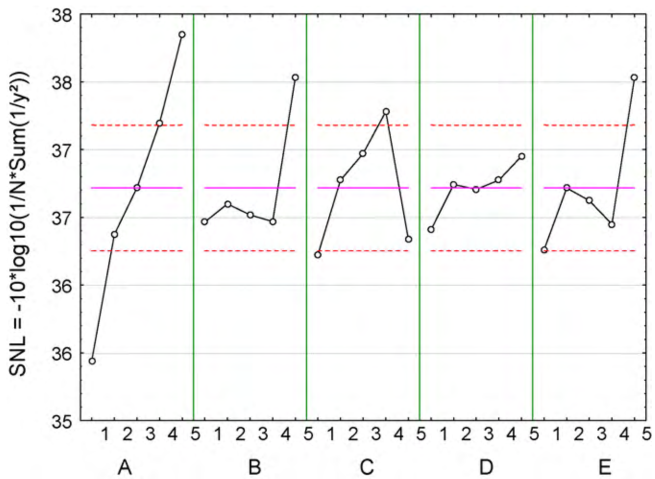

Fig. 1. The effect of each parameter on the performance statistics for zinc.

3.2. Statistical analysis

The collected data were analyzed for evaluating the effect of each parameter on the optimization criteria. A statistical analysis of variance (ANOVA) was performed to see which process parameters were statistically significant. *F*-Test is a tool to see which process parameters have a significant effect on the dissolution rate. Usually, the larger the *F*-value is, the greater the effect on the dissolution will be. The optimal combination of process parameters can be predicted with the performance characteristics and ANOVA analyses [14]. The results of variance analysis are given in Tables 4 and 5. To obtain optimal dissolution performance, the higher (larger)-the-better performance characteristic in Eq. (1) was used for the dissolution of Zn and Cd. The order of graphs in Figs. 1 and 2 is according to the degrees of influence of parameters on the performance characteristics. The optimal level of a process parameter is the highest SN value calculated by Eq. (1).

The numerical value of the maximum point in each graph indicates the best value of that particular parameter. The optimum conditions for the dissolution of maximum Zn and Cd are A5 (0.1 g cm^{-3}), B5 (65 °C), C4 (48 min), D5 (700 rpm), E5 (3 M) from Figs. 1 and 2. As seen in Tables 4 and 5, while the solid-to-liquid ratio has significant effects on the dissolution process for

Table 5
Analysis of variance for cadmium.

Effect	SS	df	MS	*F*
A (solid/liquid ratio)	1043.083	4	260.7708	19.63097
B (reaction temperature)	266.902	4	66.7254	5.02313
C (reaction time)	241.910	4	60.4774	4.55278
[a]D (stirring speed)	42.945	4		
E (acid concentration)	310.755	4	77.6888	5.84846
Residual	106.269	8	13.2836	

[a] Effect pooled into error term.

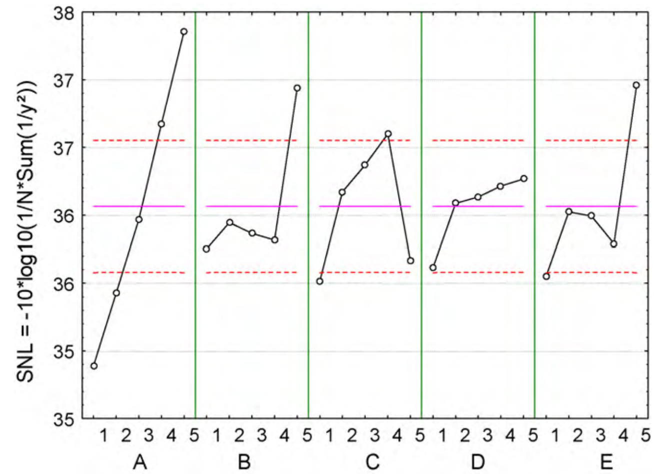

Fig. 2. The effect of each parameter on the performance statistics for cadmium.

Table 6
Optimum working conditions, observed and predicted dissolved quantities of Zn, and Cd.

Parameters	Value	Level
A. Solid/liquid ratio (g cm^{-3})	0.1	5
B. Reaction temperature (°C)	65	5
C. Reaction time (min)	48	4
D. Stirring speed (rpm)	700	5
E. Acid concentration (M)	3	5
Observed dissolved quantity of Zn%	97	
Predicted dissolved quantity of Zn%	92.6	
Confidence limits of prediction of Zn%	83.35–100	
Observed dissolved quantity of Cd%	91	
Predicted dissolved quantity of Cd%	89.38	
Confidence limits of prediction of Cd%	80.13–98.63	

Zn and Cd, the stirring speed has no effect within the working range.

If the experimental plan given in Table 3 is studied carefully together with Table 2, it can be seen that the experiments corresponding to the optimum working conditions in Table 6 were not carried out during the planned experimental work in Table 3. Thus, it should be noted that the optimum dissolution percentages are predicted results obtained by using Eqs. (5)–(7) and observed results for the same conditions (see Table 6). Also, results are within the 95% significance level confidence interval of predictions. In order to test the predicted results, confirmation experiments were carried out twice at the same working conditions. The fact that the dissolution percentages from confirmation experiments are within calculated confidence intervals shows that experimental results are within ±5% in error. This case states that there is a good agreement between the predicted values and experimental values, and interactive effects of parameters are indeed negligible. It may be concluded that the additive model is adequate for describing the dependence of this dissolution process on the various operational parameters [14].

4. Conclusion

The optimum conditions of dissolution of zinc and cadmium in the Waelz sintering waste (WSW) in hydrochloric acid solutions were investigated. The effect of some important operational parameters (solid-to-liquid ratio, reaction temperature, reaction time, stirring speed, acid concentration) was studied. The Taguchi method was used to determine the optimum conditions. The major conclusions derived from the present work are as follows:

- The optimum conditions was found to be as follows: solid to liquid ratio (g/mL): 0.1; reaction temperature (°C): 65; reaction time (min): 48; stirring speed (rpm): 700; acid concentration (M): 3. Under these conditions, the extraction efficiencies of Zn, Cd and Pb were 97%, 91% and 0.052%, respectively.
- While the solid-to-liquid ratio had significant effects on the dissolution process for Zn and Cd, the stirring speed had no effect within the working range.
- The lead is dissolved in hot condition in HCl and it is precipitated in cold condition as $PbCl_2$. Since $PbCl_2$ is highly dissolved in hot water, the precipitated $PbCl_2$ is distinguished from gang and insoluble material in water.

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