Environmental assessment of filter cake wastes in zinc processing plants

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Abstract

In this paper, results of the study on heavy metals solubility behavior of Ni-Cd filter cakes in Iranian Zinc Mine Development Company (IZMDC) plants are investigated. The effects of pH, temperature, liquid/solid ratio and contact time on the release of heavy metals (Zn, Cd, Ni and Pb) into water media was examined. Also, "Extraction procedure tests" approved by EPA were applied to the residues. Moreover, statistical data analysis was performed and the most important parameters for dissolution of Zn, Cd, Ni and Pb were found to be the pH and L/S.. The concentration of Cd and Pb in the extracts obtained from filter cakes by applying EPA extraction procedures at pH 5 are over 1.0 and 5.0 mg/L, which are toxicity limits, respectively. The concentrations of other metals in the solution are above the limits given by various quality standards for surface water.

key words

Zinc wastes

Ni-Cd purification filter cakes

EPA extraction tests

Heavy metal pollution

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1. Introduction

Owing to industrial development and population expansion, heavy metal pollution in water environment is becoming increasingly serious worldwide [1,2]. Of all the heavy metals, Zn is an essential element for plant growth and can be easily taken up by roots [3], but it is regarded as poisonous at concentrations of 150–200 μg g^{-1} in plants' tissues [4]. Zn contents of plants from some contaminated sites have reached the magnitude of 0.X% (DW) and may create an important environmental problem [5]. Cd is a toxic element and exists along with Zn in nature. It is one of the most significant pollutants to consider in terms of food chain contamination, because it is readily taken up by plant and translocated to different parts of plant [6]. Pb is found in accumulator industry sludge, toy production, printing, petroleum industry, waste water and exhaust gases [7]. This element is not essential for plant growth and considered as toxic at the concentration of 30–300 μg.g^{-1} in plant tissues [8]. It has received much attention as a hazardous pollutant to human and animals recently.

Metals are released into the environment at increasing rates by mining, industry, and agriculture, causing serious problems for environmental and human health [9].

Zinc extraction plants, located in Zanjan, Iran, practice a hydrometallurgical leaching-electrolysis production process. In this process, a great deal of residual wasteful filter cakes is generated each day. These wastes are retained for valuable elements recovery in the future and dumped in open stockpiles where they may cause heavy metal pollution problems. Generally, three types of wastes are gathered together in such dumping sites including; Leaching filter cake, Cobalt purification filter cake, and Ni-Cd purification filter cake. All of the filter cakes have a high percent of heavy metal [10]. In this study, the metal release potential of zinc production waste by-products was investigated. The concentration of metal ions leached from Ni-Cd filter cake samples into water was determined at different pH, temperature, liquid/solid ratio and contact time. Also, standard extraction tests were applied to the filter cakes in order to compare the concentration of metal ions released from the cakes and the limit concentrations of contaminants determined by [12] for surface waters.

2. Materials and methods

100 gr of waste filter cake was employed for the X-ray diffraction analysis was, to determine the phases of Ni-Cd filter cake . Result of the analysis is presented in table 1.

As for the solubility studies, different amounts of waste samples were weighed up and added to a beaker containing 200 ml of distilled water in amounts to produce liquid/solid ratios from 1 to 10 (w/w), while the pH of which was adjusted with H_2SO_4 The suspensions were tightly capped and

Table1. Chemical analysis of the sample (Wt.%)

Component	Wt. (%)
Na_2O	10.937
MgO	0.567
Al_2O_3	0.187
SiO_2	0.356
SO_3	8.395
CaO	0.308
MnO	0.168
Cd	11.061
Ni	3.339
Cu	1.397
Zn	40.37
Pb	0.795
LOI	22.12

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Table2. Special parameters in leaching treatment

Parameters	Units	Level 1	Level 2	Level 3	Level 4	Level 5
pH	-	3	4	5	6	7
Temperature	ºC	20	25	30	35	40
S/L	-	1/1	1/3	1/5	1/7	1/10
Time	Min	30	60	120	480	960

equilibrated by shaking at the rate of 250 cycle/min for a period varying from 1/2 to 16 h. At the end of predetermined shaking period, the suspensions were filtered through filter paper. the transport of heavy metals such as Zn, Cd, Ni, Pb from Ni-Cd purification filter cake were examined in which four parameters of pH, Temperature, liquid/solid ratio and contact time on the transport of above mentioned metals were studied using leaching tests. For each parameter five levels were chosen as shown in table 2.

The quantity of metal ions released from the cake samples into the water or acid solutions were determined by applying EPA approved extraction test. In the test procedure, 100 g of dried solid sample was placed in a 2.5 L jar containing 1600 ml of distilled water. Then pH was adjusted to 5 using 0.5 N acetic acid. The mixture was stirred at 100 rpm with a mechanical stirrer for 24 h. During the stirring period, the pH was kept at 5±0.2 using 0.5N acetic acid. At the end of the 24 h extraction period, deionized water was added to the extractor in an amount determined by the equation (1).

$$V = 20(W) - 16(W) - A$$

$$V = 4(W) - A \qquad \text{equation (1)}$$

where, V is the amount of deionized water to be added (ml), W is the weight of solid charged to extractor (gr) and A is the amount of 0.5 N acetic acid added during extraction (ml). The concentration of Cd, Co, Ni, Cu, Fe, Mn, Mg, Pb and Zn in the solutions was determined by atomic absorption spectrophotometry using direct aspiration technique [11,13].

3. Results and discussion

3.1. Effect of pH

Figure 1. depicts the concentrations of heavy metals ions released from the cakes at various pH. As seen in Figure 1, decreasing the pH down to 3

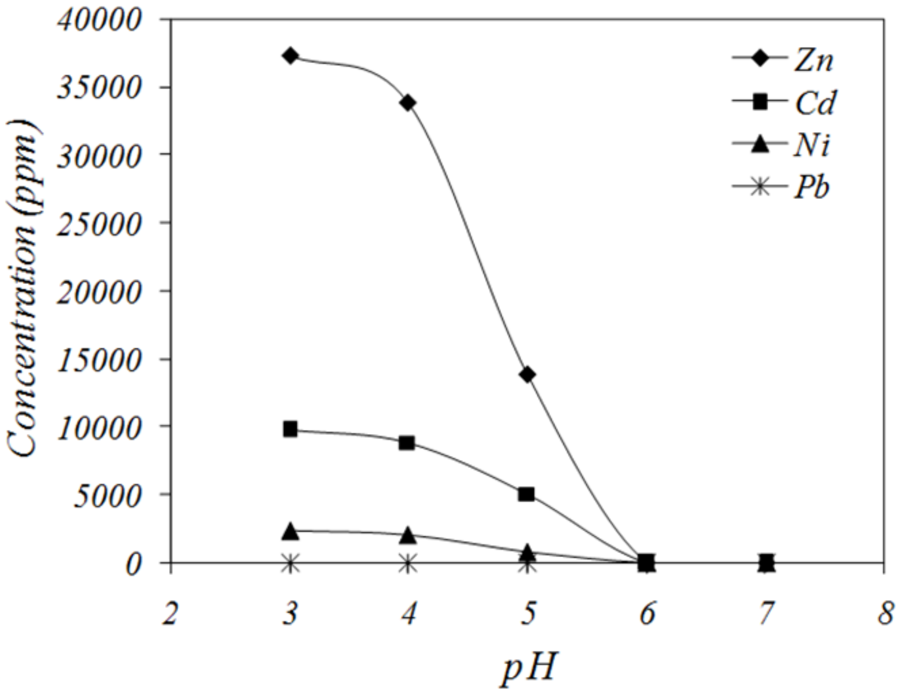

Figure 1. Effect of pH on the Zn, Cd, Ni and Pb dissolution (T: 25ºC, L/S: 10/1, t: 60min)

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made a significant change in metal concentration but at pH 7, it was observed that the solubilization of Cd, Zn, Ni and Pb decreased. The concentrations of Zn, Cd, Ni, and Pb solubilized from cake are 37340, 2367, 9755 and 3.9 mg/l at pH 3, respectively. The solubility of metal compounds in the cake is mostly dependent on acidity of solution. For that reason, it is expected that the concentration of solubilized metals in the leach solution increase at strong acidic media. The lead ions solubilized from the cakes may react with H2SO4 to form $PbSO_4$. Since solubility of $PbSO_4$ is very low, the concentration of Pb in the solutions did not increase compared to other metals. Concentration of heavy metals in pH=3 and pH=4 is near together.

3.2. Effect of temperature

Figure 2 shows the effect of temperature on the dissolution of Zn, Cd, Ni and Pb. As seen in Figure 2, increasing the temperature up to 40ºC did not make a significant change in metal concentration. The maximum concentration of Zn, Cd, Ni and Pb were found to be at the temperature of 30 ºC that equal to 39560, 11110, 2433.5, and 5.19 mg/l, respectively.

3.3. Effect of liquid/solid ratio

The effects of liquid/solid ratio on the dissolution of Zn, Cd, Ni and Pb are illustrated in Figure 3. To investigate the effect of the liquid/solid ratio on the concentrations of metals releasing into water at pH=3, experiments using different liquid/solid ratios were performed. The batch shaking experiments showed that the dissolution percent of Zn, Cd, Ni and Pb increased with an increasing liquid/solid ratio, whereas the Pb concentrations in the solutions did not change with liquid/solid ratio. The maximum dissolution percent achieved in L/S: 10/1.

3.4. Effect of contact time

Concentration of Zn, Cd, Ni and Pb for 0.5, 1, 2, 4, 8 and 16 hour of leaching time by H_2SO_4 solution are given in Figure.4. As shown in Figure.4, results indicate that the concentration of above-mentioned metals increase with increasing leaching time to 8 hr and then it reaches to constant rate.

3.5. EP toxicity results

The term “EP toxicity” refers to a test used to determine the concentrations of particular toxic constituents leached out from a solid waste disposed to improper site. If the concentration of toxic constituents from a solid waste is over the “EP toxicity” limits, this waste is considered as hazardous. The concentrations of extractable metals from filter cakes by applying extraction procedure tests are given in Table 3. As seen, the concentrations of Cd and Pb exceeded “EP toxicity” limits given by EPA (EPA 1980, EPA 1989), as 1 and 5 mg/l, respectively. The concentrations of Cd and Pb are 1527 and 12.67 mg/L which are very high compared to their toxicity limits EP toxicity limits. However, the concentrations of metals determined were compared to the water quality criteria for surface water and it was found that the concentrations of all metals except Fe and Mg are over the limits which are presented in table 3. Therefore, these cakes can be assumed as a hazardous waste for the environment.

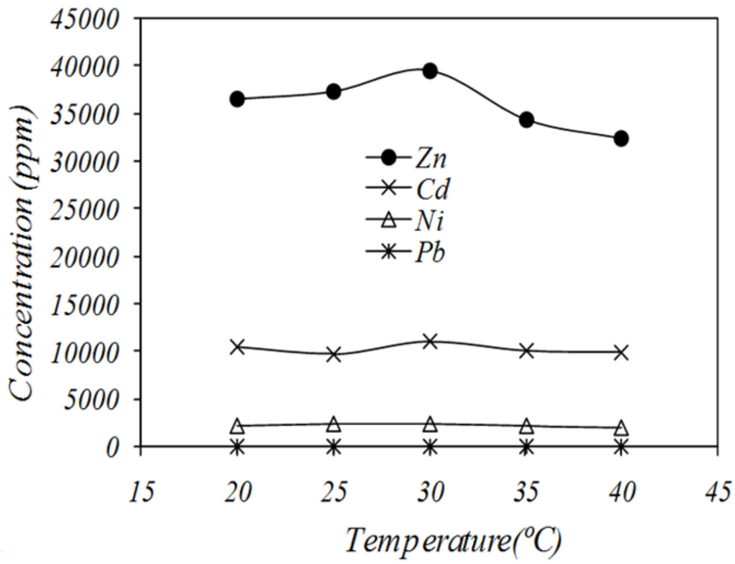

Figure.2. Effect of Temperature on the Zn, Cd, Ni and Pb dissolution (pH: 3, L/S: 10/1, t: 60min)

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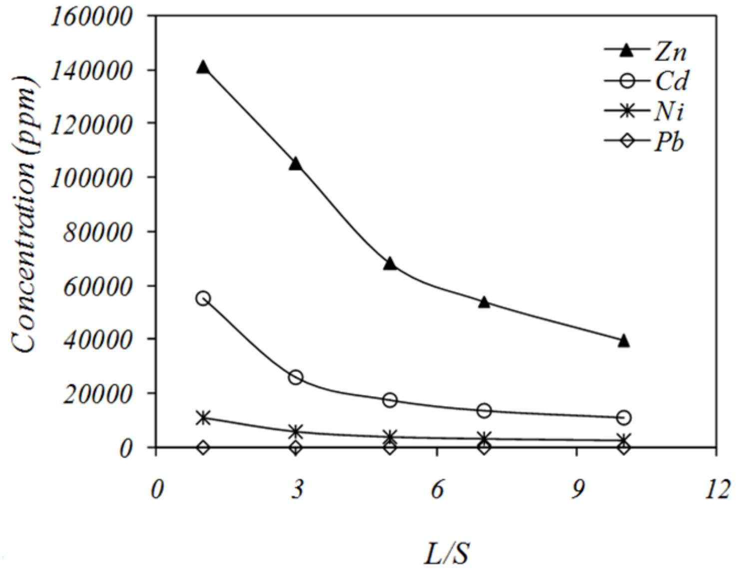

Figure 3. Effect of L/S on the Zn, Cd, Ni and Pb dissolution (pH: 3, T: 30 ºC, t: 60min)

3.6. Predicting leachability hazardous metals from cake waste

PH, Temperature, liquid/solid ratio and time were statistically analysed by SPSS14software using a multi-variable linear model.

The equation for dissolution percent of zinc is described by:

DZn = -0.825H + 0.028T + 0.273LS + 0.201t, equation (2)

Where H is input pH, T is Temperature, LS is liquid/solid and t is time.

And for the dissolution percent of cadmium, the equation is:

DCd = -0.857H + 0.087T + 0.300LS + 0.127t, equation (3)

And for the dissolution percent of nickel, the equation is:

DNi = -0.806H + 0.033T + 0.266LS + 0.323t, equation (4)

Also, the equation for dissolution percent of lead is shown by:

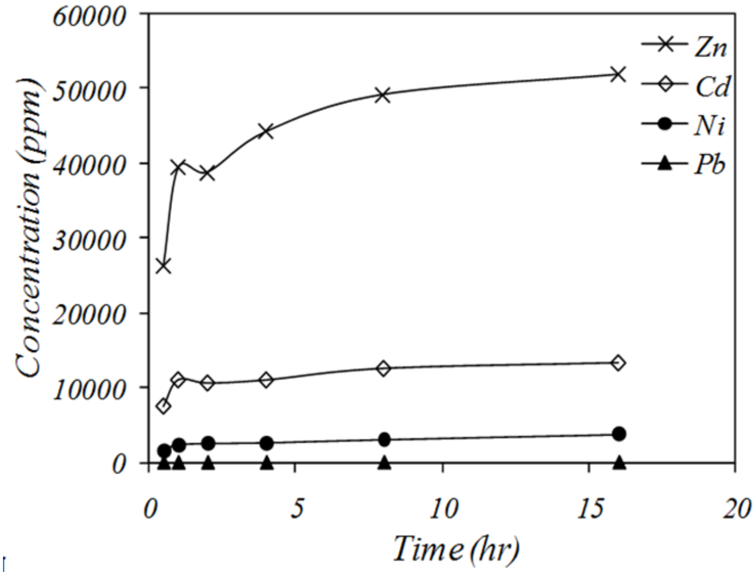

Figure.4. Effect of time on the Zn, Cd, Ni and Pb dissolution (pH: 3, T: 30 ºC, L/S: 10/1)

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Table3. EP Tests Results, EP Toxicity Criteria Quality Standard for Surface Water

Metals	Concentration of Metals in Extracts (mg/l)	Concentration Limits of Heavy Metals (mg/l)	
		Quality Standard	EP Toxicity
Co	1.26	1	-
Pb	12.67	0.05	5.0
Mn	10.745	3	-
Fe	0.02	5	-
Cu	2.87	0.2	-
Ni	294.3	0.2	-
Mg	35.65	100	-
Zn	2520	2	-
Cd	1527	0.01	1.0

$$DPb= -0.293H -0.043T + 0.262LS + 0.776 t. \quad \text{equation (5)}$$

As can be also seen in equations (2)-(3), the effective parameters to transport Zn and Cd to environment were pH and liquid/solid ratio and also equations (4)-(5) are shown that pH, time and L/S were important parameters for the Ni and Pb transport to environment.

4. Conclusion

The most significant parameters in tank leaching were determined as pH, L/S ratio, temperature and leaching time. The most of probability pollution were found the following conditions: pH=3, T=30ºC, L/S ratio= 10/1, time=8 hr. EPA tests detected the concentrations of Cd and Pb to be very high compared to their EP toxicity limits given by EPA and the concentrations of all metals except Fe and Mg are over the limits given by water quality standards. Various equations were achieved with the SPSS software for Zn, Cd, Ni and Pb dissolution. Results indicated that pH and L/S were the effective parameter for the Zn and Cd dissolution and for the Ni and Pb dissolution, pH, time and L/S ratio were the effectual factors to pollution. Water being in contact with Ni-Cd filter cakes piled in plant's area will be a potential hazardous effluent for contamination of water sources and soil. The filter cakes, retained on open areas for recovering of valuable metals, will seriously cause heavy metal pollution problems.

5. Acknowledgements

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