Heavy Metal Pollution Potential of Zinc Leach Residues Discarded in Çinkur Plant

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Abstract

In this paper, results of the study on heavy metals solubility behaviour of filter cakes from leaching of clinkerized Waelz oxide and flue dust collected during clinkerization in Çinkur plant are given. The release of heavy metals into water was investigated by subjecting the cakes to solubility tests systematically. The effect of contact time, pH, liquid/solid ratio and successive extractions on the releasing of heavy metals (Cd, Pb, Mn and Zn) into water was examined and their concentrations in the solutions were compared to the various limits for surface waters. Also, "Extraction procedure tests" approved by EPA were applied to the both residues to determine whether concentration of metals released from them are over toxicity limits given by EPA for solid wastes.

Solubilization of metals from filter cakes was found to be a function of liquid/solid ratio, contact time and pH of mixture. Depending upon these parameters, the concentration of solubilized metals from the cakes is various. However, the pH of medium is most effective parameter for the solubility of filter cakes. The release of metals into solution was accelerated by increasing acidity, whereas solubilization of Pb was not affected very much. 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 concentration of other metals in the solution are above the limits given by various quality standard for surface water. From these findings, it can be resulted that leach residues are hazardous wastes for environment.

Key Words: Zinc extraction wastes, Lead cakes, EPA extraction tests, Heavy metal pollution.

Çinkur Tesislerinde Açığa Çıkan Çinko Çözümlendirme Atıklarının Ağır Metal Kirlilik Potansiyeli

Özet

Bu makalede, Çinkur tesislerinde çinko ekstraksiyonunda açığa çıkan filtre keklerinin ağır metal çözünürlük davranışları üzerine yapılan çalışmanın sonuçları verilmiştir. Çözünürlük deneyleri yapılarak keklerden ağır metallerin suya geçişleri sistematik olarak incelenmiştir. Metallerin suya geçişlerine temas süresi, pH, sıvı/katı oranı ve ardışık ekstraksiyonların etkileri incelenmiş ve metal konsantrasyonları yüzey suları için verilen çeşitli limitler ile mukayese edilmiştir. Keklerden çözünen metallerin konsantrasyonlarını EPA tarafından verilen toksisite limitleri ile kıyaslamak amacıyla kekler ayrıca EPA tarafından önerilen "Ekstraksiyon testlerine" tabi tutulmuştur.

Filtre keklerinden ağır metallerin çözünürlüklerinin sıvı/katı oranı, temas süresi ve karışım pH'sına bağlı olduğu belirlenmiştir. Metallerin çözünen miktarları bu parametrelere bağlı olarak değişmektedir. Ancak

ortam pH'sı filtre keklerinin çözünürlükleri için en etkin parametredir. Asiditenin artmasıyla çözeltiye geçen metal miktarları artmakla beraber Pb, bu durumdan pek fazla etkilenmemektedir. EPA ekstraksiyon yöntemlerinin uygulanması ile pH 5'de filtre keklerinden çözeltiye geçen Cd ve Pb'nin miktarları toksisite limitleri olan 1.0 ve 5.0 mg/l'nin üzerindedir. Çözeltiye geçen diğer metallerin konsantrasyonları yüzey suları için çeşitli kalite standartlarıyla verilen limitlerin üzerinde olmaktadır. Buna göre çinko üretim artığı filtre keklerinin çevre için tehlikeli atıklar olduğu sonucu çıkarılabilir.

Anahtar Sözcükler: Çinko ekstraksiyon artıkları, Kurşun kekleri, EPA ekstraksiyon testleri, Ağır metal kirliliği.

Introduction

The amount and variety of waste material have increased in with the growing of technology and population. Of the priority pollutants, heavy metals cause adverse effects on aquatic ecosystem by entering into the food chain and accumulating in living organism (Moore and Ramamoorthy, 1984). The introduction of metal contaminants into the aquatic system has various sources a few of which are atmospheric fallout originating from smelting processes and fuel combustion, industrial leaks and effluents, land application of sewage materials and leaching of garbage (Förstner and Wittmann, 1983).

In metal extraction processes, large amounts of various solid wastes including flotation tailings, slags, slimes and flue dusts etc. are generated. These wastes become activated due to the process applied such as grinding, leaching, roasting, smelting, quenching etc. Exposure of these wastes to atmospheric oxygen and moisture results in solubilization of toxic metals which may seriously affect the water quality and biological life in surface waters. The potential release of toxic heavy metals from such by-products and waste materials to the surface and ground water are of particular concern (Tümen, 1988; Tümen et al., 1991; Altundoğan et al., 1992; Tümen et al., 1992)

In Çinkur plant located in Kayseri, Turkey, it is practised a leach-electrolysis process for zinc production. In this process, more than 100 tons of filter cakes as by-product are generated daily. These wastes are retained for lead reovery in he future and dumped in open stockpiles where they may cause heavy metal pollution problems. In this study, the metal releasing potential of zinc production by-products was investigated. The concentration of metal ions released from filter cake samples into water were determined at different pH, 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 with the limit concentrations of comtaminants determinde by EPA (Environmental Protection Agency) and quality standards for surface waters.

Materials and Methods

Two filtration cakes from Çinkur Zinc Plant, Kayseri-Turkey were used in this study. These will be referred to by number and are: Cake1- filtration residue from leaching of clinkerized Waelz oxide (calcine); Cake2- filtration residue from leaching of flue dust collected during clinkerization.

The cake samples were analyzed through an atomic absorption spectrophotometric method by utilizing the lithium metaborate fusion-nitric acid dissolution route (Bailey and Wood, 1974). In order to identify compounds present, the samples were also subjected to X-ray diffraction analysis.

In the solubility studies, different amounts of waste samples were weighed and added to an erlenmeyer flask containing 200 ml of distilled water, the pH of which was adjusted with H_2SO_4, in amounts to produce liquid/solid ratios varying from 10 to 400 (w/w). The suspensions were tightly capped and equilibrated by shaking at the rate of 500 cycle/min for a period varying from 1/2 to 24 h. At the end of predetermined shaking period, the suspensions were filtered through S & S-589 filter paper. In the experiments including the successive extraction, after obtaining the first extract, 200 ml of water or acid solution was added on the solid residue and the procedure was repeated. Thus, successive extractions for the same solid sample were performed until the 20th extract was obtained. Samples of each solution were acidified with HNO_3 and retained for metal analysis. All of the experiments were carried out at room temperature ($20 \mp 2°C$).

The quantity of metal ions released from the cake samples in to the water or acid solutions was also de-

termined by applying EPA approved extraction test. In the first test procedure (EP1) (Ham *et al.,* 1979), 2 g of dried solid was dispersed in 200 ml of distilled water and the pH was adjusted to 5 by the addition of NaOH or HCl. Mixtures were subjected to continuous shaking, and the pH was measured and readjusted to pH 5 every 24 h. When two consecutive measurements of pH 5 were obtained, the procedure was stopped and the suspensions were allowed to settle for another 24 h. The supernatant was then filtered and the metal concentration was determined.

In the second test procedure (EP2) (EPA, 1980) 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 by using 0.5 N acetic acid. At the end of the 24 h extraction period, deionized water was added to the extractor in an amount determined by the following equation.

$$V = 20(W) - 16(W) - A$$
$$V = 4(W) - A$$

where, V is the amount of deionized water to be added (ml), W is the weight of solid charged to extractor (g) and A is the amount of 0.5 N acetic acid added during extraction (ml).

The concentration of Ag, Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn in the solutions was determined by atomic absorption spectrophotometry using direct aspiration technique (APHA, 1976; EPA, 1979).

Result and Discussion

The chemical composition of the cakes shows that they contain ore grade lead. Other heavy metals are present in various amount in the materials tested (Table 1). X-ray diffraction analysis showed that both samples contain detectable amounts of anglesite ($PbSO_4$) and gypsum ($CaSO_4.2H_2O$).

All the heavy metals mentioned above were determined in the aqueous phase throughout the study, however, concentraions of Ag, Co and Cr were found to be below the detection limits of the method of analysis. Cu was determined only in acidified medium and at a maximum concentration of 0.8 mg/l. Although Fe was present in significant amounts (maximum about 50 mg/l) particularly in

experiments where lower liquid/solid ratios were applied, in the experiments over a long time period its concentration was found to be highly variable and inconsistent probably due to hydrolysis and/or adsorption. Therefore, this study focussed on the concentrations of Cd, Mn, Pb and Zn in the waters contacted with the cakes.

Table 1. Chemical Composition of Cakes.

Constituents	Cake 1	Cake 2
Pb (%)	25.33	54.12
Zn (%)	11.96	4.41
Cd (mg/kg)	550	4000
Mn (%)	1.89	0.81
Fe (%)	6.25	1.50
Co (mg/kg)	160	85
Cr (mg/kg)	410	250
Cu (mg/kg)	400	450
Ag (mg/kg)	220	170
Mg (%)	0.37	0.14
Ca (%)	2.40	1.50
Na (%)	0.14	0.16
K (%)	0.47	1.06
SiO_2 (%)	4.45	3.12
Loss of Ignition (105-900°C)(%)	17.70	9.85

The acidity of the cakes which are by-products of an acid-leaching process, was found to be pH 5-6, after equilibration for 24 h in distilled water at a liquid/solid ratio of 10. This shows that the cakes discarded from the zinc plant were almost free from acidity.

Effect of pH Contact Time

Figs 1 and 2 show the concentrations of heavy metal ions released from the cakes at various pH and Zn were found to be significantly solubilized from both cakes. As seen in Figs. 1 and 2, equilibrium concentrations were established within almost 2 hours of contact. Decreasing the pH down to 3 did not make a significant change in metal concentraion but at pH 2, it was observed that the solubilization of Cd, Zn and Mn increased. The concentrations of Zn, Mn, and Cd solubilized from cake 1 are 570.1, 17.8 and 1.6 mg/l at pH 2 and liquid/solid ratio of 100 for equilibration time, respectively. At the same conditions, the concentrations of these metals were found to be 262.3, 3.7 and 22.8 mg/l for cake 2. The solubility of metal compounds in the cakes is mostly dependent on acidity of solution. For that reason,

it is expected that the concentration of soulbilized metals in the leach solution increase at strong acidic media. The solubilization of Pb from both cakes did not show a considerable change with increase in acidity of medium. The lead ions solubilized from the cakes may react with H_2SO_4 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.

Effect of Liquid/Solid Ratio

To investigate the effect of the liquid/solid ratio on the concentrations of metals releasing into water at
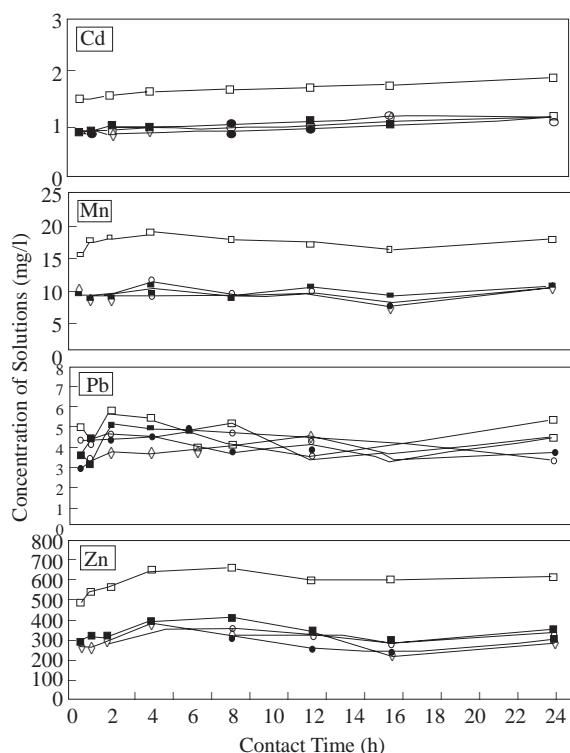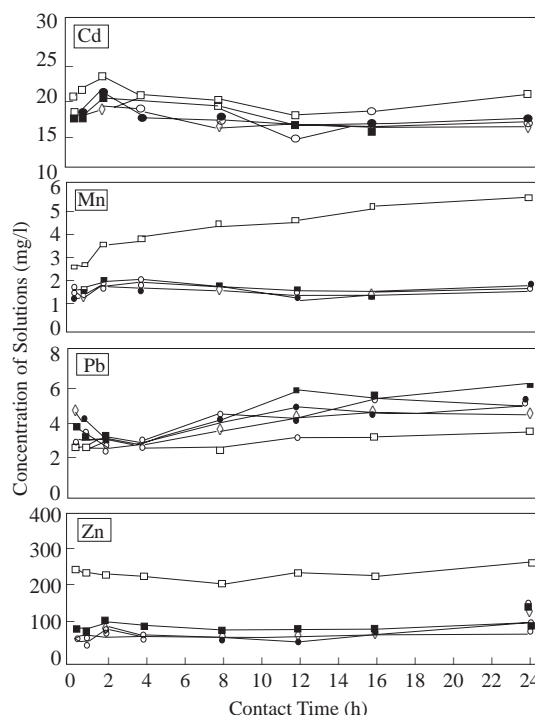

Figure 1. The Variation of Metal Concentration with Contact Time at Different pH for Cake 1 (Liquid/solid ratio: 100; □ pH 2, ■ pH 3, ○ pH 4, ● pH 5, ◇ pH 7).

Effect of Successive Extractions

The solubility of the metals was also tested by carrying out succesive extractions at a liquid/solid ration of 100 for 20 washings. The concentrations of various metals in each solution are shown in Figs 5 and 6 for Cake 1 and Cake 2, respectively. Metal concentrations in the first solutions are given in the inner tables. The initial solutions contained high levels of Zn,

different pH, additional experiments using different liquid/solid ratios were performed. The results are shown in Figs 3 and 4 for Cake 1 and Cake 2, respectively.

The batch shaking experiments showed that the concentrations of Cd, Mn and Zn in the solution increased with an increasing cake loading, whereas the Pb concenrations in the solutions did not change with liguid/solid ratio. Solubility calculations for $PbSO_4$ using $K_{sp}= 1.60.10^{-8}$ (Skoog and West, 1976) implies that concentration of Pb ions in the soltions is controlled by saturation.

Figure 2. The Variation of Metal Concentration with Contact Time at Different pH for Cake 2 (Liquid/solid ratio: 100;□ pH 2, ■ pH 3, ○ pH 4, ● pH 5, ◇ pH 7).

Mn and Cd. Subsequent extractions produced a decrease in concentrations of three metals. In contrast, Pb extractions increased by the extraction number and Pb concentrations became steady between 5-15 mg/l for both cakes representing a continual solubilization. Increasing Pb concentrations in further extractions may be due to a loose in the structure of cakes by the phenomena of hydration and hydrolysis.

The amounts of solubilized metals per kg of cakes

are shown in Figs. 7 and 8. The cumulative amounts of Cd, Pb, Zn and Mn extracted from Cake 1 were calculated as 250, 920, 68250 and 1400 mg/kg at the end of 20th extraction for pH 2, respectively. The same values are 1430, 1090, 22400 and 540 mg/kg for Cake 2 (Fig. 8). With the exception of pH 2, cumulative curves show that for both cakes a significant fraction of the soluble Cd, Mn and Zn went into solution in the first 5 extractions. Soluble Pb increased for all pH ranges. However, Pb solubilizes at a relatively low rate at acidic pH probably due to the buffering effect of sulphate ions stemming from

added H_2SO_4.

Figure 9 represents the percentage of metal solubilization calculated for 20 washings at liquid/solid ratio of 10. In 20 extractions, solubilized Zn aggregated 50-60 % of its content for pH 2. In case of neutral or mildly acidic media (pH 5-7), it changed in the range of 20-25 %. For both cakes, solubilized Pb constitutes a small percentage at the end of 20 washings. However, Pb appears to have continual solubilization pattern giving the concentration level 10-15 mg/l.
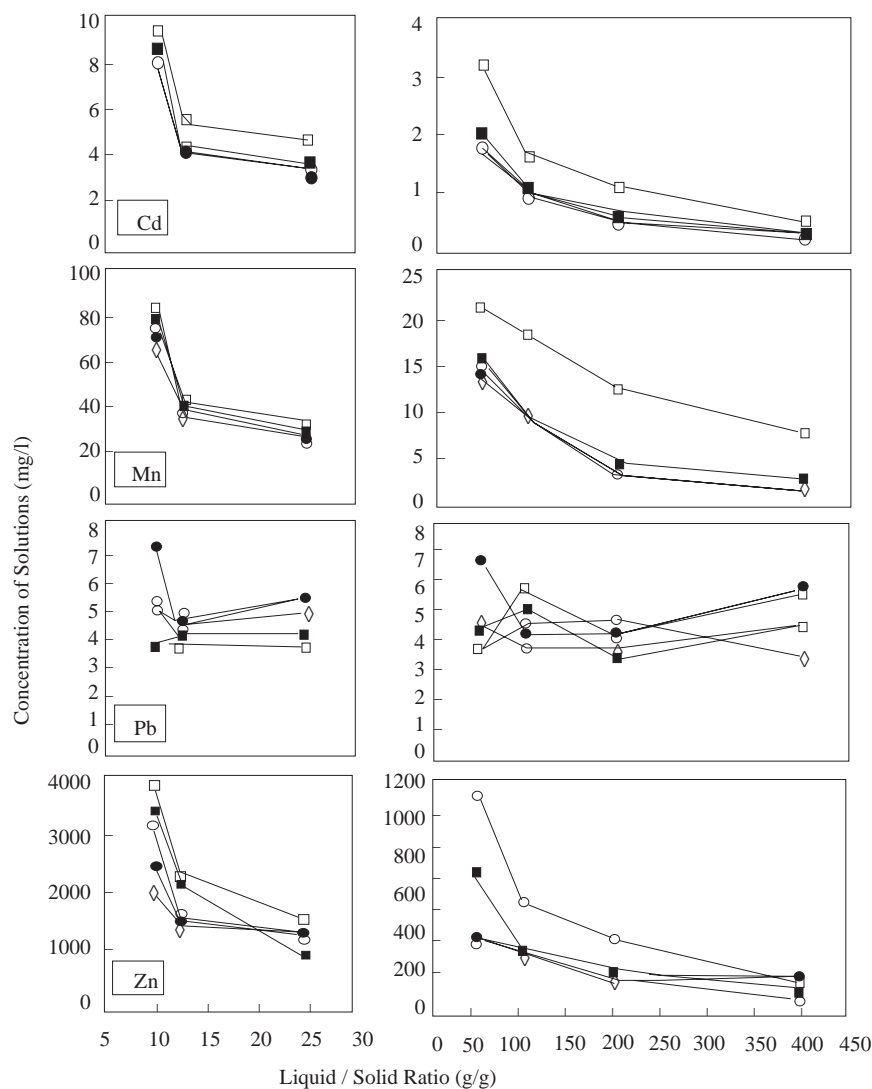

Figure 3. The Variation of Metal Concentration with Liquid/Solid Ratio at Different pH for Cake 1 (Contact time: □ pH 2, ■ pH 3, ○ pH 4, ● pH 5, ◇ pH 7).

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EP Toxicity Results

The term "EP toxicity" refers to a test that used to determine the concentrations of particular toxic constituents leached out from a solid waste disposed to improper site. If the concentraiton of toxic constituents from a solid waste are over the "EP toxicity" limits, this waste is considered as hazardous.

The concentrations of extractable metals from filter cakes by applying extraction procedure tests (EP1 and EP2) are given in Table 2. As seen, the concentrations of Cd and Pb exceed "EP toxicity" limits given by EPA (EPA, 1980; Wentz 1989), as 1 and 5 mg/l, respectively. The concentrations of Cd

and Pb from Cake2 by applying EP2 test method are 65.4 and 10.54 mg/L which are very high compared to their toxicity limits EP toxicity limits for Zn and Mn are not reported by EPA. However, the concentrations of metals determined were compared to the water quality criteria for surface water (Anonymous, 1992; Uslu and Türkman, 1987) and it was found that the concentrations of all metals are over the limits which are presented in Table 2. Therefore, these cakes can be assumed as a hazardous waste for the environment.
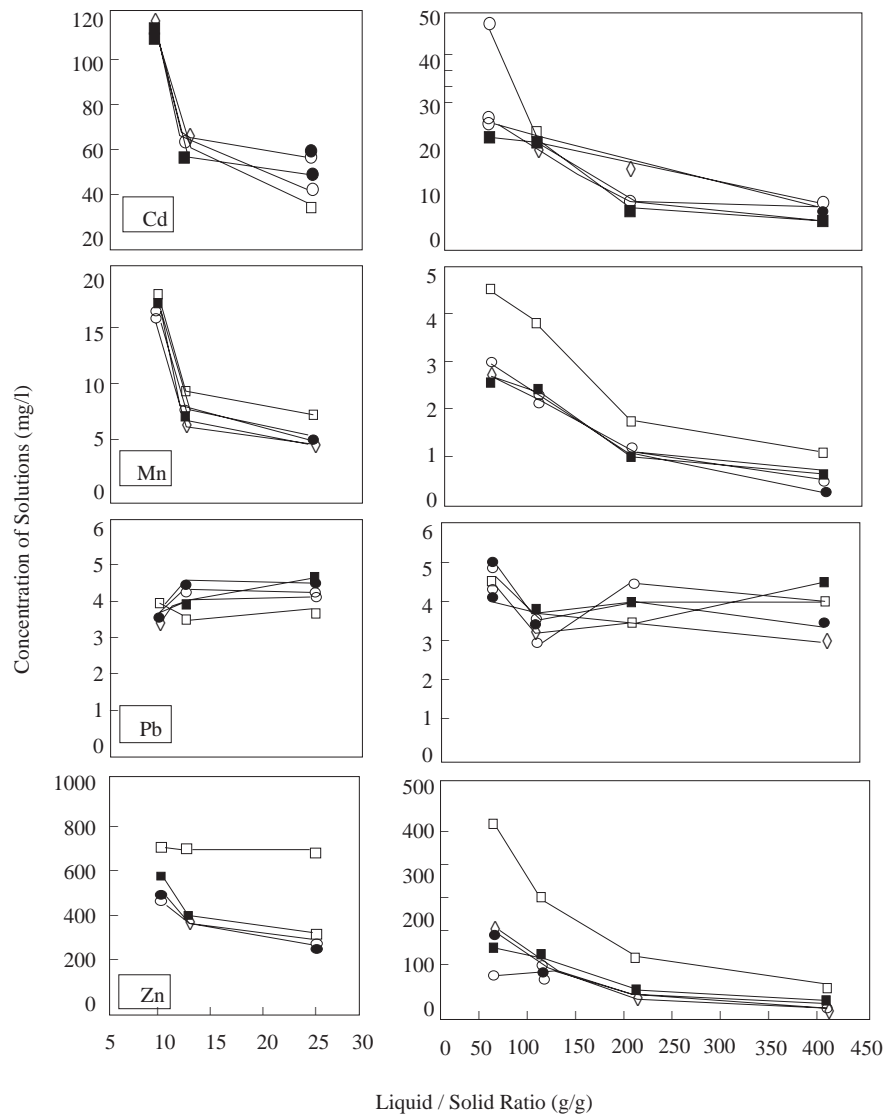

Figure 4. The Variation of Metal Concentration with Liquid/Solid Ratio at Different pH for Cake 2 (Contact time: □ pH 2, ■ pH 3, ○ pH 4, ● pH 5, ◇ pH 7).
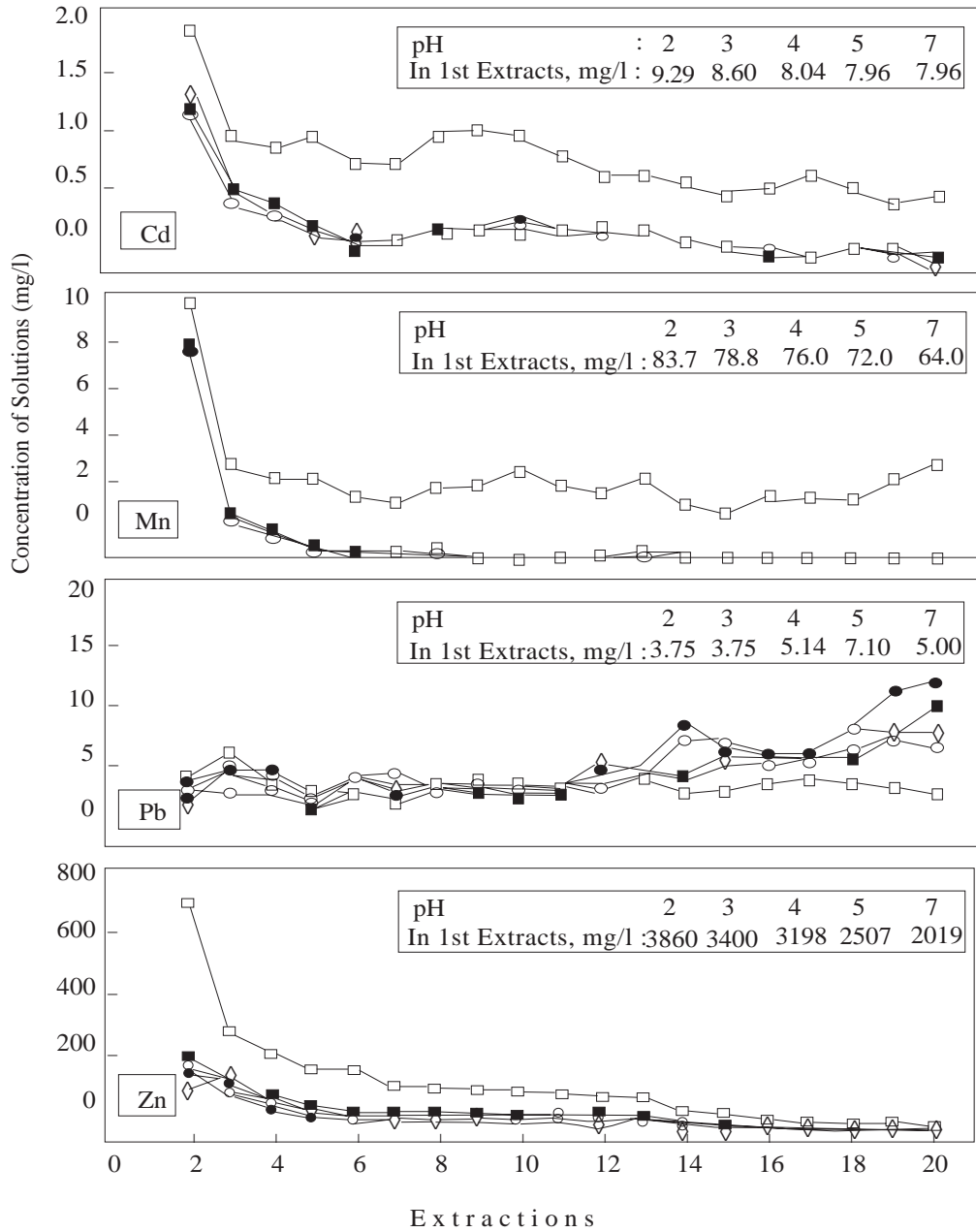
Figure 5. The Variation of Metal Concentration with the Extraction Number at Different pH for Cake 1 (Liquid/solid ratio: 10;contact time for each extraction: □ pH 2, ■ pH 3, ∘ pH 4, • pH 5, ◇ pH 7).

Table 2. EP Tests Results, EP Toxicity Criteria and I to IV Quality Standard for Surface Water

Metals	Concentration of Metals in Extracts (mg/l)				Concentration Limits of Heavy Metals (mg/l)				
	EP1		EP2		EP* Toxicity	Quality Standard**			
	Cake 1	Cake 2	Cake 1	Cake 2		I	II	III	IV
Cd	1.61	12.91	8.48	65.4	1.0	0.003	0.005	0.01	>0.01
Cu	0.07	0.10	0.10	0.56	-	0.02	0.05	0.2	>0.2
Fe	5.83	0.80	60.2	1.62	-	0.3	1	5	>5
Mn	8.11	1.26	50.1	6.90	-	0.1	0.5	3	>3
Pb	5.00	5.32	6.57	10.54	5.0	0.01	0.02	0.05	>0.05
Zn	443	224	2475	1025	-	0.2	0.5	2	>2

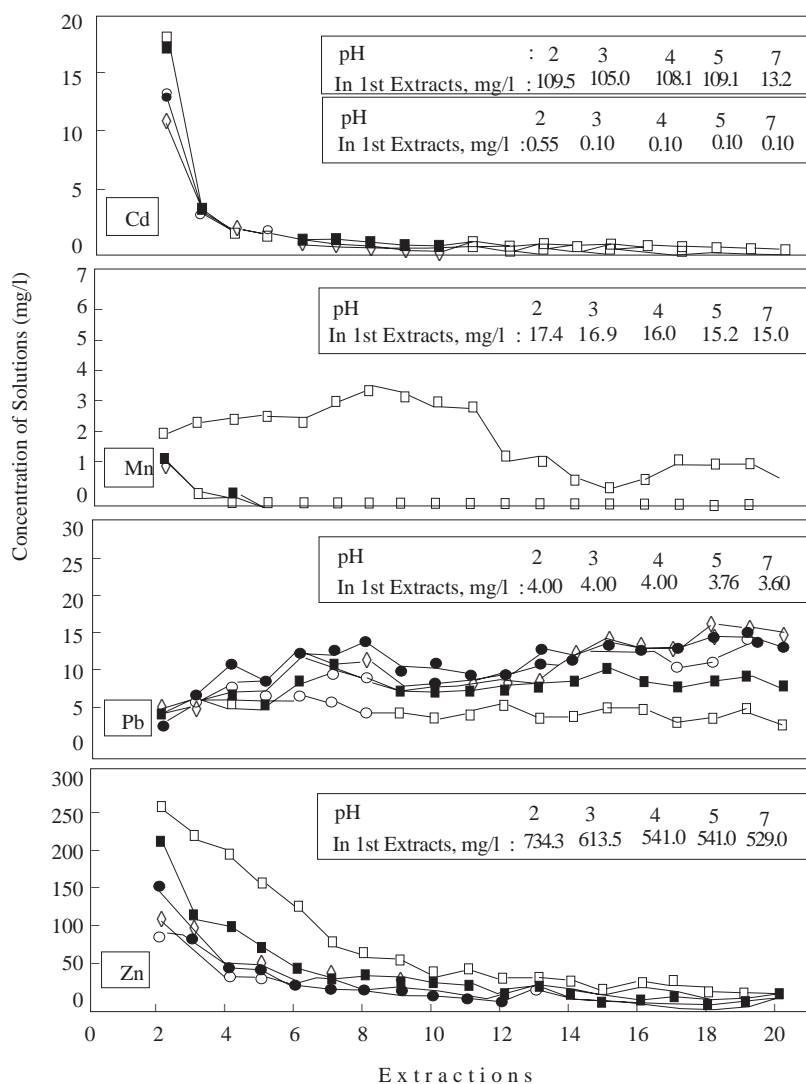*EPA, 1980
** Anonymous, 1992; Uslu and Türkman, 1987

Figure 6. The Variation of Metal Concentration with the Extraction Number at Different pH for Cake 1 (Liquid/solid ratio: 10;contact time for each extraction: 2h; □ pH 2, ■ pH 3, ○ pH 4, ● pH 5, ◇ pH 7).
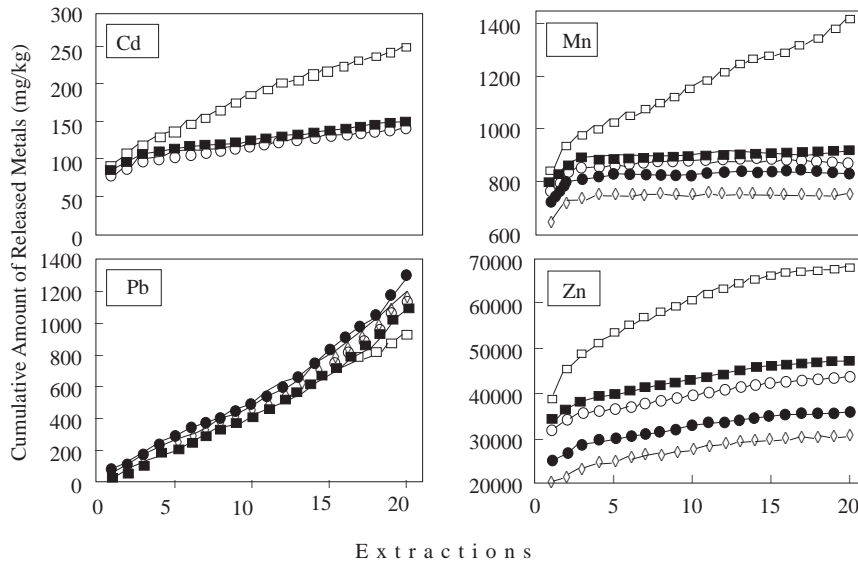
Figure 7. The Cumulative Amount of Metals Solubilized at Different pH in Succesive Extractions for Cake 1 (Liquid/solid ratio: 10;contact time for each extraction: 2h; □ pH 2, ■ pH 3, ○ pH 4, ● pH 5, ◇ pH 7).
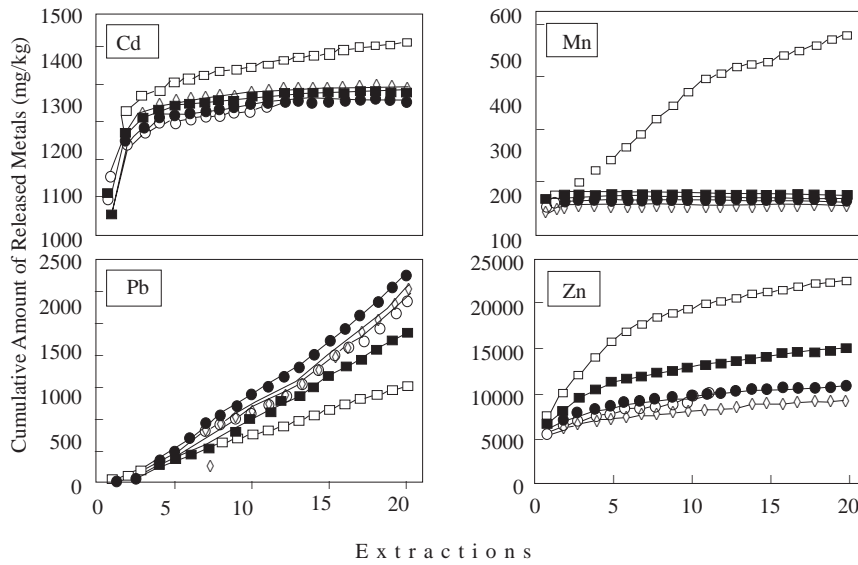

Figure 8. The Cumulative Amount of Metals Solubilized at Different pH in Succesive Extractions for Cake 2 (Liquid/solid ratio: 10;contact time for each extraction: 2h; □ pH 2, ■ pH 3, ○ pH 4, ● pH 5, ◇ pH 7).
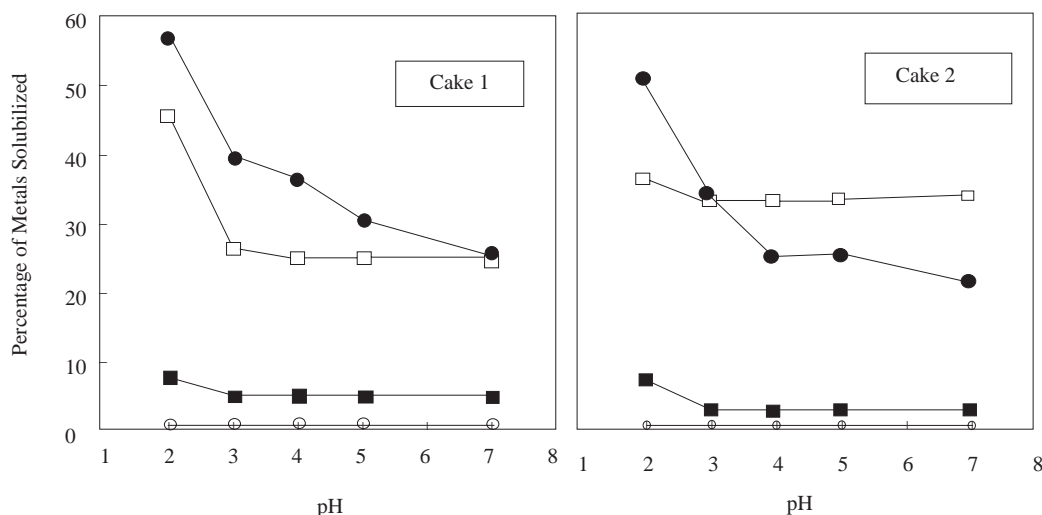
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Figure 9. The Percentage of Solubilized Metals at the End of 20 Succesive Extractions for Cake 1 and 2 (Liquid/solid ratio: 10; contact time for each extraction: 2h; □ Cd, ■ Mn, ○ Pb, ● Zn).

Conclusions

Following conclusions can be drawn from the results of present study dealing with the heavy metal pollution potential of the lead-rich residues discarded in a leach-electrolysis process of zinc production.

It was found that Cd, Mn and Zn significantly solubilized from the filter cakes contacted with water. Solubilization study has showed that contact time, pH and liquid/solid ratio are effective parameters. The concentration levels of metals in water extracts were found to be over permissible limits given in various quality standards for surface waters.

Successive washing tests showed that significant amounts of Zn and Cd were solubilized from both cakes compared to Pb and Mn. The percentages of Zn, Cd, Mn and Pb solubilized from Cake 1 (produced in leaching of calcinated ore) were calculated as 57.1, 45.6, 7.4 and 0.37 during 20 extractions period at pH 2 and liquid/solid ratio of 100, respectively. The same values for cake 2 (produced in leaching of flue dusts) are 5.08, 35.8, 6.7 and 0.20. On the other hand, it was found that sicnificant fraction of Cd, Mn and Zn went into the solution in the first

5 extraction and showed a continual solubilization depending upon extraction number.

The results of two different "Extraction procedure tests" applied to solid wastes at pH 5 showed that the concentrations of Cd an Pb in extracts exceeded the "EP toxicity" limits given by EPA. The concentration of Zn and Mn in the extracts was found to be over the limits given by water quality standards.

As a conclusion, water being in contact with Pb-rich 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 future lead production, will seriously cause heavy metal pollution problems.

To prevent the potential hazards setemming from these by-products, to a certain extent, they must be piled in a suitable site coated with impermeable materials. The stockpile runoff and leachates caused by rains must be collected in a pond. Thereafter, these waters must be treated throught a way such as precipitation before discharging to the environment.

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