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Caustic Soda Leach of Electric Arc Furnace Dust

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Abstract

The annual process dust output of Turkish EAF steel plants is approximately 120,000 t. EAF dust contains about 15-35 % Zn and some toxic metals such as Pb, Cd and Cr. It is well known that EAF dust is used as a substitute for zinc ores in many countries. Turkey imports about 25,000 tonnes of metallic zinc to meet its demand (about 50,000 t/y) mainly due to the shortage of zinc ores. Therefore, the recycling of Turkish EAF dust could contribute greatly to the economy.

In this study, caustic soda leach experiments were conducted with an EAF dust sample containing 23 % Zn, 5 % Pb and 30 % Fe obtained from by a plant located in Aliağa/İzmir. Optimum leach conditions were determined. Extraction yields for Zn and Pb were 80 % and 85 %, respectively. The relatively low Zn extraction yield was mainly due to the presence of insoluble zinc ferrite ($ZnFe_2O_4$). The bulk leachate was cleaned using zinc powder to precipitate lead and other impurities. After solid/liquid separation, zinc metal with 99.27 % Zn was recovered by electrolysis of the purified solution. These experiments indicated that the caustic soda leach-electrolysis process may be technically applicable to Turkish EAF dust.

Key Words: Zinc, dust, leach, electric arc furnace

Elektrik Ark Ocağı Tozlarının Kostik Soda Liçi

Özet

Türkiye'deki elektrik ark ocaklı çelik fabrikalarından üretim esnasında çıkan toz yaklaşık 120 000 tondur. Bu tozlar % 15-35 arasında Zn, Pb, Cd ve Cr gibi toksik metalleri içermektedirler. Birçok ülkede ark ocakları tozlarının çinko üretiminde çinko cevheri yerine kullanıldığı bilinmektedir. Türkiye çinko cevherlerinin azlığı nedeniyle yıllık 50 000 ton Zn metal talebini karşılamak için 25 000 ton Zn metali dış alımı yapmaktadır. Bu yüzden, elektrik ark ocağı tozlarının içerdiği Zn ve diğer metallerin geri kazanımı, Türkiyenin ekonomisine büyük bir katkı sağlıyacaktır.

Bu çalışmada, İzmir Aliağa'da bulunan elektrik ark ocaklı çelik üretimi yapan bir tesisten temin edilen % 23 Zn, % 5 Pb ve % 30 Fe içeren toz numunesi kullanılarak kostik-soda liç deneyleri yapılmıştır. Optimum liç koşulları tespit edilmiştir. Deneylerde çinko % 80, kurşun % 85 verimle kazanılabilmiştir. Çinko ekstraksiyon verimindeki düşüklük, çözünmeyen çinko ferritlerin varlığından ($ZnFe_2O_4$) ileri gelmektedir. Liç çözeltisindeki kurşun ve diğer safsızlıklar toz Zn ile çöktürülerek, çözelti temizlenmiştir. Katı-sıvı ayrımından sonra, bu çözeltinin elektrolizi ile % 99.27 saflıkta Zn metali elde edilmiştir. Deneyler, elektrik ark ocağı tozlarından kostik-soda liçi-elektroliz yöntemi ile çinkonun üretilebileceğini ortaya koymuştur.

Anahtar Sözcükler: Çinko, toz, liç, elektrik ark ocağı

Introduction

Currently, more than 60 % of Turkish steel is being produced by the electric arc furnace process. Encouraged by low capital investment costs and the possibility of small capacities starting from 40,000 t/y, EAF steel making is increasingly preferred by private sector. Table 1 shows the operating EAF steel plants, their capacities and the 1994 production figures. EAF operators in Turkey are mainly using steel scrap for the production of carbon steel, which is cast as semi-finished products and/or further processed to commercial steel, mainly long products. Only a very small amount of sponge iron or HBI (hot briquetted directly reduced iron) is imported for the production of high quality steel.

Extremely fine dust is formed in the electric arc furnace by metal vaporisation, subsequent reaction with the oxygen within furnace, and deposition on condensed nuclei. Since metals such as zinc, lead and cadmium are highly volatile at the temperature of molten steel, they are concentrated in furnace dust. The dust particles are generally spherical, ranging from 0.1 to 10 microns in size (Bethlehem Steel Corporation, 1985).

The yearly dust output of Turkish EAF plants amounts to 120,000 t/y. However, it is highly questionable whether the dust generated in EAF plants is entirely recovered for disposal. Dust emission from some EAF plants is always noticeable. According to common practice, the waste gas containing fine dust is cleaned by dust collectors and the recovered dust is dumped into landfills near the plants. EAF dust is disposed in some plants after wetting or pelletizing with water to facilitate its handling and to prevent any wind dispersal of the dust. At present, EAF dust is not processed further because EAF operators consider further treatment to be uneconomical and legally unnecessary. However, this situation will change rapidly due to stricter environment protection laws and local pressures to reduce pollution. On the other hand, increased value of metals and the need to reduce imports will certainly encourage the utilisation of this waste as a source of valuable metals such as zinc and lead.

Table 1. Turkish Electric Arc Furnace Steel Plants (Turkish Iron and Steel Producers Assosiations Journal, 1995)

Plant	Location	Owner	Designed Capacity (t/y)	Production 1994 (t/y)
ASIL ÇELIK	Bursa	Private	250 000	222 442
AYPAŞ	Kocaeli	Private	110 000	125 827
ÇEBİTAŞ	İzmir	Private	286 500	217 280
ÇEMTAŞ	Bursa	Private	120 000	114 136
ÇOLAKOĞLU	Kocaeli	Private	1 400 000	1 150 109
ÇUKUROVA	İzmir	Private	2 050 000	1 351 361
DİLER	Kocaeli	Private	316 000	379 393
EGEMETAL	İzmir	Private	600 000	65 431
EKİNCİLER	İskenderun	Private	675 000	565 470
HABAŞ	İzmir	Private	1 200 000	843 405
İÇDAŞ	İstanbul	Private	640 000	653 335
İST.METAL.	İstanbul	Private	40 000	19 253
İZMİR D.Ç.	İzmir	Private	590 000	614 764
KROMAN	Kocaeli	Private	420 000	404 758
METAŞ	İzmir	Private	750 000	467 216
SIVAS D.Ç.	Sivas	Private	450 000	89 059
TUBER	İstanbul	Private	236 000	191 643
YAZICI	İskenderun	Private	722 000	228 372
MKEK	Kırıkkale	State	60 000	
TOTAL			10 915 500	7 661 254

The hazardous nature and the value of EAF dusts as a Zn and Pb source have attracted the attention of many Turkish researchers (Duman and Dikeç, 1994). There are many pyrometallurgical and hydrometallurgical processes for treating EAF dust (Falt, 1979, Maczec and Kola, 1980, Higley and Fine, 1977, Fosnacht, 1981, Frenay et al., 1986, Eacott et al., 1984, Duman and Kırdar, 1994, Çiçek et al., 1996). Some plants for processing EAF dusts are in commercial operation in the USA, Sweden, Germany and Japan.

Among the hydrometallurgical methods, the caustic soda leach process has the advantage that iron is not soluble in caustic soda. Therefore, leaching with caustic soda is the most promising method of the leaching processes.

1. Hydrometallurgical Recovery of Zinc From Eaf Dust

In these processes, the metals are extracted by a liquid leach stage, and then recovered in metallic form by electrolysis. Principally, two types of leaching methods are applicable to EAF dust, namely acid (e.g. H_2SO_4) and basic (e.g. NaOH) leaching. The acidic leach process can be used to extract zinc in the form of $ZnSO_4$. If high-quality zinc is to be produced, a considerable purification of the solution is required since iron is also readily soluble in acid. Tests have shown that acid leaching of EAF dust seems to be uneconomical due to problems caused by the high Fe content of the dust (Akdağ and Mordoğan, 1992). Some caustic soda leach tests performed using a composite sample containing EAF dust and waelz-oxide have proved the viability of the caustic leaching on such materials (Duman and Kırdar, 1994). Duman and Kırdar could extract Zn and Pb with 78 % and 80 % yield, respectively. In some tests the sample was prereduced by heating with coke at 600-800 °C, in order to facilitate the dissolving of zinc ferrite.

The main reactions of caustic soda leaching are as follows:

$ZnO + 2\ NaOH \rightarrow Na_2ZnO_2 + H_2O$

$PbO + 2\ NaOH \rightarrow Na_2PbO_2 + H_2O$

$SiO_2 + 2\ NaOH \rightarrow Na_2SiO_3 + H_2O$

During leaching, Na, K, Cl and F dissolve completly. Na_2SiO_3 can be precipitated as $CaSiO_3$ using $Ca(OH)_2$ according to the following chemical reaction:

$Na_2SiO_3 + Ca(OH)_2 \rightarrow 2\ NaOH + CaSiO_3$

Purification of the leachate will be achieved with Zn powder according to the following reactions:

$Zn + Na_2PbO_2 \rightarrow Na_2ZnO_2 + Pb$

$Zn + Na_2CuO_2 \rightarrow Na_2ZnO_2 + Cu$

The purified leachate should not contain more than 100 mg/l Pb and 1 mg/l Cu for an efficient electrolysis.

The main reactions during electrolysis are given as follows:

Cathode:

$Na_2ZnO_2 + 2H_2O{+}2e \rightarrow Zn{+}2NaOH{+}2OH^-$

Anode:

$2\ OH^- \rightarrow H_2O{+}1/2O_2{+}2e$

Total:

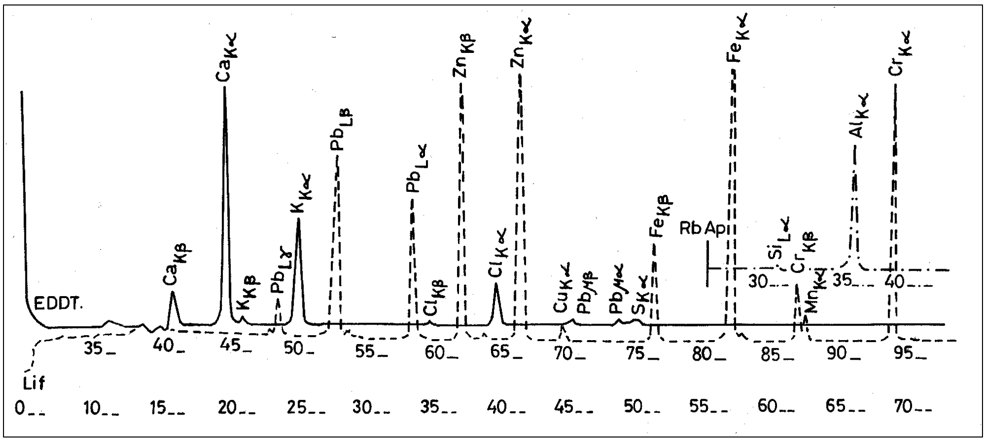
$Na_2ZnO_2 + H_2O \rightarrow Zn + 2\ NaOH + 1/2\ O2$

The primary aim of this study was to determine the optimum caustic soda leaching conditions for a local EAF dust sample.

2. Experiments

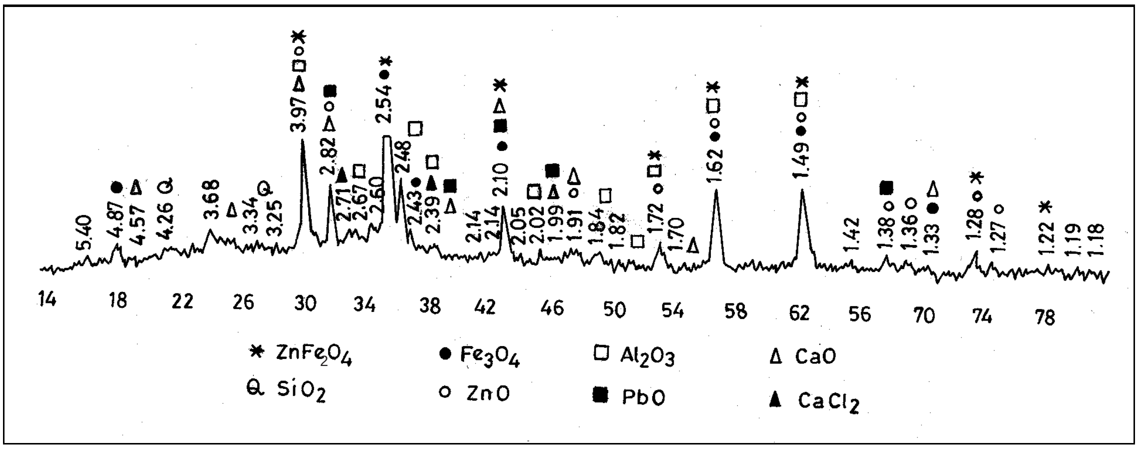
2.1. Physical and chemical properties of the dust sample

The sample for the experiments was taken from the dust collector of a EAF steelplant in İzmir. XRF and XRD analysis were carried out by using Jeol-Sax-100 S4 X-ray analyser in order to determine the components of the sample. The results of XRF and XRD analyses are shown in Figure 1 and 2.



Major elements: Fe, Zn, Pb, Si, Al, Ca, Mn, Na, K, Cl

Figure 1. X-Ray Flourescence spectrum of the dust sample



Compounds: ZnO, $ZnFe_2O_4$, Fe_3O_4, PbO, Al_2O_3, $CaCl_2$, CaO, SiO_2

Figure 2. X-Ray Diffraction spectra of the dust sample

A wet chemical analysis of the sample is given in Table 2. Malvern 2600 Laser Master Size Analyser was used to out size analyses of the head sample. The results of size analyses can be seen in Table 3. In the last column of Table 3 the distribution of particle size weight percentage as weight % per micron are given. A high concentration of dust particles was indicated, around 3-5 microns

Table 2. Wet chemical analyses of EAF dust sample

Elements /Compounds	weight %
Total Fe	30.18
Total Zn	23.00
ZnO+Zn	22.31
$ZnFe_2O_4$	16.68
Pb	5.05
Cu	0.26
Cd	0.15
Al	0.70
Cr	0.15
Mn	0.97
Ca	3.11
Mg	0.42
Na	1.88
K	0.94
SiO_2	3.80
S	0.62
C	0.35
P	0.01
Cl	5.88

2.2. Leaching tests

Leaching tests were carried out with Fisher leaching test equipment (Figure 3) consisting of 5 leaching glass jars of 1 litre capacity, a thermostative-controlled water bath and a speed-controlled stirring mechanism (50-1000 rpm). This equipment was run at different temperatures and stirring rates.

2.2.1. Water leach tests

A water leach stage is necessary prior to the caustic leach stage in order to remove elements such as Na, K and Ca, usually as chlorides that are detrimental to electrolysis. Water leach tests were carried out with 10, 20 and 30 % solid content of the leach pulp and at pulp temperatures of 20 and 40 °C. Leaching time was 2 hours, and stirring speed was 600 rpm.

2.2.2. Caustic soda leach tests

A series of caustic soda leach tests were performed whereby the influence of caustic soda concentration, temperature, leaching time, stirring rate and solid content upon leach results were investigated. In the experiments, the above mentioned test parameters were varied as follows:

Caustic soda concentration (g NaOH/l) : 62, 104, 135, 165, 260, 355
Temperature (°C) : 20, 40, 60, 80
Leaching time (min.) : 30, 60, 90, 120, 150, 180
Stirring Rate (rpm) : 200, 400, 600, 900
Solid content (%) : 5, 10, 20, 30

Table 3. Particle size distribution of EAF dust

Particle size Microns	Weight %	Cum. Screen undersize %	Cum. screen oversize%	Wt./d %
30/20	5.7	100.0	5.7	0.57
20/10	20.5	94.3	26.2	2.05
10/5	32.4	73.8	58.6	6.48
5/3	26.4	41.4	85.0	13.20
3/2	7.1	15.0	92.1	7.10
2/1	7.9	7.9	100.0	7.90

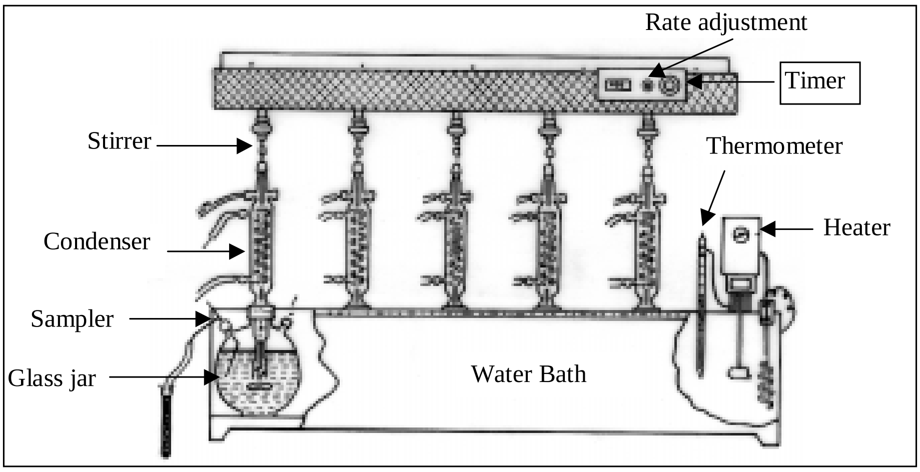
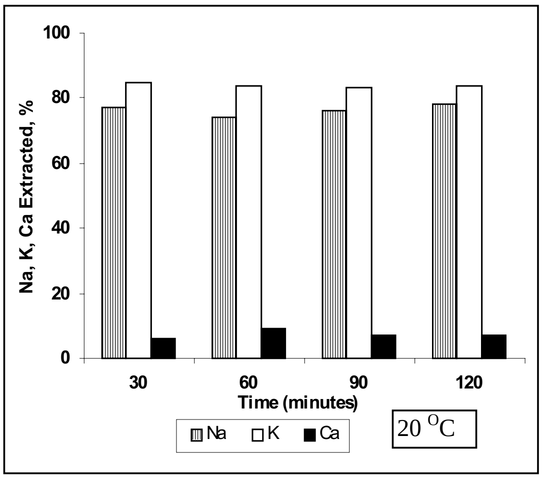


Figure 3. Fisher leaching test equipment

3. Results and Discussion

3.1. Result of water leach tests

Water leach tests of the sample at 20 and 40 °C showed that the solubility of Na and K chlorides was about 90 % and increased with increasing water temperature. As seen in Figure 4, Ca chloride was less soluble than Na and K chlorides (10 %).



3.2. Results of caustic soda leach tests

3.2.1. Influence of NaOH concentration

Figure 5 shows the influence of the NaOH concentration on the zinc extraction rates. Increasing the NaOH concentration increased the dissolution of Zn. In general, NaOH concentrations above 260 g/l seemed to yield satisfactory results.

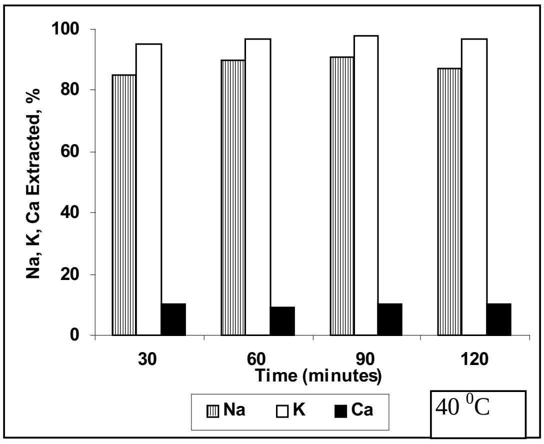


Figure 4a-b Water solubility of Na, K, Ca (20, 40 °C)

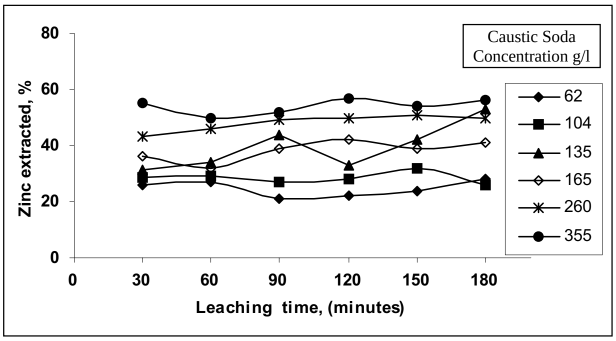


Figure 5. Influence of caustic soda concentration on caustic soda solubility of zinc (leach cond.: 20 °C, solid content 10 %, stirring rate 600 rpm)

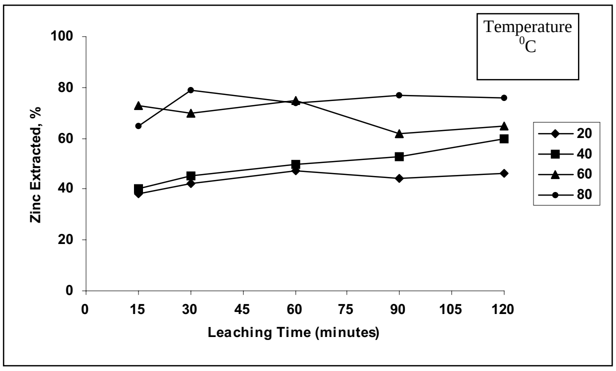


Figure 6. Influence of temperature on caustic soda solubility of zinc (Leach cond.: 260 g NaOH/l, solid cont. 10 %, stirring rate 600 rpm)

3.2.2. Influence of Temperature

The solubility of Zn increased with increasing pulp temperature, as seen in Figure 6, while Zn extraction was 42 % after a leaching time of 30 minutes at ambient temperature, reaching almost 80 % at 80 °C.

3.2.3. Influence of leaching time

As seen in Figure 6 at 80 °C and after 30 minutes of leaching time zinc solubility did not change significantly. Therefore, a leaching time of 30 minutes seemed to be reasonable for higher temperatures. At lower pulp temperatures, however, longer leaching time was required for higher Zn recoveries.

3.2.4. Influence of solid content

Figure 7 shows the solubility of Zn for different solid contents of the leach pulp depending on leaching time. It was found that 10 % solids yielded better results. Above 20 % solids the extraction yield for Zn detoriated, probably due to flocculation of fine dust particles.

3.2.5. Influence of stirring rate

As seen in Figure 8, when the stirring rate was increased, the solubility of zinc also increased. Stirring prevented flocculation and hence promoted leach reaction

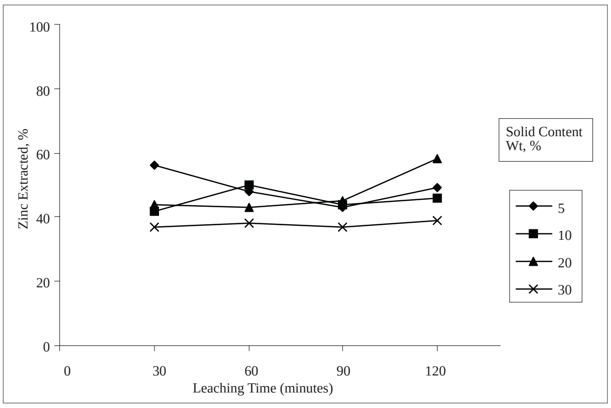


Figure 7. Influence of solid/liquid ratio on caustic soda solubility of zinc (Leach cond.: 20 °C, 260 g/l NaOH, stirring rate 600 rpm)

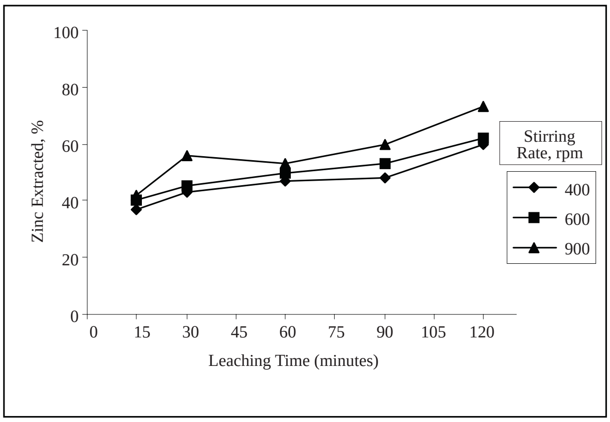


Figure 8. Influence of stirring rate on caustic soda solubility of zinc. (Leach cond.: 40 °C, 260 g/l NaOH, solid content 10 %)

3.2.6. Optimum caustic soda leach conditions

Based on the test results the optimum parameters for the caustic leach process could be given as follows:

Caustic soda concentration : above 260 g/l
Temperature : 80 °C
Time : 30 minutes
Solid content : 10 % (w/w)
Stirring rate : 900 rpm

At the above given conditions, the total recovery for zinc was 80-85 %.

Extraction yields obtained for Pb were in general 10-20 % higher than those obtained for Zn. The solubility of Pb increased with the increasing temperature of the pulp; however, the increase was not so pronounced as that experienced by zinc.

3.3. Solid/liquid separation and purification

After caustic leach under optimum conditions, solids were separated from leachate by filtering. Chemical analyses of leach residue are given below:

	Fe	Zn	Pb	Na	Cu	K
Wt-%	48.6	8.2	0.9	0.35	0.42	0.15

The XRD diffraction analyses of leach residue given in Figure 9 showed that the residue consisted mainly of magnetite and zinc ferrite.

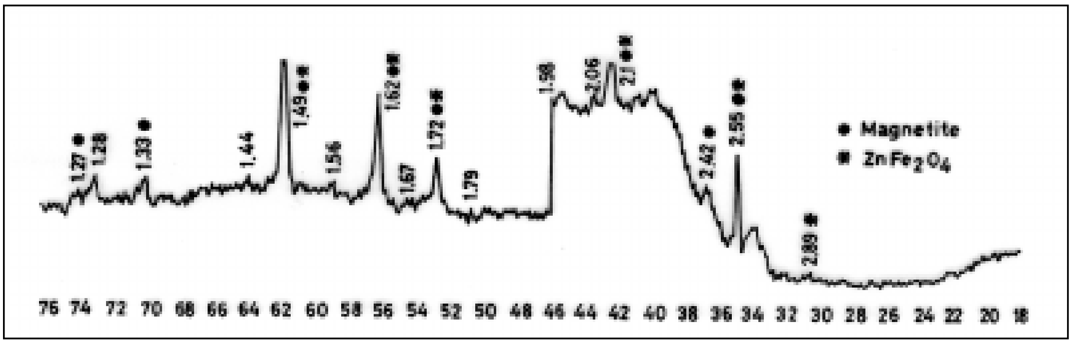


Figure 9. X-Ray Diffraction spectra of leach residue

Purification was performed with zinc powder at an amount 4 times greater than that stoichiometrically required, in order to remove Pb, Cu and Cd, which are not desired in Zn electrolysis. The purification took place at an ambient temperature by stirring at 300 rpm. The duration of the purification was 60 minutes. The Zn, Pb, Cu and Cd concentrations of caustic leachate before and after purification were as follows:

		Before	After
Zn (g/l)	:	18.00	22.00
Pb (g/l)	:	3.20	0.21
Cu (mg/l)	:	0.70	0.20
Cd (mg/l)	:	22.00	1.00

After cementation, the cement was analysed and the results were as follows:

	Pb	Zn	Cu	Fe	Cd
Wt. %	75.4	5.8	1.6	0.12	0.21

As seen from the analyses, the cement obtained could be a suitable raw material for the further recycling of metals such as Pb and Cd.

3.4. Electrolysis

For electrolysis, a laboratory type IKA-Werk electrolysis cell was used. A copper cathode and a stainless steel anode measuring 25x40 mm were used as electrodes. The electrical current was held at 0.5 A at the beginning of the electrolyses for about 10 minutes. After the temperature was increased to 60 °C, the electrolysis was continued at 1.5 A for about 45 minutes.

Although the concentration of Zn with 22 g/l was low for an efficient electrolysis, a cathodic deposition of fine zinc was obtained. Results of cathodic zinc analysis are given below:

	Zn	Pb	Fe	Cu	Cd	K	Na
Wt. %	99.27	0.08	0.09	0.01	0.35	0.02	0.17

4. Conclusions

Based on the results of this study, the following can be concluded:

- Caustic leaching of EAF dust is technically possible and seems to be economical since the recovery of zinc and lead are above 80 % and purification is done simply with zinc powder.
- Optimum leach conditions were as follows:

Caustic soda concentration: + 260 g/l
Temperature : 80 °C
Leach time : 30 minutes
Solid content :10 %
Stirring rate : 900 rpm

- The caustic soda leach process has the advantage that iron is not soluble in caustic soda. Furthermore, the waste of a caustic soda leach plant is not so hazardous as in the case of acidic leach plants. Therefore, leaching with caustic soda is the most promising of the leaching processes
- The caustic leach-electrowinning process is flexible in scale and can also be applied to small and medium scale operations. This will certainly encourage the private sector.
- Solid/liquid separation could, however, cause some problems in industrial application due to the extremely fine material and high viscosity of the leach pulp.
- The principle flow sheet for caustic soda leach and electrowinning of Zn from EAF dust is given in Figure 10 .

It is known that EAF dusts are being dumped inappropriately, and this may contaminate the environment. As a result of the investigation, the production of zinc and lead from EAF dust by using caustic leaching method will greatly contribute to the country's economy and will also reduce pollution.

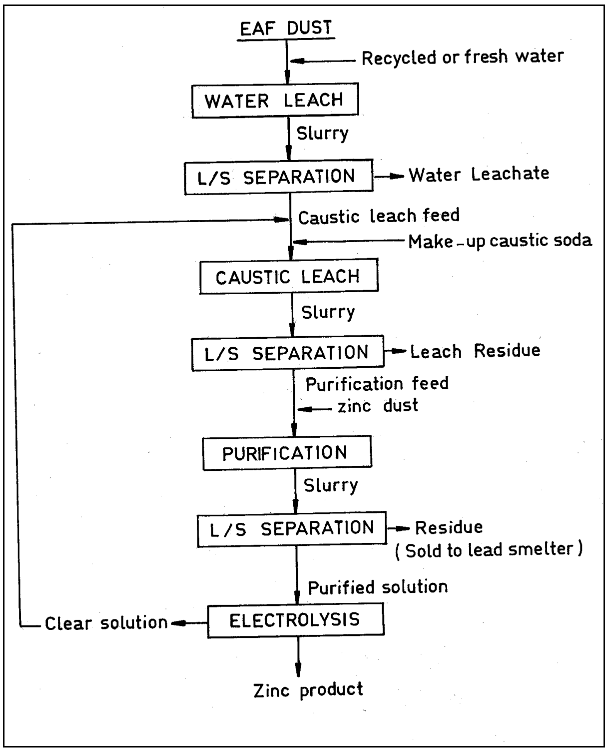


Figure 10. Principle flow sheet for caustic soda leach (Eacott, J.G., et al,1984)

References

Akdağ, M., Mordoğan, H., The Evaluation of Steelmill Dust in terms of Economical and Environmental Factors, 4th International Mineral Processing Symposium, Proceedings Volume 2, Turkey, 1992.

Betlehem Steel Corporation, Research Department, Electric Arc Furnace Dust - Disposal Recycle and Recovery, Final Report, project Nr. RP-2570-1-2, Pennsylvania, 1985.

Çiçek, T., Mordoğan, H., Cöcen, I., Çilingir, Y., Disposal and Treatment of Electric Arc Furnace Dust, Proceedings of the First International Symposium on Mine Environmental Engineering, Kütahya, Turkey, 1996.

Duman, İ and Dikeç, F., Elektrik Ark Fırını Baca Tozları: Ekolojik Sorun-Ekonomik Değer, Metal Dünyası, sayı 10, Şubat 1994.

Duman, İ. and Kyrdar, A, Çelik Ark Fırını Baca Tozlarının Hidrometalurjik Değerlendirilmesi, Metal Dünyası, sayı 10, Şubat 1994.

Eacott, J.G., Robinson, M.C. and others, Technoeconomic Feasibility of Zinc and Lead Recovery from Electric Arc Furnace Baghouse Dust, CIM Bulletin, Sept. 1984.

Falt, I., Metal Recovery from Steelworks Furnace Dust, 2nd Symposium on Environmental Control in the Steel Industry, Chicago, June 1979.

Fosnach, D.R., Recycling of Ferrous Steel Plant Fines State-of-the-Art Iron and Steel Maker, April 1981.

Frenay, J., Ferlay, S., Hissel, J., Zinc and Lead Recovery from EAF Dusts by Caustic Soda Process, 44 th Electric Arc Furnace Conference, Dallas, Texas, 1986.

Higley, L.W. and Fine, M.M., Electric Arc Furnace Steelmaking Dusts- A Zinc Raw Material, Report of Investigations 8209, U.S. Department of the Interior, Bureau of Mines, 1977.

Maczec, H. and Kola, R., Recovery of Zinc and Lead from Electric Arc Furnace Steelmaking Dusts at Berzelius, Journal of Metals, Jan. 1980.

Turkish Iron and Steel Producer Associations Journal, 1995.