

# LEACHING RECOVERY OF ZINC, COBALT AND MANGANESE FROM ZINC PURIFICATION RESIDUE

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**Abstract** This paper reports on the recovery of zinc, cobalt and manganese by two-step leaching of zinc-plants purification residue with sulfuric acid. The residue, hot filter press cake (HFC), contains 14 % ZnO, 4.8 % Co<sub>3</sub>O<sub>4</sub> and 22.9 % MnO. Effects of different parameters are determined and used to optimize the process. With acid to hot filter press cake (HFC) stoichiometry of 0.85, acid concentration of 30 g/L and temperature of 25°C, it took two minutes to separate zinc from zinc plant residue. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was used as an oxidation agent. The most suitable acid concentration for leaching of both cobalt and manganese was 50 g/L. Recovery of cobalt and manganese increased with peroxide concentration in the leaching solution.

**Keywords** Leaching, Recovery, Hydrometallurgy, Zinc Plant Residue, Filter Press Cake

**چکیده** در این مقاله تاثیر پارامترهای مختلف بر بازیابی فلزات روی، کبالت و منگنز طی دو مرحله انحلال پسماند تصفیه کارخانجات تولید روی با اسید سولفوریک مطالعه شده است. این پسماند، فیلتر کیک گرم حاوی ۱۴٪ اکسید روی (ZnO)، ۴/۸٪ اکسید کبالت (Co<sub>3</sub>O<sub>4</sub>) و ۲۲/۹٪ اکسید منگنز (MnO) می باشد. شرایط بهینه بازیابی روی در نسبت استوکیومتری اسید به فیلتر کیک گرم معادل ۰/۸۵، غلظت اسید سولفوریک ۳۰ g/L و دمای ۲۵°C و حداقل زمان ۲ دقیقه بدست آمد. از پسماند لیچینگ این مرحله برای بازیابی منگنز و کبالت با استفاده از حلال حاوی آب اکسیژنه (H<sub>2</sub>O<sub>2</sub>) استفاده شد. مشاهده شد که بهترین شرایط برای بازیابی این فلزات محلول آبی حاوی ۳۰ g/L اسید سولفوریک بوده و افزایش مقدار آب اکسیژنه باعث زیادتیر شدن مقدار انحلال کبالت و منگنز می شود.

## 1. INTRODUCTION

With an ever-increasing demand for Co, Mn and

Zn, it is worthwhile to exploit secondary resources. Cobalt-bearing manganese wad [1], spent lithium-ion batteries [2], waste dust generated by glass

industry [3], copper smelter slag and converter slag [4,5], spent cobalt/manganese bromide oxidation catalyst, spent ammonia cracker catalyst [6], fly ash generated from municipal incineration plants [7] and zinc plants residue [8,9] are a number of secondary resources.

During recent years, several hydrometallurgical processes have been developed for Co, Mn and Zn from these resources. These processes generally include the following major unit operations: 1 roasting (not always), 2 leaching by acids, bases or water, 3 removal of impurities such as iron, 4 separation and recovery processes and 5 refining of recovered metals [2-4,7,9-11]. A lot of researchers have worked to improve the extraction methods and promote the recovery efficiency of these processes [10,12-18].

Leaching is the most important starting point of most hydrometallurgical processes. Suitable leaching conditions can be determined for an appropriate design of the leaching system. These parameters consist of leachant concentration, reaction time, size of solid particles, shape of solid particles, solid to liquid ratio and temperature. A leaching process can often be selected for dissolving valuable metals from an ore or a secondary resource; whilst leaving most of the gangue largely unaffected. Thermodynamic parameters such as concentration and temperature of the leachant can be used to predict and control the general conditions required for dissolution of secondary resources into water. A large number of studies have been carried out to optimize these processes [2,4,9-11,16-18]. Previous researches have rationalized the kinetics of dissolution of zinc, manganese and cobalt in a few leachant solutions [19-22].

Zhang, et al. introduced a hydrometallurgical process for the recovery of metals from spent secondary batteries [2]. In this study hydrochloric acid was found as the best leachant. At 80°C, the efficiency of the cobalt leaching process became more than 99 % in 1 hour.

From the literature it seems that the sulfuric acid is commonly used as a leachant in many cases [3,4,6, 8-12,15-17,20]

A process was invented by Nguyen for simultaneous electrolyte production of manganese dioxide and zinc from waste materials consisting of spent batteries and other electronic components

[23]. This process included acidic leaching and electrolysis of the spent parts. Landucc et al. introduced a hydrometallurgical process for the treatment of zinc plant residue [24]. This process included a two-step leaching of the residue in sulfuric acid at atmospheric pressure and a temperature above 60°C. The final product of the process was a purified zinc sulfate solution.

Senanayake introduced an equation for the kinetics of leaching mono-sized pyrolite, which was based on a shrinking sphere model [19]. The kinetics of cobalto-cobaltic ( $\text{Co}_3\text{O}_4$ ) dissolution in sulfuric acid was also investigated by Hubli, et al. [21]. It was found that the rate controlling step for this reaction was diffusion.

In the zinc production industry, leaching is a one or two step procedure using a batch or a continuous system. Although the single-step procedure used requires small capital investment, it must be carefully controlled for minimization of the amount zinc that is lost. New zinc plants use various modifications of leaching procedures because it includes the recovery of zinc and some other valuable metals. Residue from diluted acid leaching is one of the most important resources which should be considered for this purpose. Zinc plant leaching residue can contain zinc ferrite, entrained zinc sulfate, undissolved zinc oxide and other valuable materials such as lead, copper, cadmium, cobalt, nickel, manganese, silver and gold. Turan et al. has studied the recovery of zinc and lead from zinc plant residue [8]. The residue was discarded as a cake. It contained more than 11 % zinc and near 25 % lead. This residue was blended with  $\text{H}_2\text{SO}_4$  and subjected to a process comprising of roasting, water leaching and finally NaCl leaching. The recovery percentage of zinc and lead at the end of this multi stage process was about 86 % and 89 %, respectively.

Another work on the treatment of the zinc plant residue has been developed by Wang and Zhou [9]. Their recommended process consisted of six major unit operations: 1 washing, 2 roasting, 3 leaching, 4 precipitation of iron and manganese, 5 separation of zinc, 6 separation of nickel and 7 precipitation of cobalt.

Leaching of zinc concentrate is a well-known method for producing zinc sulfate solution. In the Iranian national Lead and Zinc Company located in Zandjan, Iran, sulfuric acid leaching of zinc

concentrates is carried out in two stages under certain conditions: (a) acidic leaching and (b) neutralized leaching. Acidic leaching has been done in an adjusted pH value of 1 to 2. In this step, almost all Zn is dissolved. In the second step, the neutralized leaching is carried out at 70°C. A zinc concentrate and/or limestone are added to the solution and pH of the solution increases to 5. After the second step, impurities such as Fe, Co, Cd and Ni are dissolved in the leaching liquor. These impurities should then be removed from this liquor. During the first purification step, addition of  $\text{KMnO}_4$  at a temperature equal of 90°C results in  $\text{Fe}^{+2}$  and  $\text{Co}^{+2}$  conversion into  $\text{Fe}^{+3}$  and  $\text{Co}^{+3}$ , respectively. Calcium hydroxide ( $\text{Ca(OH)}_2$ ) is then added to the leach liquor and the iron and cobalt are precipitated in the form of hydroxide at the pH value of 5. After separation of this precipitated solid phase, which is named hot filter press cake (HFC), zinc powder is added to the leach liquor at a temperature of 70°C. Ni and Cd are thus cemented and removed from the leach liquor. After separation of this precipitated solid phase, which is named Cold Filter Press Cake (CFC), the pregnant leach liquor (PLS) is used to make up zinc electro-

wining solution cycle.

A substantial part of the zinc and other metals such as cobalt, cadmium, nickel and manganese remains therefore as residue. These residues must be further treated to provide an economic recovery of zinc, cadmium, cobalt, nickel, and manganese. This study gives details of investigations carried out recently in our laboratory on the recovery of zinc, cobalt and manganese from HFC zinc plant residue of Iran.

## 2. EXPERIMENTS AND METHODS

**2.1. Materials** A hot filter press cake (HFC) of cobalt from the National Iranian Lead and Zinc Company located in Zandjan, Iran was used in this research. X-ray fluorescence (XRF) analysis of the material is given in Table 1. X-ray diffraction (XRD) of the material shows an amorphous filter cake structure. Both sulfuric acid and ammonium hydroxide used in this research are of an analytical grade produced by Baran Company located in Tehran, Iran. Hydrogen peroxide, potassium nitrate

TABLE 1. Chemical Composition of Zandjan, Iran Zinc Plant Residue.

Component	wt %
CaO	13.5
CdO	0.17
$\text{Co}_3\text{O}_4$	4.8
CuO	0.079
MnO	22.9
NiO	0.07
PbO	0.62
$\text{SO}_3$	25.8
ZnO	14.00
LOI.	17.54

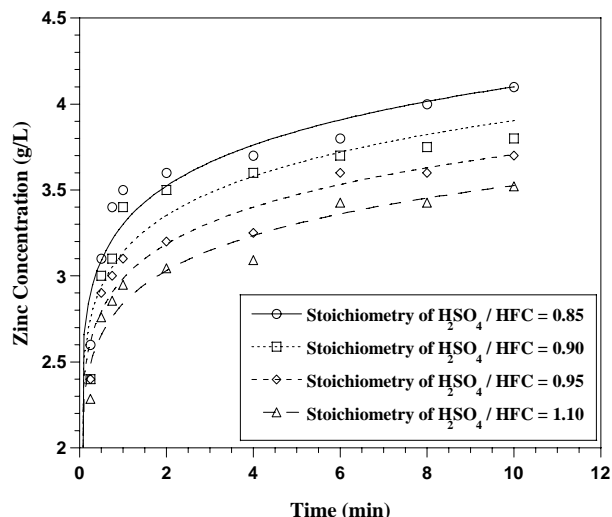
and reagents used in this research are made by MERCK (a chemical company of Germany).

**2.2. Experimental Procedure** Leaching was carried out in a 0.5-L batch glass reactor. A mechanical mixer agitated the liquor at a speed of 300 rpm and ambient temperature. A water bath was used to control the temperature. Atomic adsorption spectroscopy was used to determine the concentration of Zn, Mn and Co in the leaching liquor. The leaching ability of the zinc filter cake was investigated. Solid stoichiometry, acid concentration and the time for leaching were optimized. Cobalt/manganese filter cake recovery was determined. Acid concentration and  $H_2O_2/KNO_3$  consumption were also evaluated.

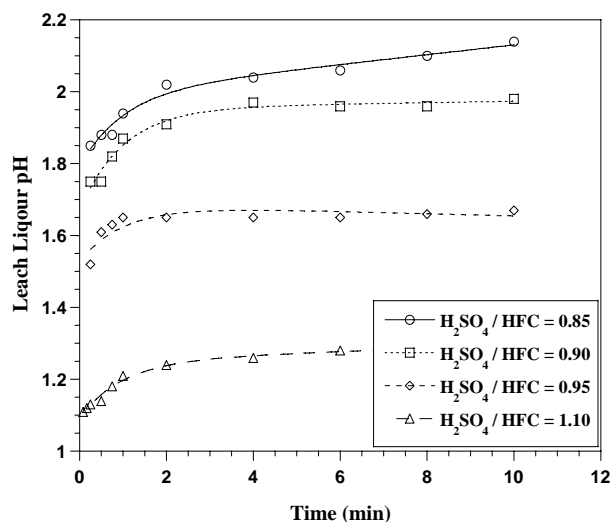
### 3. RESULT AND DISCUSSION

**3.1. Effect of Acid Stoichiometry on HFC Zinc Leaching** Figure 1 shows the effect of acid to HFC stoichiometric ratio and the leaching time on the dissolution of HFC in 5 g/L sulfuric acid. The experiments were carried out in four stoichiometric ratios of 1.1, 0.95, 0.9 and 0.85. As can be seen, for a constant acid concentration of 5 g/L, the best performance is obtained with the acid to HFC stoichiometric ratio of 0.85. Also, This figure shows that the zinc concentration decreases with the increasing of the acid to HFC stoichiometric ratio. Also Figure 2 indicates that the pH value produced during the leaching process, decreases with increasing the ratio of  $H_2SO_4/HFC$ . Lower pH means greater impurity dissolution and acid consumption. From these results it can be concluded that the best acid stoichiometry to HFC is 0.85.

**3.2. Effect of Time and Acid Concentration on Leaching of the HFC Zinc Content** Figure 3 shows the effect of time on the zinc concentration of the liquor obtained from leaching HFC with sulfuric acid at a stoichiometric ratio of 0.85. As is obvious from the figure, it takes less than 60 sec for the reaction to reach to 80 % completion. With all acid concentrations, the zinc dissolution reaction completes in approximately two minutes. Greater time does

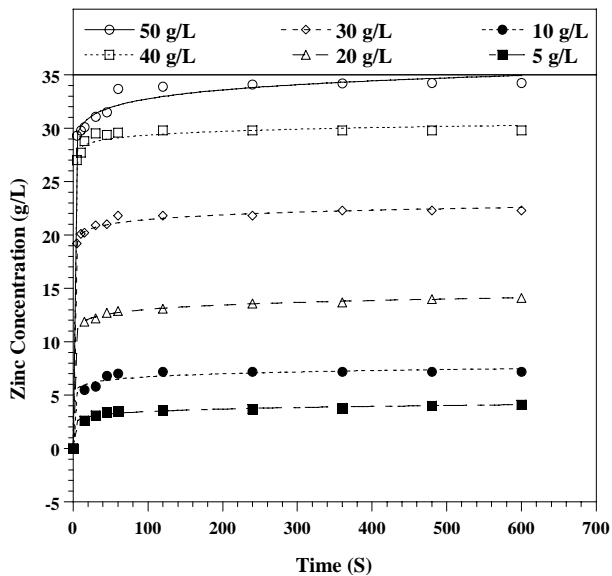


**Figure 1.** Effects of leaching time and acid to HFC stoichiometric ratio on zinc concentration in a solution containing 5 g/L of sulfuric acid.



**Figure 2.** Leach liquor pH against time at different acid stoichiometries.

not considerably change the zinc recovery percentage. Two minutes is, therefore, an appropriate time for the leaching of HFC zinc. Due to the fast leaching rate, kinetic parameter measurements and the controlling step determination seems to be practically impossible.



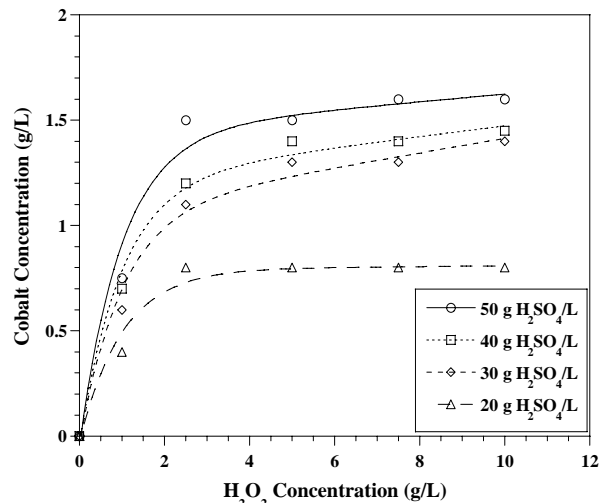
**Figure 3.** Kinetics of zinc leaching, using different concentrations of acid and at constant stoichiometry ratio equal to 0.85.

The effect of acid concentration on the leaching of HFC was determined. For the stoichiometric ratio of 0.85, Figure 3 was obtained. The figure indicates that with the increasing of the acid concentration from 5 to 50 g/L, the zinc concentration increases from 4 to 34 g/L at  $t = 2$  minutes. Using acid concentrations greater than 30 g/L produces filtration problems during solid/liquid phase separation.

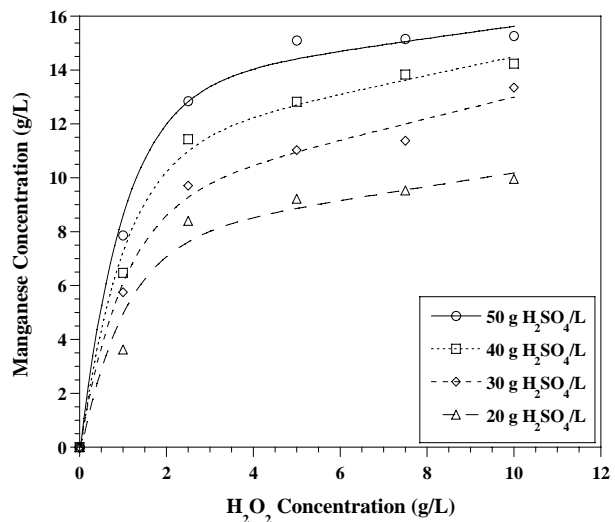
The procedure resulted in partial leaching of the HFC Mn and Co, too. Acid concentrations exceeding 30 g/L also dissolved the Fe content of the HFC. This led to furtherance of an HFC iron removal step. With the solid stoichiometry of 0.85, the best result corresponded with an acid concentration of 30 (g/L). After optimizing the zinc leaching parameters and removing it from the filter cake, the remained residue was treated for recovery of Co and Mn. Hence, the optimized conditions for Co and Mn recovery were determined.

### 3.3. Effect of Acid Concentration on Leaching of the HFC Cobalt and Manganese Contents

The effect of acid concentration on leaching of the



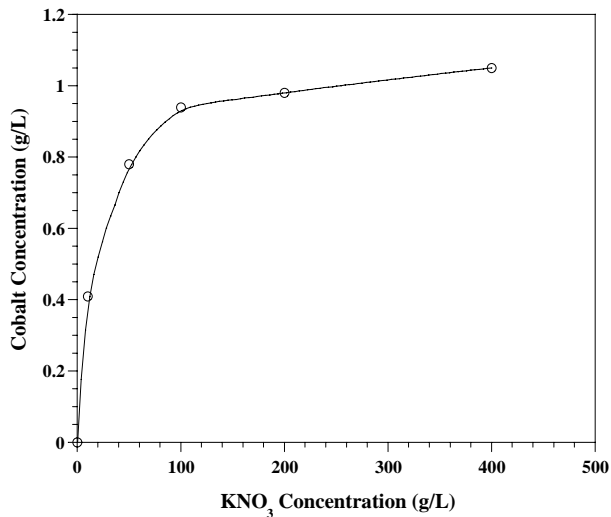
(a)



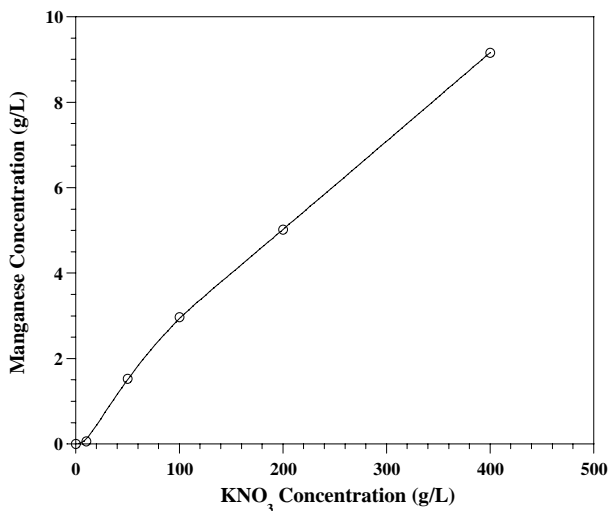
(b)

**Figure 4.** Effect of addition of  $H_2O_2$  on (a) cobalt and (b) manganese concentration after 10 minutes leaching with different acid concentrations.

HFC cobalt and manganese was also investigated. For a constant  $H_2O_2$  addition ( $5cm^3$ ), the leaching was facilitated with a greater acid content (Figure 4). Figure 4a and 4b show that with increasing the acid concentration from 20 to 50 (g/L), the respective concentrations of Co and Mn increase



(a)



(b)

**Figure 5.** Effect of KNO<sub>3</sub> on (a) cobalt and (b) manganese concentrations after 10 minutes leaching with 50 g/L sulfuric acid.

from 0.8 to 1.5 (g/L) and 9 to 15 (g/L) in the leaching solution. Based on these results, 50 g/L is a suitable acid concentration for the leaching of the HFC cobalt and manganese residual content.

### 3.4. Effect of H<sub>2</sub>O<sub>2</sub> and KNO<sub>3</sub> on Leaching

#### of the HFC Cobalt and Manganese Contents

The effect of H<sub>2</sub>O<sub>2</sub> addition on leaching of cobalt and manganese is shown in Figure 4. From the Figures, it seems that the addition of 5 g/L of H<sub>2</sub>O<sub>2</sub> has the best influence on both on the cobalt and manganese leaching process. Greater amounts of H<sub>2</sub>O<sub>2</sub> do not have a significant effect.

According to Figure 5, it can be seen that the maximum leaching value of Co is obtained when a minimum of 100 g/L KNO<sub>3</sub>, as a reductive agent, is added. Similar results are obtained with 1.5 g/L of H<sub>2</sub>O<sub>2</sub> (with compares Figure 5a). For reduction of Mn, the KNO<sub>3</sub> concentration should be more than 400 g/L and a similar result is obtained with 1.1 g/L of H<sub>2</sub>O<sub>2</sub> (with compares Figure 5b). This is of course not an economical procedure.

## 4. CONCLUSIONS

A process was developed for the recovery of zinc, cobalt and manganese from filter-cake zinc plant residue. Leaching of the residue in sulfuric acid led to the dissolution and extraction of all three elements. The best acid concentration for separation and removal of zinc from the residue with a solid stoichiometry of 0.85 was 30 g/L. Zinc recovery was increased with acid concentration. Solid phase separation from the solution became, however, more difficult at concentrations greater than 30 g/L.

At an acid concentration of 30 g/L, the zinc dissolution reaction reached completion in 2 minutes without any cobalt or manganese dissolution. The maximum leaching rate of cobalt was obtained at 100 g/L of KNO<sub>3</sub> concentration. This was added as a reductive agent to the leaching solution. H<sub>2</sub>O<sub>2</sub> showed similar effects when up to 1.5 g/L was added to the leaching solution. A KNO<sub>3</sub> concentration greater than 400 g/L was suitable for Mn reduction. This did not seem economically feasible.

The most suitable sulfuric acid concentration for leaching of cobalt was 50 g/L. At this concentration, almost all cobalt content of the HFC became solvable. Leaching conditions for

manganese and cobalt were both optimized in this research. Both elements (cobalt and manganese) existed in the leaching solution. For separation and recovery of both elements, a solvent extraction process proved to be usable.

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