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Article

# Recovery of Metal Values from Ni-Cd Cake Waste Residue of an Iranian Zinc Plant by Hydrometallurgical Route

Sushanta Kumar Sahu <sup>1,2,\*</sup>, Maryam Kargar Razi <sup>3</sup>, Mathieu Beuscher <sup>4</sup> and Alexandre Chagnes <sup>1,\*</sup> 

<sup>1</sup> CNRS, GeoRessources, Université de Lorraine, 54000 Nancy, France

<sup>2</sup> Metal Extraction & Recycling Division, CSIR-National Metallurgical Laboratory, Jamshedpur 831007, India

<sup>3</sup> Tehran North Branch-Faculty of Chemistry, Azad University, QF8F+4H Tehran, Iran; m\_kargarrazi@iau-tnb.ac.ir

<sup>4</sup> Euro Persia Processing Company-N1, Emdad Alley, Emam Reza Street, Miyamay, Semnan Province, Iran; mbeuscher@euro-persia-processing.com

\* Correspondence: sushanta29@gmail.com (S.K.S.); alexandre.chagnes@univ-lorraine.fr (A.C.); Tel.: +91-9431521200 (S.K.S.); +33-372-744-544 (A.C.)

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**Abstract:** This paper concerns the development of an environment-friendly hydrometallurgical flowsheet dedicated to the recovery of zinc and nickel from a waste residue collected from an Iranian zinc plant. In particular, valuable metals from Ni-Cd cake waste generated at this plant were recovered by a simple hydrometallurgical process using minimum acid for leaching, and solvent extraction step was designed such that addition of sodium hydroxide was not required and the effluent generated is safe to dispose off. The waste was leached with a mixture of hydrochloric acid and sulfuric acid in the presence of hydrogen peroxide in order to achieve a good selectivity towards iron and calcium. Afterwards, cementation was performed at pH 5 in order to remove cadmium. Liquid–liquid extraction was then implemented to produce high-purity solutions of zinc and nickel. Zinc-nickel separation was obtained at pH 2 by using a mixture of bis-(2-ethyl-hexyl)-phosphoric acid (HDEHP) and tris-2-ethylhexyl amine (TEHA) diluted in an aliphatic kerosene. TEHA did not directly participate but helped in the extraction of zinc by scavenging the protons released by HDEHP. Therefore, no alkaline solution was necessary for maintaining the equilibrium pH during liquid–liquid extraction. Finally, this flowsheet allowed to recover more than 95% of zinc and nickel from the residue with more than 99% purity.

**Keywords:** tailings; hydrometallurgy; value metals; flowsheet; solvent extraction

## 1. Introduction

Zinc is the third most non-ferrous metal following aluminum and copper. About 13.8 million tons of zinc was produced in 2018. Out of the total zinc production, 90% of zinc is produced by hydrometallurgical route using primary or secondary resources. The hydrometallurgical processing option involves leaching and a few purification steps producing high pure zinc solution suitable for electrowinning. During this operation, various kinds of waste residues are generated at different stages. These waste residues contain toxic but valuable heavy metals. Due to the potential release of toxic heavy metals into the surface and ground water, these waste residues are classified into a hazardous category. Therefore, such wastes are securely stored inside the industrial premises, encroaching valuable land mass. However, these wastes may serve as the secondary resources of valuable metals if technologically and economically feasible extraction techniques are developed.

The hydrometallurgical extraction of metals from low grade ores, secondary resources and wastes is a highly attractive process. This attractiveness is due to economic, environmental and technical reasons. Reports are available on hydrometallurgical recovery of zinc and other valuable metals from industrial wastes [1,2]. In a research conducted by Kul and Topkaya [3], the extraction of germanium and other valuable metals was studied, whereas in the study of Wang and Zhou [4], a hydrometallurgical process was reported for the recovery of cobalt oxide from zinc plant residue. A process was developed by Moradkhani et al. [5] for the recovery of cobalt and manganese from zinc plant residue. The process involved reductive leaching of zinc plant residue followed by solution purification by cadmium, and cobalt-manganese separation by precipitation of cobalt with beta-naphthol. The sulfuric acid leaching of cadmium from zinc plant has been examined by Garabaghi et al. [6]. In the study of Palencar et al. [7], the purification of steel making dust by cementation was described and the highest removal efficiency (>99%) of cadmium and lead was achieved from chloride solution.

A zinc ore concentrate obtained from various mines in and out of Iran, mixed in different ratios, is processed by the leach-electrolysis process to produce a high purity zinc metal. The process flowsheet followed by the industry is given in Figure 1. The zinc concentrate processing generates a variety of solid wastes. These solid wastes contain a number of toxic but valuable metals. These metals must be recovered prior to waste disposal for environmental and economic benefits.

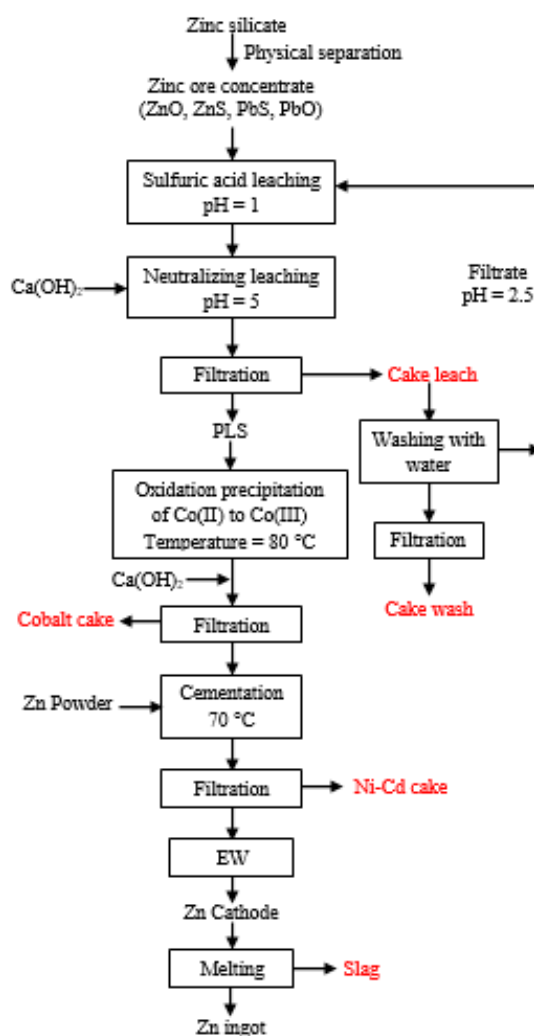


Figure 1. General flowsheet of ziterite process by hydrometallurgical route.

As shown in the process flowsheet (Figure 1), zinc from the concentrate is recovered by leaching with dil. sulfuric acid at pH 1. After leaching, the slurry is neutralized to pH 5 by adding lime. The slurry

is then filtered to generate pregnant leach solution and a solid waste (Cake leach). The cake leach is washed with water. The washing at pH 2.5 is recirculated to initial leaching stage. The wastes cake leach and cake wash may mainly contain gypsum and minor quantities of minerals of zinc concentrate.

The pregnant leach solution (PLS), apart from zinc, contains other impurity elements like Co, Ni, Cd, etc. Cobalt from the PLS is removed by oxidative precipitation with  $\text{KMnO}_4$  and lime at pH 3.7. At this stage, cobalt is precipitated as cobalt cake. This waste is expected to contain  $\text{Co}(\text{OH})_3$ , gypsum as major phases.

Nickel and cadmium impurities in the PLS are removed by cementation using zinc powder at 65–70 °C. The waste (Ni-Cd cake) generated at this stage is separated through filtration. The Ni-Cd cake residue contains zinc, nickel and cadmium. The purified leach solution is then electrowon to produce zinc metal at the cathode, which is then re-melted to produce zinc ingot. During the melting process, a slag is generated.

The solid wastes generated during the zinc concentrates processing include: Cake leach, Cake wash, Cobalt cake, Ni-Cd cake and Slag. Chemical analyses of the residues are given in Table 1. Out of the above waste residues, with respect to valuable metal contents, cobalt cake, Ni-Cd cake and slag are worth investigating for the development of process to recover metal values. In this paper, development of a process for recovery of metal values from Ni-Cd cake is presented.

**Table 1.** Chemical analyses of zinc process residues in % (weight).

Name	Ti	Fe	Mn	Ca	Mg	Ni	Cd	Zn	Pb	Co
Cake leach	0.167	5.19	0.23	13.96	0.78	0.03	0.089	4.94	2.96	0.030
Cake wash	0.185	5.85	0.08	15.35	0.74	0.02	0.047	2.04	3.05	0.012
Cobalt cake	0.007	0.32	11.35	9.62	1.28	0.20	0.361	19.94	0.12	1.372
Ni-Cd cake	0.011	0.314	0.311	2.161	0.499	3.113	9.017	47.131	0.46	0.019
Slag	0.005	0.12	0.04	0.34	0.40	0.00	0.004	77.96	0.08	0.002

## 2. Experiments

Waste residues generated at various stages of zinc production in an Iranian industry were obtained through International Center for Industrial and Mineral Researches on Wastes. Among the five residue samples received, Ni-Cd cake was selected to develop a process for the recovery of zinc and nickel. Hydrochloric acid (analytical grade), sulfuric acid (analytical grade), zinc powder, kerosene, bis-2-ethylhexyl phosphoric acid (HDEHP, purity >98) and tris-2-ethylhexyl amine (TEHA, purity >98%) were provided by Aldrich Chemicals. All other chemicals were of analytical grade.

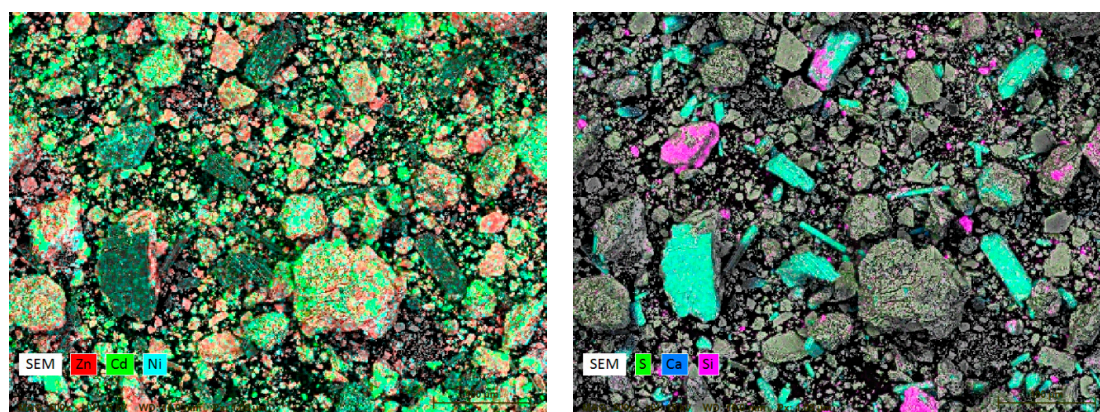
Elemental analyses were carried out using ICP-OES (ICAP 6000 Series, Thermo Scientific, Dardilly, France). Solid phases in residues were determined by X-ray diffraction after mixing the sample with 10wt% finely ground pure calcite. XRD spectra were recorded between  $2\theta = 3^\circ$  and  $2\theta = 90^\circ$  by means of the diffractometer D8 Advance Bruker, Bremen, Germany, (cobalt anode,  $\lambda_{\text{CoK}\alpha} = 1.79 \text{ \AA}$ ) equipped with a linear detector LynxEye. Residues were examined by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDX) equipment (SEM HIROX-SH 3000 with integrated EDS Bruker Nano, Bremen, Germany).

Initial preliminary leaching experiments were separately carried out with sulfuric acid and hydrochloric acid solutions. Based on the leaching efficiency and extractability studies of metal values from the leach solution by solvent extraction with mixture of bis-(2-ethyl-hexyl)-phosphoric acid (HDEHP) and tris-2-ethylhexyl amine (TEHA), the leaching of metal values from Ni-Cd cake was optimized using the mixture of hydrochloric acid and sulfuric acid solution. Cadmium from the leach solution was removed through cementation using zinc powder. After cadmium removal, zinc and nickel were separated by solvent extraction using the mixture of HDEHP and TEHA as extractants in kerosene as diluent. Zinc and nickel from the respective loaded organic phases were stripped with sulfuric acid solutions of desired concentration to produce highly pure zinc sulfate and nickel sulfate solutions.

### 3. Results and Discussion

#### 3.1. Characterization of Ni-Cd Cake Waste Residue

Prior to the development of process for the recovery of metal values, Ni-Cd waste residue was characterized by XRD and SEM-EDS. In Ni-Cd cake, mineral phases related to Ni and Cd were not detected. The lack of Ni and Cd peaks may be due to their amorphous phases. The appearance of Zn bearing phases may be due to the use of Zn metallic powder for cementation, oxidized in the solution after the precipitation in the electrochemical reaction between  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ . Major mineral phases in Ni-Cd cake were found to be gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), quartz ( $\text{SiO}_2$ ), zincite ( $\text{ZnO}$ ) and zinkosite ( $\text{ZnSO}_4$ ). The SEM micrograph with overlaid EDX mapping (Figure 2) shows that zinc, cadmium and nickel bearing phases are accumulated together indicating their generation as a result of cementation reaction. Calcium and silicon bearing phases were also observed separately. Zinc, nickel and cadmium contents in this sample are about 47%, 3% and 9%, respectively. The characterization of Ni-Cd cake waste residue indicates that valuable metals like zinc, nickel and cadmium can be recovered by leaching with mineral acid.



**Figure 2.** SEM micrograph with overlaid EDX (Energy Dispersive X-ray Spectroscopy) mapping of Ni-Cd cake waste residue.

#### 3.2. Preliminary Studies on the Recovery of Metal Values from Ni-Cd Cake

Leaching of metal values from Ni-Cd cake generated at various zinc processing plants has been reported in literature. In a study conducted by Altundogan et al. [8], 85% of zinc and 90% of lead were recovered from Ni-Cd cake by roasting with concentrated sulfuric acid followed by two successive leaching with water and sodium chloride solution, respectively. The research results of Safarzadeh et al. [9,10] reported the leaching of zinc, cadmium and nickel from Ni-Cd cake with dilute sulfuric acid followed by the removal of cadmium and nickel through cementation with zinc. In another study, the leaching behavior of valuable metals from residue generated during the purification of zinc electrolyte has been studied by Bae and Yoo [11]. It was reported that baring lead, all other metals viz. cadmium, zinc, copper, cobalt, nickel and antimony were recovered by leaching with 1M sulfuric acid at 50 °C.

In view of the above data from literature, preliminary experiments focus on the use of hydrochloric acid, sulfuric acid and a mixture of sulfuric acid and hydrochloric acid to leach Ni-Cd cake followed by cementation to remove impurities and solvent extraction to produce highly pure zinc and nickel solutions.

### 3.2.1. Sulfuric Acid Leaching of Metal Values from Ni-Cd Cake Waste Residue and their Separation by Solvent Extraction

In order to recover metal values, Ni-Cd cake waste residue was leached with 0.5 mol/L, 1.0 mol/L and 1.5 mol/L sulfuric acid solution at 60 °C and 150 g/L pulp density for 1h. It was found that leaching of metal values increased with the increase of acid concentration. With 0.5 mol/L sulfuric acid solution, about 50% of metal values were recovered, while with 1.5M sulfuric acid, the metal recovery increased to 90–95%. After leaching with 1.5 mol/L sulfuric acid, concentration of zinc, cadmium and nickel were found to be 68.5 g/L, 12.1 g/L and 4.2 g/L, respectively and pH of the leach solution was ~0.5.

bis-(2-ethyl-hexyl)-phosphoric acid (HDEHP) has been proved to be a good extractant for the extraction of base metals, and amine extractants are known to extract acid from the aqueous phase. Therefore, the mixture of HDEHP and tris-2-ethylhexyl amine (TEHA) was tested for the extraction of metal ions from the leach solution, which will also control the acidity of the aqueous phase during extraction [12]. When the leach solution was contacted with 1M HDEHP solutions containing various concentrations of TEHA in the range from 0.2 mol/L to 1.0 mol/L, no extraction of any metal ion present in the leach solution was observed. Similarly, extraction was negligible with 1 mol/L TEHA in the presence of various concentration of HDEHP (0.2 to 1 mol/L HDEHP). Equilibrium pH of the aqueous phase in all cases remained almost unchanged in the range 0.7 to 0.75.

### 3.2.2. Chloride Leaching of Ni-Cd Cake Waste Residue and Recovery of Metal Values by Solvent Extraction

Due to the negligible extraction of metal ions from sulfate leach solution, extraction of metal ions was also tested using the chloride leach solution. This solution was produced by leaching Ni-Cd cake waste residue with 2.5 mol/L hydrochloric acid at 60 °C and 150 g/L pulp density for 1h. The resulting chloride leach solution contained 63 g/L Zn, 12 g/L Cd and 4.1 g/L Ni with a recovery of about 90% of metals from the waste residue. The leach solution was contacted with different organic phases totally containing 1 mol/L HDEHP and TEHA together (0.2 mol/L TEHA + 0.8 mol/L HDEHP; 0.4 mol/L TEHA + 0.6 mol/L HDEHP and 0.6 mol/L TEHA + 0.4 mol/L HDEHP). When extracted with mixture of 0.4 mol/L TEHA and 0.6 mol/L HDEHP, a maximum of ~30% Zn and 23% Cd was extracted from the chloride leach solution with an increase in equilibrium pH of leach solution from 0.20 to 0.42. It is clear from the above observation that (HDEHP + TEHA) is a better extraction system for chloride leach solution than sulfate leach one. Therefore, chloride leach solution was generated, and the separation of zinc, cadmium and nickel using the mixture of HDEHP and TEHA was studied.

### 3.3. Optimization of Ni-Cd Cake Waste Residue Leaching

Exploratory experiments on leaching of Ni-Cd cake waste residue with 1.5 mol/L sulfuric acid or 2.5 mol/L hydrochloric acid for 1h showed that although ~90% of Zn, Cd and Ni was recovered, the leach solution which still contained high concentration of unutilized acid with pH of the leach solution was 0.1 and 0.5, which had an adverse effect on the solvent extraction of metal ions with HDEHP. Furthermore, both sulfate and chloride leach solutions contained 0.40 to 0.45 g/L Fe(II). Iron(II) from the leach solution had to be removed in order to avoid interferences during solvent extraction separation of Zn, Cd and Ni. Iron from the leach solution was removed by precipitation at pH 4.5 and aeration for 6 h at 60 °C. However, the iron removal process was time consuming and only 60% of iron present in the leach solution was removed. Calcium present in the Ni-Cd cake waste residue was also quantitatively leached when hydrochloric acid was used as the leaching reagent. Calcium gradually precipitated from the solution and interfered in solvent extraction separation of valuable metal ions.

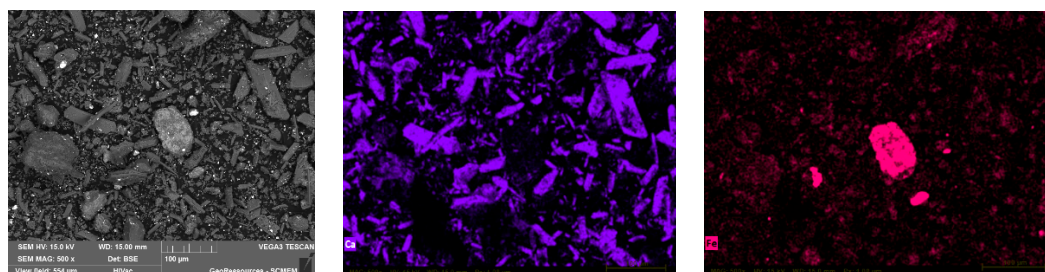
Considering the above difficulties, a leaching process was developed such that the maximum metal values were recovered with optimum utilization of lixiviant and in-situ removal of calcium and iron from the leach solution. The Ni-Cd cake waste residue was leached with a mixture of hydrochloric acid (1.38 N) and sulfuric acid (0.36 N) (total acid (H<sup>+</sup>) concentration: 1.74 N) at 130 g/L pulp density for 2 h at 60 °C. The reason being, the use of sulfuric acid in the lixiviant removed calcium from the leach

solution as calcium sulfate precipitate. After 2 h of leaching, 2 mL of H<sub>2</sub>O<sub>2</sub> per liter of lixiviant was added to the leaching vessel and leaching reaction was continued for another 1 h. Addition of H<sub>2</sub>O<sub>2</sub> led to the oxidization of Fe(II) to Fe(III) and in-situ precipitation as ferric hydroxide [13]. After 3 h of leaching, pH of the leach solution was found to be 4.5, indicating the maximum consumption of acid during leaching. Before arriving at this leaching condition several experiments were carried out to understand the effect of acid concentration and leaching time on leaching efficiency and final pH of the leach solution. However, detailed results are not included here. In the above process, 96.7% of Zn, 98% of Cd and 98% of Ni were recovered from the Ni-Cd cake waste residue. Compositions of leach solution and leach residue along with those of Ni-Cd cake waste residue are given in Table 2.

**Table 2.** Chemical composition of Ni-Cd waste residue, leach solution and leach residue.

Element	Ni-Cd Cake Waste Residue (%)	Leach Solution (mg/L)	Leach Residue (%)
Ti	0.01	<0.1	0.13
Fe	0.31	<0.1	3.71
Mn	0.31	369	0.12
Ca	2.16	122	17.12
Mg	0.50	566	0.55
Ni	3.11	3960	0.03
Cd	9.02	11480	0.05
Zn	47.13	59140	0.68
Pb	0.46	90	4.43
Co	0.02	20	0.001

Characterization by XRD and SEM methods reveals that leach residue, obtained after leaching with mixture of hydrochloric and sulfuric acid, is mainly composed of calcium phase (Figure 3). This indicates efficient recovery of metal values from Ni-Cd cake waste residue.

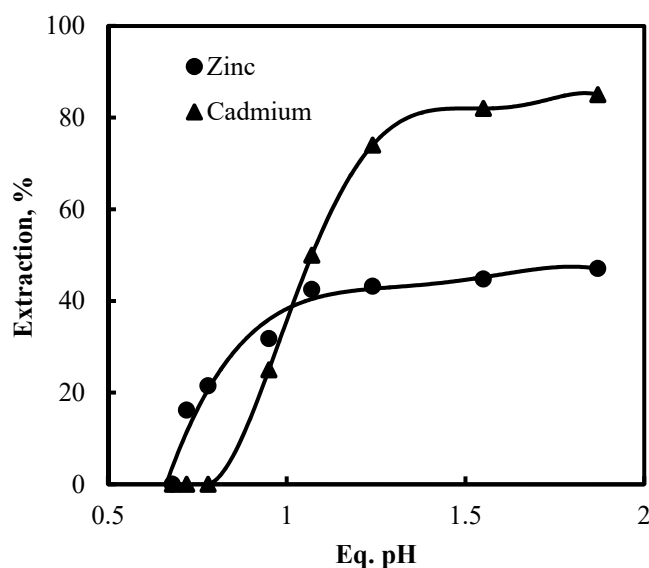
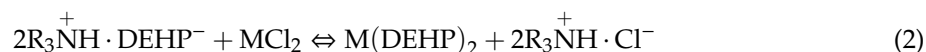
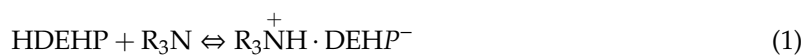


**Figure 3.** SEM image with overlaid EDS mapping of leach residue obtained after of Ni-Cd cake waste residue with mixture of hydrochloric acid and sulfuric acid.

### 3.4. Purification of Leach Solution

As mentioned above, the leach solution generated by the leaching of Ni-Cd waste cake residue with mixture of hydrochloric acid and sulfuric acid contained 59.14 g/L Zn, 11.47 g/L Cd and 3.95 g/L Ni along with other impurities. To obtain purified solutions of zinc and nickel, the leach solution was subjected to solvent extraction and separation of metal values using the mixture of HDEHP and TEHA as extractants. When the leach solution at initial pH 4.5 contacted with 1 mol/L HDEHP containing various concentrations of TEHA (0 to 1 mol/L TEHA) at phase ratio of O/A = 1:1, equilibrium pH of the leach solution decreased. At the same time, equilibrium pH gradually increased with the increase of concentration of TEHA. It was also found that extraction of zinc and cadmium increased with the increase in TEHA concentration, i.e., with the increase of equilibrium pH (Figure 4). This indicates that TEHA does not directly participate in the extraction of metal ions, but helps in the extraction of metal ions with HDEHP by neutralizing the acid released during extraction process. The advantage of using a combination of HDEHP and TEHA is that no external addition of alkali is required to control

the equilibrium pH. The mechanism of extraction of a divalent metal ion ( $M^{2+}$ ) with combination of HDEHP and TEHA ( $R_3N$ ) is given below.



**Figure 4.** Effect of equilibrium pH on the extraction of zinc and cadmium from the leach solution with 1 mol/L HDEHP in presence of various concentration of TEHA (0–1M TEHA) in kerosene.

However, as it is observed from Figure 4 that extraction of zinc and cadmium from the leach solution increased with the increase of equilibrium pH, whereas extraction of nickel and other impurity elements was negligible. At equilibrium pH of 1.87, a maximum of 47.1% Zn and 85% Cd were extracted into the organic phase. As far as selectivity between zinc and cadmium is concerned at higher equilibrium pH though extraction efficiency was high, selectivity was very poor. This is due to the fact that concentration of zinc (59.14 g/L) as compared to cadmium (11.47 g/L) in the leach solution was very high. Further, selectivity of zinc over cadmium was very low ( $D_{Zn}/D_{Cd} = 0.16$ ). Thus, extracted zinc (e.g., 47% extraction at equilibrium pH 1.8) was always contaminated with co-extracted cadmium (85% extraction). Separation of zinc and cadmium by solvent extraction will require several stages of counter current extraction. At low equilibrium pH (0.7 to 0.9), extraction efficiency was poor. Thus, recovery of pure zinc from the leach solution by solvent extraction may not be a good strategy. Therefore, cadmium from the leach solution was removed by cementation process.

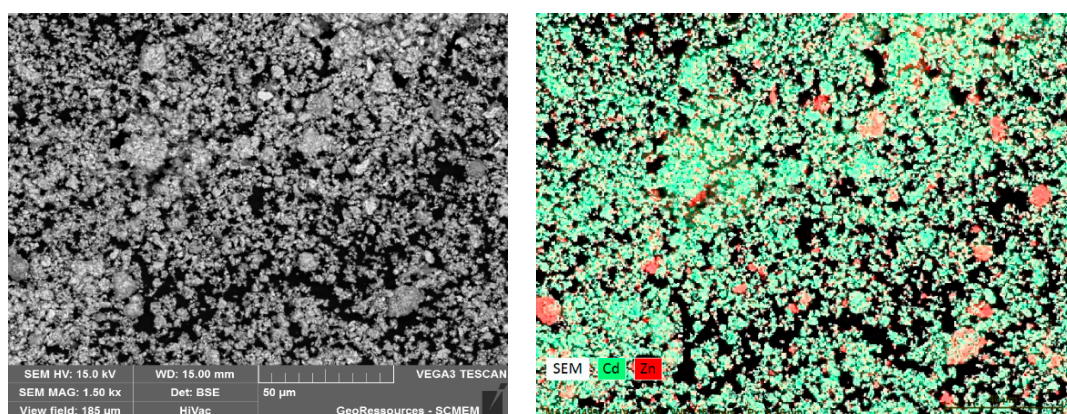
Cementation process is considered as an environment-friendly and economic refining operation. Several works on cementation from synthetic solutions or leach solutions of steel making dust have been reported in literature. Cementation was carried out both from acidic and alkaline media using zinc dust as cementing material. The cementation of cadmium and lead from acidic sulfate and chloride media has been studied by Palencar et al. [7]. Literature review [14–16] shows that in an acidic medium, effective cementation takes place in the temperature range of 25–45 °C and pH 5–6. In this case, 1000 mL of leach solution containing 59.14 g/L Zn, 11.48 g/L Cd and 3.96 g/L Ni at initial pH of 4.5 was added with 10.5 g zinc dust and stirred for 15 min at room temperature. During stirring, pH of the leach solution increased up to 6. Therefore, pH was kept constant at 5.0 by the adding 10% HCl solution. Within 15 min of reaction, cadmium concentration in the leach solution decreased to 64 mg/L and lead concentration decreased to 1.5 mg/L. This is equivalent to more than 99% removal of cadmium and lead from the leach solution. Zinc concentration of the leach solution in the process increased to



68.5 g/L. However, nickel concentration decreased to 3.4 g/L. In the above cementation process, 17.2 g of cement was generated and characterized by chemical analysis, XRD and SEM. For comparison, total chemical analysis of leach solution, purified leach solution and cement material are given in Table 3. Phase analysis of cement material confirmed the presence of major Cd, Cd(OH)<sub>2</sub> and minor zinc and nickel phases. Chemical analysis and XRD phase analysis are corroborated by SEM image of cement material as shown in Figure 5.

**Table 3.** Chemical composition of leach solution, purified leach solution and cement material.

Element	Leach Solution (mg/L)	Purified Leach Solution (mg/L)	Cement Material (%)
Ti	<0.1	<0.1	0.001
Fe	<0.1	<0.1	0.002
Mn	369	366	0.003
Ca	122	81	0.1
Mg	566	562	0.005
Ni	3960	2450	4.7
Cd	11,480	64	63.6
Zn	59,140	68,520	9.6
Pb	90	1.5	2.1
Co	20	20	0.001



**Figure 5.** SEM image with overlaid EDS mapping of cement material obtained after cementation of cadmium from leach solution.

### 3.5. Recovery of Zinc and Nickel from the Purified Leach Solution

Zinc from the purified solution, containing 68.52 g/L Zn, 3.45 g/L Ni and other impurities as shown in Table 3, was recovered by solvent extraction using the mixture of HDEHP and TEHA diluted in kerosene. Extraction isotherm for zinc was obtained by contacting the above purified solution with mixture of 1 mol/L HDEHP and 0.5 mol/L TEHA in kerosene at different phase volume ratios (O/A = 1:5 to 5:1) with initial pH of 5.0. At all the phase volume ratios, equilibrium pH reduced to a constant value of pH 2.0 without adjusting pH using acid or alkali. Extraction of zinc increased from 13% to 95% with the increase of phase volume ratio (Figure 6). Extraction of nickel and other impurities present in the solution was negligible.

In order to determine the number of counter current extraction stages required for complete extraction of zinc from the purified leach solution, extraction data obtained from Figure 6 was used to plot Mc-Cabe Thiele diagram (Figure 7). Mc-Cabe Thiele diagram indicates that two counter current stages are sufficient for the complete extraction of zinc with 1 mol/L HDEHP and 0.5 mol/L TEHA at phase volume ratio of 2.5:1 and equilibrium pH of 2.0.

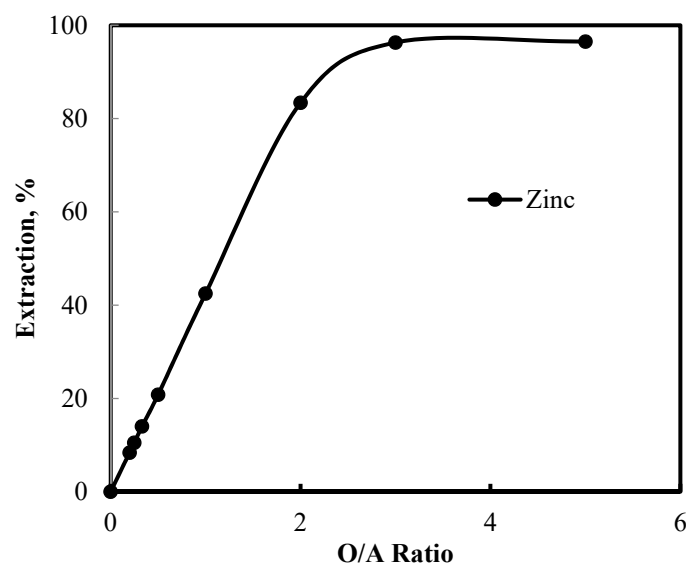


Figure 6. Effect of phase volume ratio (O/A) on the extraction of zinc from purified leach solution.

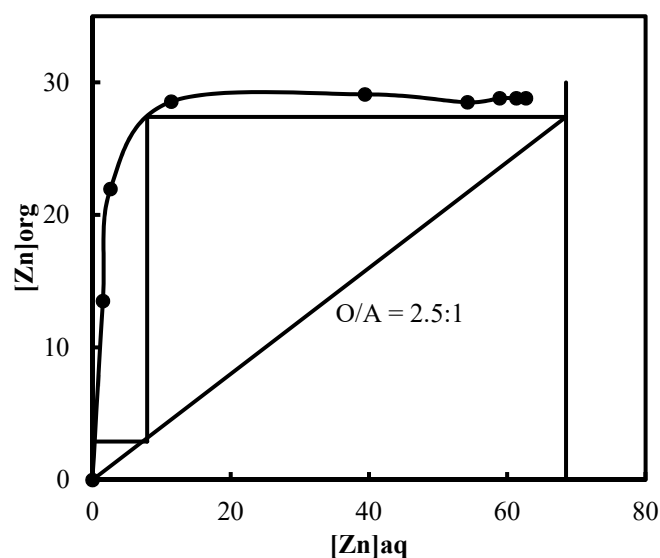


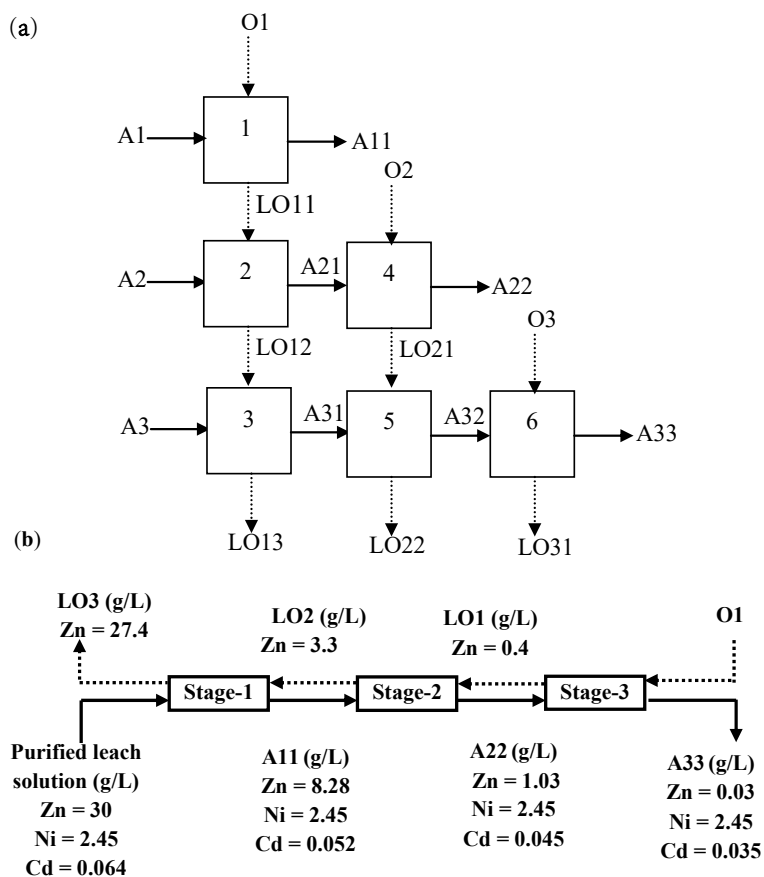
Figure 7. Mc-Cabe Thiele diagram for the solvent extraction of zinc from purified leach solution.

Simulation of counter current extraction of zinc from the purified leach solution following a model reported in Figure 8a shows that 27.4 g/L Zn loaded into the organic phase and the raffinate contained 2.45 g/L Ni, 0.03 g/L Zn and other impurities at the end of three stages (Figure 8b).

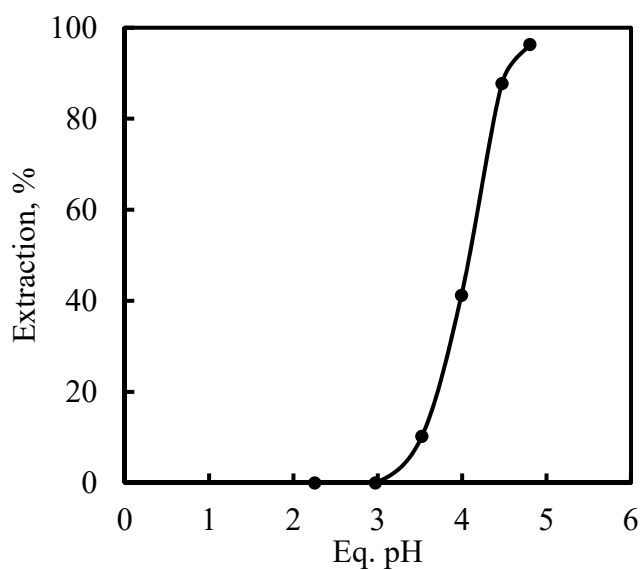
The raffinate obtained after the recovery of zinc from the purified leach solution contained 2.45 g/L Ni, 0.03 g/L Zn, 0.03 g/L Cd, 0.36 g/L Mn, 0.55 g/L Mg, 0.020 g/L Co with pH of ~2.0. The raffinate was contacted with mixture of 1 mol/L HDEHP and 0.5 mol/L TEHA at different equilibrium pH to recover nickel. In this case, equilibrium pH was kept constant by adding 1 mol/L NaOH solution during mixing of aqueous and organic phases. As nickel concentration was only 2.45 g/L (0.04M) in the raffinate, equilibrium pH was maintained with minimum addition of NaOH solution. It was found that extraction of nickel increased with increase of equilibrium pH (Figure 9). At equilibrium Ph = 4.8, quantitative extraction of nickel was obtained in a single stage at phase volume ratio of O/A = 1:1. Extraction of other impurities was negligible.

The loaded organic phases containing 27.4 g/L Zn and 2.45 g/L Ni were stripped in a single stage by contacting with 200 g/L and 50 g/L sulfuric acid solutions, respectively. The chemical analysis shows that stripped solutions have more than 99% purity. Thus, the high pure stripped solutions of zinc and

nickel could be used for preparation of various value-added products like metal powder or their salts and oxides for targeted applications.



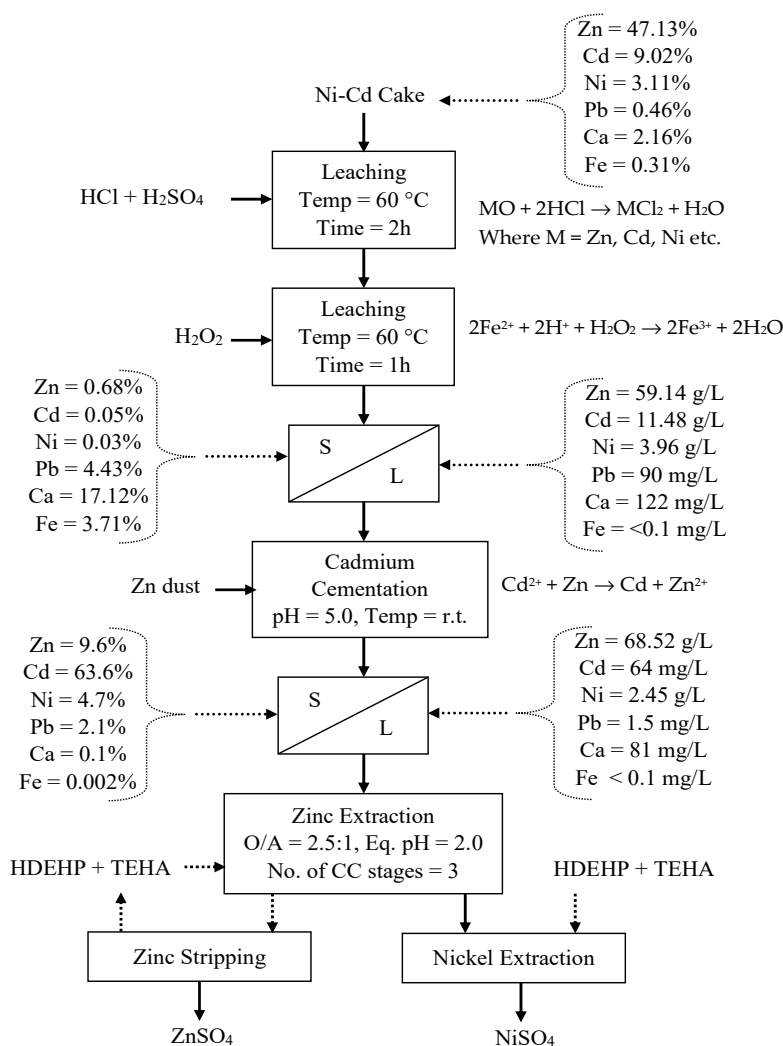
**Figure 8.** (a) Simulation model for counter current extraction of zinc from purified leach solution using mixture of 1 mol/L HDEHP and 0.5 mol/L tris-2-ethylhexyl amine (TEHA) as extractant. (b) Counter current extraction showing concentration of metal ions in the aqueous and loaded organic phases at different stages.



**Figure 9.** Effect of equilibrium pH on the extraction of nickel with mixture of HDEHP and TEHA.

#### 4. Conclusions

A complete process has been developed to recover high purity solutions of zinc and nickel from Ni-Cd cake waste residue generated in a zinc processing plant in Iran. The process flowsheet is given in Figure 10. The main advantage of the process is that leaching of metals has been carried out using lixiviant containing minimum but maximum utilization of acid. The process has been designed such that iron was removed in-situ during leaching. Zinc and nickel from the leach solution were recovered by solvent extraction after removing cadmium through the cementation process. For solvent extraction, a mixture of HDEHP and TEHA was used as extractant. During solvent extraction process, TEHA did not directly participate but helped in the extraction of zinc by scavenging the  $H^+$  ion released by HDEHP. Therefore, it was not required to add NaOH solution for maintaining the equilibrium pH. However, for solvent extraction of nickel, a little amount of sodium hydroxide was required to be added as nickel extracts at high equilibrium pH (4.8). In the above process, more than 95% of zinc and nickel were recovered with more than 99% purity. The high pure solutions of zinc and nickel could be used for the preparation of value added products like metal powders and salts for targeted applications. The effluent generated could be disposed of after the removal of impurity metals by neutralization. Overall, the process is environment-friendly and can be adopted for industrial practice.



**Figure 10.** Complete process flowsheet for the recovery of metal values from Ni-Cd cake from an Iranian zinc plant.

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