

## Processing of the Nickel existing in the mineral waste of a mine in Azerbaijan region, Iran

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**Abstract:** The raw material used in the present research was the waste of lead and zinc mines of Iran named CFC, stands for cold filter cake. CFC contains considerable amounts of nickel (2.5-4%). Annually, a large amount of CFC residue is produced in Iran's Lead and Zinc Project. The residue of Ni-Cd purification step can be used as the second source of production of zinc, nickel, and cadmium. First of all, the zinc existing in the waste was separated from CFC in two steps in order to find the ability of purification and conversion into metal. This operation was performed by sodium hydroxide solution.

The rest of the waste which was just solid converted into solution by sulfuric acid. Solvent extraction operation with D2EHPA diluted kerosene was done at the optimal pH. The optimal pH for 80% kerosene and 20% D2EHPA was obtained to be 3-3.5. Given the amount of impurities in the solution, solvent extraction operation was done by D2EHPA (Di-2-Ethyl Hexyl Phosphoric Acid) which produced pure solution of cadmium-nickel. In this solution, nickel is in the form of sulfate in an acidic environment. In order to achieve more industrial results, Iranian laboratory materials with purity close to industrial one were used.

**Keywords:** Nickel, Solvent extraction, Waste.

### Introduction

Nickel is a strategic metal which is used in electroplating industries and production of alloys and steels. Today, overuse of extracted sources of initial chemical industries is considered a serious threat to raw materials extraction. Due to providing sufficient initial resources needed for industrial units, the waste of industrial processes of various metallurgies and secondary resources such as catalysts, soil, batteries, and slug (accumulated residue of industries and mines) have recently attracted a lot of attention and started to replace the raw materials. Since there is valuable waste containing nickel in Zanjan Lead and Zinc Mine and considerable reserves of this waste have been accumulated in this mine, the present research is focused at using this waste for nickel processing.

The cause of Alzheimer's disease (AD) is poorly understood. About 70% of the risk is believed to be genetic with many genes usually involved. Other risk factors include a history of head injuries, depression, or hypertension. The disease process is associated with plaques and tangles in the brain. A probable diagnosis is based on the history of the illness and cognitive testing with medical imaging and blood tests to rule out other possible causes. Initial symptoms are often mistaken for normal ageing. Examination of brain tissue is needed for a definite diagnosis. Mental and physical exercise and avoiding obesity may decrease the risk of AD; however, evidence to support these recommendations is not strong [1-3].

The nicotinic  $\alpha 4\beta 2$  acetylcholine receptor is an important target for diagnostic neuroimaging and drug development because of its involvement in learning

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This filter cake contains high cadmium. Production of hydrometallurgical cadmium from filter cake has been previously done experimentally [1]. According to the

chemical and mineralogy analysis of filter cake, quantitative analysis of above-mentioned compound is as shown in Table 1.

**Table 1:** Chemical and mineral analysis of cold filter cake (CFC)

Compound	CdO	ZnSO <sub>4</sub>	ZnSO <sub>3</sub> .2.5H <sub>2</sub> O	Zn	ZnO	NiO	CaO	L.O.I
Weight percentage	15.04	22.45	21.19	25.27	0.88	4.37	3.17	5.00

### *Theoretical foundations:*

Alkaline agents such as sodium hydroxide, ammonium hydroxide, and sodium carbonate can selectively absorb the metals from waste into solution and leave iron, nickel, and manganese in the residual [2]. Various methods have been proposed for leaching of zinc ores in different solutions and the best result have been obtained from alkaline leaching [3-5]. Depending on its chemical and mineral composition, nickel can be extracted in both pyro metallurgy and hydrometallurgy methods. Caron and HPAL (high pressure acid leaching) are two techniques of hydrometallurgy. Caron process, which involves reduction and then ammonia leaching of oxidation, has been used in mines such as Queensland in Australia [6]. In HPAL, nickel ore is leached by sulfuric acid at high pressure and temperature and then nickel is separated from other impurities such as cobalt by hydroxide sequestration. This method has been used in Ravensthorpe and Cawe industries in Australia [2]. In both above-mentioned processes, nickel and cobalt are extracted by amine complexes. There are several methods for separation and recovery of nickel from leached ammonia solutions such as sequestration [8], solvent extraction [9], and membranes [10]. Among these methods, solvent extraction is the best; because of ease of operation and ease of use on large scales [11]. The laboratory operation required at this stage of separation is solvent extraction, because the grade of this compound in Iran's mines is low and the best method at this grade is solvent extraction. The type of solvent may vary depending on the impurities remaining at the end of leaching operation. However, according to the studied references on solvent extraction of metals existing in this waste, tri-butyl phosphate and D2EHPA are recommended as the best solvents [12-16].

### **Results and discussion**

This research on nickel sulfate production was started for the following reasons: High consumption of nickel and its compounds in various industries in Iran

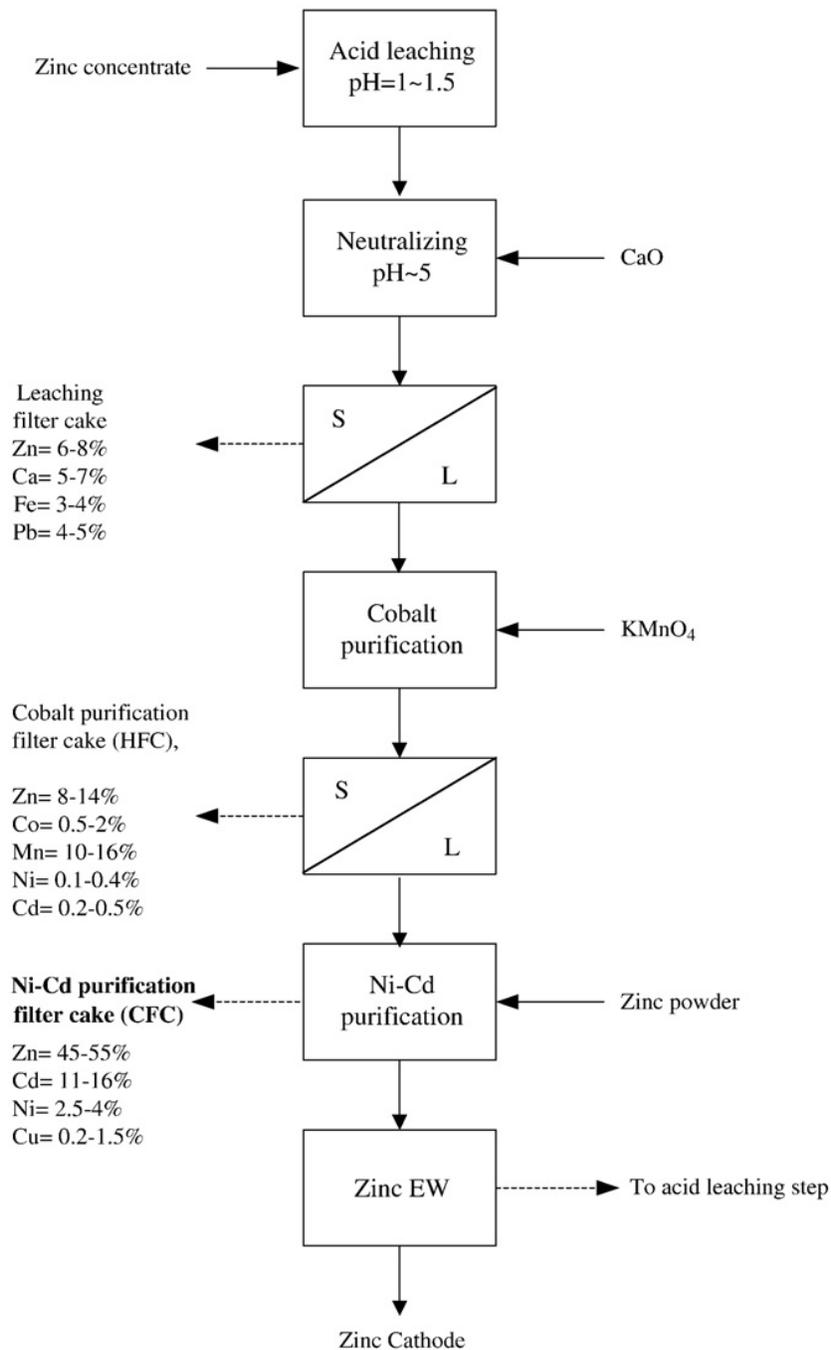
- Strategic position of nickel and its compounds due to their special applications
- Value of this metal in terms of price
- Non-production of the compounds of this metal in Iran
- Existence of this metal in waste of some mines which is considered as an environmental pollutant

Nickel exists in northeastern mines of Iran at low grade. To extract these compounds from mines, solvent extraction methods are enrichment operations. In other words, the heart of this project is the solvent extraction process.

Annually, a large amount of CFC residue is produced in Iran's Lead and Zinc Project. The residue of Ni-Cd purification step can be used as the second source of production of zinc, nickel, and cadmium. Unfortunately, despite its dangerous content, waste has remained in a way that many of its dangerous compounds can easily enter the environment. 50 kg of CFC is produced per each ton of zinc ingot production. For the process of zinc cathode production in Iran's Lead and Zinc Project, a considerable accumulation of residual waste of filter cake is produced. This filter cake contains high cadmium. Production of hydrometallurgical cadmium from this filter cake has been previously done experimentally [17]. Due to the limited budget and industrial nature of this project, it was tried to be carried out with the minimum analyses and raw materials. In addition, in order to make the project cost-effective, the cheapest possible materials which can be easily found in Iran were used.

The model of XRD device was Philips PW-1800, in which  $K_{\alpha}$  was 40 kV, 30 mA (Figure 2). Analysis of cold filter cake in the National Iranian Lead and Zinc Company (NILZ) is shown in Table 1. According to this analysis, it can be found that the nickel ore existing in the waste is of oxide type (limonite nickel). In sampling process, as professional samplers are present in mines and conduct sampling based on

international standards, project executors do not need to do sampling themselves



**Figure 1:** Flow sheet of zinc cathode in Iran's zinc and lead industries and the origin and production process of cold filter cake (CFC)

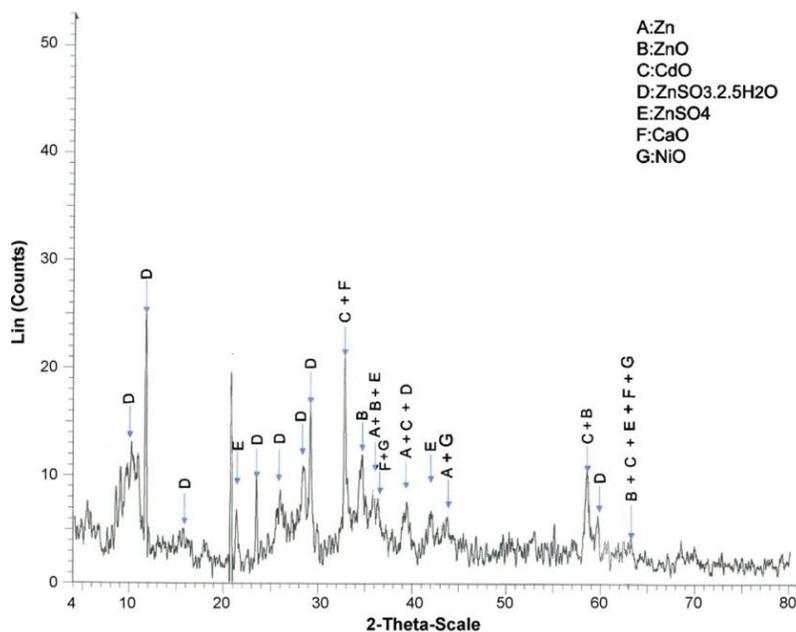


Figure 2: XRD of cold filter cake (CFC)

#### Alkaline leaching tests:

According to all mentioned above, for nickel separation, zinc should be first completely separated from the waste by alkaline leaching. Alkaline agents such as sodium hydroxide, ammonium hydroxide, and sodium carbonate can selectively absorb the metals from waste into solution and leave iron, nickel, and manganese in the residual [18]. Various methods have been proposed for leaching of zinc ores in different solutions and the best result have been obtained from alkaline leaching [19-23]. Alkaline leaching can absorb a limited number of metal oxides with amphoteric property, such as zinc oxide and aluminum oxide, into the solution and leave the remaining part in the solid. Hence, zinc and aluminum enter the solution and nickel and cadmium remain in the solid. Alkaline leaching operation of CFC has been optimized in various references [24-27]. The optimal condition for this process which was used in this study is as follows: 8 M sodium hydroxide, a temperature of 75°C, duration of 1 hour, stirring speed of 500 rpm, and liquid/solid ratio of 1:10. The objective of alkaline leaching is rapid dissolving of the zinc existing in the CFC in the solution. In practice, it is not possible to achieve this goal in one step. Therefore, the second stage of alkaline leaching was performed with the same optimal conditions. In two replicates of alkaline leaching, about 96% of the zinc existing in the CFC entered the solution.

#### Acidic leaching of the waste of alkaline leaching from the second stage:

Almost all existing nickel with some impurities such as cadmium and copper can be added to the aqueous phase by using sulfuric acid. Leaching operation of this cake in sulfuric acid has been studied and optimized [17], dissolving of the metals existing in this cake is done through the reaction shown in Table 4 [28]. Copper cannot dissolve as long as other metals remain undissolved. In addition, lead comes in the form of insoluble  $\text{PbSO}_4$ , so it exits the leaching cycle and, as result, copper and lead easily get out of this cycle. According to above numbers, it is expected that the tendency power of metals in leaching process to be as follows:

$$R_{\text{Zn}} > R_{\text{Cd}} > R_{\text{Ni}} \quad (3)$$

In a paper, this tendency power was consistent with experimental operations [29]. Calcium reaction is more exothermic than other ones. Acidic leaching of the waste of alkaline leaching of the second stage is done in order to transfer all metals to sulfate solution. The optimal conditions of leaching, according to the references is as follows: duration 1.5 hours, temperature of 75°C, and liquid/solid ration of 1:10. The color of solution obtained from colander turned dark green. As a result of this operation, 99.9% of the existing nickel was absorbed into the solution.

Analysis of the leaching solution has been shown in Table 2.

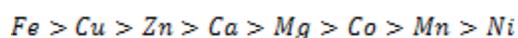
**Table 2:** Conditions and behaviors of the metals existing in CFC and their oxide compounds in sulfuric acid

$Zn + H_2SO_4 = ZnSO_4 + H_2$	$E^0_{Zn^{2+}/Zn} = -0.763V$
	$\Delta H^0_{298} = -39.352kcal$
	$G^0_{298} = -43.46kcal \Delta$
$ZnO + H_2SO_4 = ZnSO_4 + H_2O$	$\Delta H^0_{298} = -23.896kcal$
	$G^0_{298} = -23.74kcal \Delta$
$Cd + H_2SO_4 = CdSO_4 + H_2$	$E^0_{Cd^{2+}/Cd} = -0.403V$
	$\Delta H^0_{298} = -28.55kcal$
	$\Delta G^0_{298} = -31.76 kcal$
$CdO + H_2SO_4 = CdSO_4 + H_2O$	$\Delta H^0_{298} = -34.967kcal$
	$G^0_{298} = -33.63kcal \Delta$
$NiO + H_2SO_4 = NiSO_4 + H_2O$	$\Delta H^0_{298} = -25.107kcal$
	$G^0_{298} = -23.41kcal \Delta$
$Ni + H_2SO_4 = NiSO_4 + H_2$	$E^0_{Ni^{2+}/Ni} = -0.25V$
	$\Delta H^0_{298} = -14.082kcal$
	$\Delta G^0_{298} = -17.308kcal$
$Cu + H_2SO_4 = CuSO_4 + H_2$	$E^0_{Cu^{2+}/Cu} = +0.337V$
	$\Delta G^0_{298} = -6.9kcal$
$Pb + H_2SO_4 = PbSO_4 + H_2$	$E^0_{Pb^{2+}/Pb} = -0.126V$
	$\Delta G^0_{298} = -30.182 kcal$
$Ca + H_2SO_4 = CaSO_4 + H_2$	$\Delta H^0_{298} = -65.618 kcal$
	$\Delta G^0_{298} = -64.309kcal$

#### Solvent extraction operation for separation of nickel:

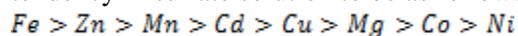
There are several methods for separation and recovery of nickel from leached ammonia solutions such as sequestration, solvent extraction, and membranes. Among these methods, solvent extraction is the best. According to the studied references on solvent extraction of metals existing in this waste, tributyl phosphate and D2EHPA are recommended as the best solvents [12-16].

The optimal pH and temperature for solvent extraction of nickel from impurities have been reported by Hoh *et al.* [30]. Ritcey *et al.* [31, 32] reported that the order to tendency of different cations to solvent extraction process is as follows:



(4)

Yao *et al.* [33] also reported the above-mentioned tendency in sulfate solution to be as follows:



(5)

Cheng reported separation of nickel from copper, calcium, zinc, and manganese at a pH range of 3-3.5 [35]. According to the practical experience on the nickel solvent extraction, the following reaction was designed in which all metals are extracted by the organic phase and nickel remains in the aqueous phase. Analysis of the aqueous solution was as shown in Table 3. The final solution, which contains nickel

sulfate, can be used for production of nickel or its compounds.

### **Presentation of results and analysis of findings:**

1- Zinc was separated from CFC in two steps with the ability of purification and conversion into metals. These operations were done by sodium hydroxide solution and the optimal reaction conditions were as follows: 8 M sodium hydroxide, a temperature of 75°C, duration of 1 hour, stirring speed of 500 rpm, and liquid/solid ratio of 1:10.

2- Other metal materials in waste were absorbed into the solution by sulfuric acid. Conditions of this reaction for complete recovery of nickel were optimized as follows: duration 1.5 hours, temperature of 75°C, and liquid/solid ratio of 1:10.

3- Solvent extraction operation by D2EHPA was done with diluted kerosene at an optimized pH. The optimal pH for 80% kerosene and 20% D2EHPA was obtained to be 3-3.5.

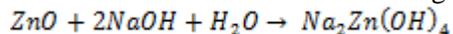
### **Experimental**

Sulfuric acid 98%, sodium hydroxide 99% (both industrial grade), distilled water, sodium sulfate, industrial boric acid 98%, ammonia 99% (industrial grade), and digital pH meter and thermometer were used in this research. In addition, all analyses were done by atomic absorption spectrometry AAS (Analyst 300 Perkin Elmer spectrophotometer).

CFC waste, as the raw material of this study, was crushed into pieces of 100-120 microns in order to increase the rate of chemical reactions.

#### **Zinc extraction by sodium hydroxide solution:**

The reaction carried out at this stage is as follows:

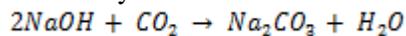


(1)

Various operations have been performed on CFC waste in terms of dissolving in alkaline and acidic systems. According to these operations, the following reactions were designed. In these reactions, zinc is added to the solution as Zn(OH)<sub>2</sub> because it has amphoteric property and cause other element remains solid. Dissolving of this waste in sodium hydroxide has been examined in different conditions, a summary of which is as follows:

A) Reaction efficiency in different molarities: Efficiency at molarities 3, 6, 8, and 10 was reported to be 48.6%, 92.1%, 95%, and 95%, respectively. Therefore, 8 M (molarity) sodium hydroxide was selected for this study.

B) The higher temperature, the more efficient reaction. However, at temperature above 75°C, some problems may occur. For instance at 90°C, a lot of sodium waste that is because of CO<sub>2</sub> absorption by sodium hydroxide solution.



(2)

In addition, existence of Na<sub>2</sub>CO<sub>3</sub> increases viscosity and corrosion and cause some problems with filtration. Thus, the best temperature is 75°C.

C) When liquid/solid ratio is 3; efficiency was 51.8%, while when this ratio reached 10, then efficiency increased to 95%.

D) The optimum time to achieve 95% efficiency was 1 hour. Longer reaction times have no significant impact on efficiency.

E) When the stirring speed is 500 rpm (round per minute), reaction efficiency is 95%, while when it is increased to 600 rpm, efficiency slightly increases to 95.9%. Therefore, the stirring speed of 500 rpm is suitable.

By considering optimizations above, the following reaction was designed:

8 grams of the CFC sample was weighted and added to 80 ml of 8 M sodium hydroxide. Then, the temperature and stirring speed were set at 75°C and 500 rpm, respectively, and the solution was stirred for 1 hour. Then, the sediment was separated from the solution. The solid on the filter was kept for the next step. In order to increase the zinc dissolving efficiency, zinc extraction operation was repeated again. The sediments separated in the previous stage were added to 80 ml of 8 M sodium hydroxide. The temperature and stirring speed were set to 75°C and 500 rpm, respectively, and the solution was stirred for 1 hour. Then, the sediment was separated from the solution. The resulting black solid on the filter was dried and kept for the next stage.

#### **Leaching process by sulfuric acid:**

When waste is leached in sulfuric acid, almost all materials existing in waste enter the solution. Thus, the following operation was performed on waste:

5 grams of dried sediment was weighted and dissolved in 50 ml of 80 mg/l sulfuric acid in order to change the phase of nickel and zinc from solid to liquid. Stirring of the solution was done at a temperature of 70°C and pH of 1-1.5 for 1.5 hours at a speed of 500 rpm (according to the existing references). Then, the sediment was separated from the solution and the obtained solution, which was green and contained nickel and cadmium ions and small

amounts of zinc and copper, was kept for the next stage and the remaining sediment was discarded. Analysis of the obtained solution was as mentioned in Table 3.

#### **Solvent extraction operation for removing the impurities:**

According to the practical experience on the nickel solvent extraction [12-16], the following reaction was designed:

For the removal of copper, zinc, and cadmium ions remained in the solution, solvent extraction operation was done. In this process, D2EHPA (Di-2-Ethyl Hexyl

Phosphoric Acid) as the solvent and kerosene as the diluter and improve the extraction properties. The organic solvent was composed of 20% D2EHPA and 80% kerosene with volume ratio. Each extraction operation was stirred in a shaker for 10 minutes. Firstly, 10 ml of the organic solution with 10 ml of the aqueous solution obtained from the third stage with a pH of 3-3.5 were poured in a separator funnel and shaken for 10 minutes. Then, organic phase was separated from aqueous phase and the aqueous phase was kept for further analyses. Analysis of this aqueous solution has shown in Table 4.

**Table 3:** Analysis of the solution obtained from leaching process by sulfuric acid

Element	Cd	Ni	Zn	Cu	Pb	Fe
Amount (g/l)	45.66	13.69	3.78	1.25	0.12	0.45

**Table 4:** Analysis of the aqueous solution after the solvent extraction process

Element	Cd	Ni	Zn	Cu	Pb	Fe
Amount (g/l)	0.24	11.56	0.003	0.003	0.004	0.002

#### **Conclusion**

1- Zinc was separated from CFC in two steps with the ability of purification and conversion into metals. These operations were done by sodium hydroxide solution and the optimal reaction conditions were as follows: 8 M sodium hydroxide, a temperature of 75 °C, duration of 1 hour, stirring speed of 500 rpm, and liquid/solid ratio of 1:10.

2- Other metal materials in waste were absorbed into the solution by sulfuric acid. Conditions of this reaction for complete recovery of nickel were optimized as follows: duration 1.5 hours, temperature of 75 °C, and liquid/solid ration of 1:10.

3- Solvent extraction operation by D2EHPA was done with diluted kerosene at an optimized pH. The optimal pH for 80% kerosene and 20% D2EHPA was obtained to be 3-3.5.

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