



## Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336

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### ABSTRACT

Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions by solvent extraction technique were studied using different forms of Aliquat 336 diluted with kerosene. The extraction percent of each metal ion was found to increase with increasing pH and extractant concentration. Co(II) was preferentially extracted by different forms of Aliquat 336 over Ni(II) under the same extraction conditions. From analysis of the experimental results, the extraction mechanism of R<sub>4</sub>N-forms was proposed with Co(II). It was found that the highest separation factor ( $S_{Co/Ni}$ ) value of 606.7 was obtained with 0.36 M R<sub>4</sub>N–SCN in kerosene from 2.0 M H<sub>2</sub>SO<sub>4</sub> solution at pH 4.8 and shaking time of 20 min. Stripping of the two metal ions from the organic phase was also investigated. Based on the experimental results, a separation method was developed and tested to separate high purity Co(II), Ni(II) and Ln(III) from Ni–MH batteries leached by 2.0 M H<sub>2</sub>SO<sub>4</sub>. Based on the experimental results, a flow sheet was developed and tested and 0.34 g Co, 1.39 g Ln and 5.2 g Ni were obtained from the leaching process.

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### 1. Introduction

Cobalt and nickel are amongst the most important nonferrous metals. Increasing demand for these metals is leading to a fast depletion of their rich sources [1]. Cobalt demand has recently risen due to its promising use in super-alloys materials, catalysts, nuclear field, chemical applications, most notably rechargeable batteries and other industry fields. Extraction and separation of cobalt and nickel from chloride and sulfate solutions have been of interest to hydrometallurgists from a long time. The separation of cobalt and nickel is difficult from weak sulfate solutions due to the fact that both metals have similar chemical behavior in aqueous solutions to make the development of separation route is needed [2]. Different solvent extraction studies were carried out for separation of cobalt and nickel using different extractants [3].

Many investigations have been performed to develop extractants selective for one of the metal ions. Although some of the reagents have been developed for the selective extraction of Ni(II) from Co(II), the more usual route has been to extract Co(II) leaving Ni(II) in the aqueous phase [4]. Different studies by solvent extraction technique involving Co(II) and Ni(II) species were carried out by different organophosphorus extractants in weak and/or strong acidic media [5–12]. The extraction and separation of cobalt and nickel from sulfate solution was carried out also using different extractants as di(2-ethylhexyl) phosphoric acid (DP-8R), LIX 860 in

Exxsol D100 diluent [13], mixtures of di(2-ethylhexyl)phosphoric acid (DP-8R) and hydroxyoxime (ACORGA M5640) in Exxsol 13100 [14], CYANEX 272 in kerosene [4] and HDEHP in toluene [15].

Nickel–metal hydride (Ni–MH) batteries contain valuable metallic components and can be regarded as a source for these metallic components. The average cycle life of these batteries is nearly 2 years, it can be concluded that an appreciable amount of these spent batteries is generated every year. Recycling of these batteries at the end of their life is necessary and important both from an economic point of view and due to the increased requirement for environmental protection.

Rabah et al. [16] studied the recovery of nickel, cobalt and some salts from spent nickel–metal hydride (Ni–MH) batteries leached by sulfuric acid at <90 °C for 3 h. Zhang et al. [17] reported a hydrometallurgical method for the separation and recovery of nickel and cobalt by CYANEX 272 from the leaching solution of Ni–MH spent batteries. In this process, the electrode material of batteries was dissolved in 2.0 M sulfuric acid at 95 °C.

Thiocyanate forms moderately stable anionic complexes with many metals. With respect to hydrometallurgical applications, there appears to have been only a modest amount of work presented in the literature. However, a more extensive body of work exists which is related to analytical chemistry [18,19] investigated in details the chemistry of amines extraction of thiocyanate complexes. A process based on solvent extraction involves the use of anion exchangers to load anionic thiocyanate complexes was used for separation of cobalt from nickel [20,21]. In this case, Aliquat 336 in the thiocyanate form was used to separate cobalt, zinc and

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copper from nickel from sulfate solution. The solvent extraction of Co(II) and Ni(II) into xylene solutions of a quaternary ammonium thiocyanate ( $R_4N \cdot NCS$ ) has been investigated from different media by Perston [22].

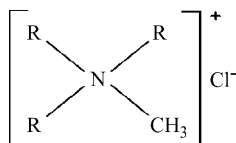
In the present study, the extraction and separation of Co(II) from Ni(II) in sulfate solutions using Aliquat 336 in the thiocyanate or sulfate form are studied. The effects of agitation time, hydrogen ion concentration, extractant concentration, sulfate concentration and temperature on the extraction systems were studied. Stripping of the two metal ions from the organic phases was also investigated. Based on the experimental results obtained a process for separation of high purity cobalt, nickel and lanthanides from Ni–MH batteries leached by 2.0 M sulfuric acid solution was developed and tested. A flow sheet is developed and tested to produce a high purity cobalt oxide, nickel oxide and lanthanides oxides.

## 2. Experimental

### 2.1. Reagents and analysis

All chemicals and reagents used in this work were reagent grade. Double distilled water was used to prepare the different aqueous solutions. Stock solutions of Co(II) and Ni(II) sulfate (0.2 M each) were prepared by dissolving AR grade Co(II) and Ni(II) sulfate in double distilled water.

Aliquat 336 chloride, ( $R_4N-Cl$ ), (Aldrich, USA) diluted with kerosene (supplied from Misr Company, Egypt) was used in the preparation of the organic phase. Generally, Aliquat 336 is a water insoluble quaternary ammonium salt composed of a large organic cation associated with a chloride ion as shown below:



Since the ammonium structure has a permanent positive charge, Aliquat 336 forms salts with different anions over a wider pH range than primary, secondary and tertiary amines. This was reflected on its use in many applications in recovery of several metals from solutions [23].

The analysis of the metals concentrations was carried out using atomic absorption spectrophotometer, Model S Series, Thermo-electron Corporation. FT-IR of  $R_4N-Cl$ ,  $R_4N-SCN$  and  $(R_4N)_2-SO_4$  and their complexes with cobalt were carried out with FT/IR spectrometer 6300, JASCO Corporation Tokyo, Japan.

Analysis for both cathode and anode of the Ni–HM battery was carried out by Energy Dispersive X-ray fluorescence (EDX) spectrometer Model; OXFORD attached with SEM Model JEOL–JSM–5400.

The hydrogen ion concentration of the different solutions was measured using digital pH-meter of the type CG820, with error of  $\pm 0.01$ . The scale of the pH-meter was calibrated before use by suitable standard buffer solutions.

Cobalt and nickel product were analyzed by XRD using a Shimadzu (Japan) diffractometer. The conditions of these measurements were obtained using Cu  $K\alpha$  radiation and Ni filter. Analysis of the diffraction patterns was made by the whole-powder pattern-fitting computer program intra-connected to the system.

### 2.2. Preparation and characterization of $R_4N-SCN$ and $(R_4N)_2-SO_4$

Aliquat 336 chloride solution (10 g) in 200 ml xylene was washed with 600 ml of 0.1 M HCl and then with 400 ml water. This treatment was necessary for removal of traces of iron, which

form a red color in the organic phase when it is converted to the thiocyanate form [22].

A purified Aliquat 336 chloride was then converted to the thiocyanate and sulfate forms by mixing with an aqueous solution of 1.6 M KSCN and 1.6 M  $Na_2SO_4$  at an A/O ratio of unity for different time periods. After the extractant solution was mixed well with fresh thiocyanate or sulfate solutions, the chloride ions in the extractant were quantitatively replaced by thiocyanate or sulfate groups. The removal of the chloride ions was followed by testing the aqueous solution by chloride precipitation using  $AgNO_3$  [24].

FT-IR analyses spectra obtained for the functionalized  $R_4N-Cl$ ,  $R_4N-SCN$  and  $(R_4N)_2-SO_4$ , Fig. 1, exhibited enhanced stretching bands between 3000 and 2850  $cm^{-1}$  corresponding to  $CH_2$ –, and  $CH_3$  groups in addition to bending bands below 1500  $cm^{-1}$  corresponding to the same group. A band at 1475  $cm^{-1}$  may be due to  $(CH_3)N^+$  stretching bending and characterized for quaternary amine. Two bands at 2053  $cm^{-1}$  and 720  $cm^{-1}$  were observed in the  $R_4N-SCN$  spectrum due to  $SCN^-$  stretching vibration, which indicate the substitution of  $Cl^-$  by  $SCN^-$  in Aliquat 336. The IR spectrum of  $(R_4N)_2-SO_4$  showed absorption bands in the region 1130–1080  $cm^{-1}$  which can be assigned to the  $SO_4^{2-}$  stretching vibrations, and indicates the substitution of  $Cl^-$  by  $SO_4^{2-}$  in Aliquat 336 ( $R_4N-Cl$ ). In all IR spectra measured, Fig. 1, a wide absorption band near 3340  $cm^{-1}$  which can be assigned to the stretching vibration of the OH of the water soluble in different  $R_4N$ -forms [25].

### 2.3. Procedures

In the extraction process, the aqueous phase (5 ml) containing 0.01 M of each Co(II) and Ni(II) sulfate dissolved in 2.0 M  $H_2SO_4$  was equilibrated by shaking with equal volumes of 0.09, 0.18, 0.27, 0.36, 0.45 and 0.54 M different  $R_4N$ -forms in kerosene. When we studied the effect of pH, the initial pH of the solutions was adjusted by  $H_2SO_4$  or NaOH to the desired value. The samples were equilibrated for 20 min, unless otherwise stated, and after phase separation; the equilibrium pH of the aqueous phase was measured. The leakage of Cl or SCN from the organic to the aqueous sulfate solution during the extraction processes by  $R_4N-Cl$  or  $R_4N-SCN$  forms were tested by either  $AgNO_3$  or  $FeCl_3$ , respectively. The results obtained show that neither white precipitate nor red complexes are formed, which indicate that leakage of Cl or SCN from the organic to the aqueous solution is absent. All the extraction and stripping experiments were carried out at ambient temperature  $25 \pm 1^\circ C$ . In all experiments the phase ratio was kept at 1 except otherwise stated.

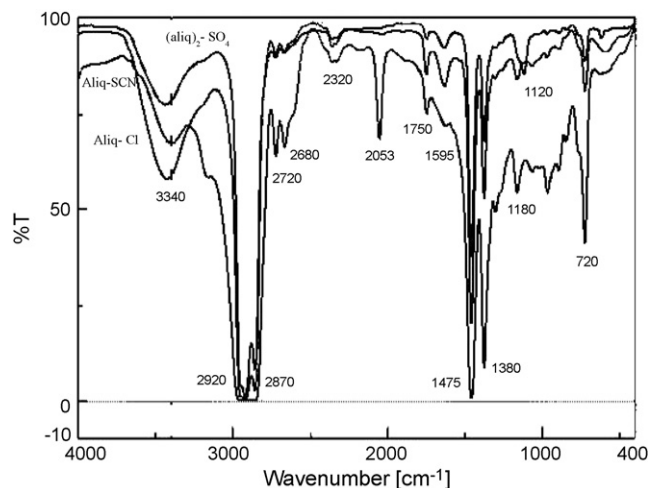


Fig. 1. FT-IR spectra of  $R_4N-Cl$ ,  $R_4N-SCN$  and  $(R_4N)_2-SO_4$ . ( $[R_4N-Cl]$ : 0.36 M,  $[R_4N-SCN]$ : 0.36 M,  $[(R_4N)_2-SO_4]$ : 0.36 M.)

**Table 1**  
Metal content in the anode and cathode of spent Ni–MH battery.

Element	Ni	Co	Ln(III)	Fe	Zn	Al	Mn
Content, g	5.56	0.43	1.47	0.70	0.19	0.10	0.25

The distribution ratio,  $D$ , was calculated from the relation:

$$D = \frac{C_o - C}{C} \quad (1)$$

where,  $C_o$  is the original metal ion concentration in the aqueous phase before extraction and  $C$  is the metal concentration in the aqueous phase after extraction.

The separation feasibility of Co(II) from Ni(II) was evaluated in terms of the separation factor,  $S_{(Co/Ni)}$ , between Co(II) and Ni(II) and defined by the following equation;

$$S_{(Co/Ni)} = \frac{D_{Co}}{D_{Ni}} \quad (2)$$

In the application section, cylinder-shaped Ni–MH batteries (Siemens, XNTY type, 650 mAh) were used. The cells weighed an average of 11.95 g each. Analysis of the anode and cathodes showed that the components are mainly composed of nickel (63.9%), cobalt (5%), lanthanides (16.9%), iron (8.0%), zinc (2.18%), aluminum (1.15%) and manganese (2.87%), Table 1. The leaching process of Ni–MH battery was carried out by adding 8.7 g from the anode and cathode, the weight of the positive electrode was about 3.5 g and that of the negative electrode was about 5.2 g, to 55.0 g of 2.0 M  $H_2SO_4$  in a 500 ml flask under electromagnetic stirring (350 rpm) for 3.0 h at 80 °C. After leaching, the leach solution and the reminder residue were separated by filtrations. Analyses for cobalt content were determined in the leach solution by atomic absorption. After leaching, the small amount of the insoluble residue ( $\approx 0.4$  g) was filtrated and washed with water. The resulting liquor solution was a dark green solution of pH about 2.4. The leaching efficiency of cobalt, nickel, iron and lanthanides was 99%, 95%, 99% and 96%, respectively.

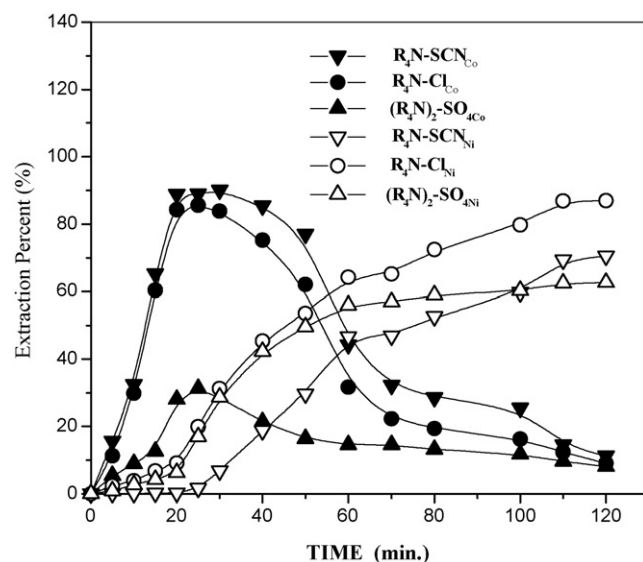
The extraction process which applied on the leaching solution that contains both Co(II), Ni(II) and other impurities was carried out by  $R_4N-SCN$  and  $R_4N-Cl$ . In each route, the scrubbing and stripping processes were investigated by different reagents.

### 3. Results and discussion

#### 3.1. Extraction of Co(II) and Ni(II) from sulfate solution

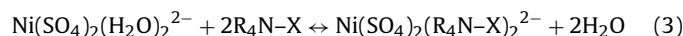
##### 3.1.1. Effect of agitation time

To study the effect of mixing time on the extraction of Co(II) and Ni(II), an aqueous sulfate solution (pH 5.6) containing 0.01 M of Co(II) and Ni(II) and an organic phase of 0.36 M Aliquat 336 in kerosene in the forms of chloride ( $R_4N-Cl$ ), thiocyanate ( $R_4N-SCN$ ) and sulfate ( $(R_4N)_2-SO_4$ ) were contacted at a 1:1 phase ratio for various mixing periods of time from 0 min to 120 min at 25 °C, Fig. 2. The data obtained shows that for Co(II), the extraction increases with the increase in contact time to reach a maximum extraction percent with a plateau within 20–30 min. This is followed by a gradual decrease in the extraction of cobalt. In case of nickel, the extraction was found to increase slowly to reach a maximum value after 110–120 min with a plateau. Preston [22] reported that Ni(II) in the aqueous sulfate solution is present as a hydrated octahedral sulfate complex as  $Ni(SO_4)_2(H_2O)_2^{2-}$  entity. Further, he stated that the poor extractability of the Ni(II) complex compared with that of Co(II) is due to the greater secondary aequation of the former resulting from the presence of the two coordinated water molecules. This can also affect the extraction kinetics of Ni(II). Unfortunately, he did not mention the time of equilibration in his work. Further, the fol-



**Fig. 2.** Effect of time on the extraction of Co(II) and Ni(II) from sulfate media by different Aliq-forms. [Co(II)], [Ni(II)]: 0.01 M, pH 5.6, [Aliquat 336]: 0.36 M in kerosene (O/A): 1. temp.: 25 °C.

lowing mechanism can be proposed for extraction of Ni, where with nitrogen donor ligand replacement of the water molecules in the octahedral  $Ni(SO_4)_2(H_2O)_2^{2-}$  by the hydrophobic amine entities, could exist,



where X is  $Cl^-$ ,  $SCN^-$  or  $1/2SO_4^{2-}$ .

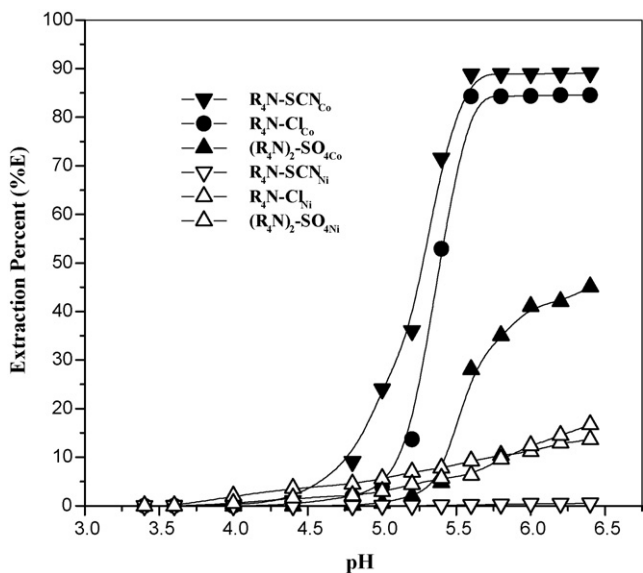
The gradual decrease in the extraction of cobalt which is accompanied by gradual increase in the extraction of nickel can be explained by the competition between cobalt and nickel and by a progressive replacement of the cobalt by nickel as nickel is loaded into the organic phase [26]. While the extraction of cobalt is relatively fast, it is well known that generally the extraction of nickel is quite slow [26]. Therefore, the equilibrium of Co(II) in sulfate medium at 20 min in presence of Ni(II) was studied. From the obtained data, the separation factor was calculated for each case and the higher separation values were found at 20 min, at the equilibrium time proposed for Co(II). Subsequently, the effects of different parameters on the extraction were carried out at 20 min.

Further, it is found that the sequence of the extraction of cobalt in terms of the different forms of Aliquat 336 is the following;  $R_4N-SCN > R_4N-Cl > (R_4N)_2-SO_4$ , while that of nickel is  $R_4N-Cl > (R_4N)_2-SO_4 > R_4N-SCN$ .

##### 3.1.2. Effect of pH

The extraction of Co(II) and Ni(II) was studied from aqueous sulfate solutions containing 0.01 M metal ions each by 0.36 M  $R_4N-Cl$ ,  $R_4N-SCN$  and  $(R_4N)_2-SO_4$  after 20 min mixing at a 1:1 phase ratio at different pH values ranged from 0.0 to 6.5. It was found that, for the different  $R_4N$ -forms, the extraction for cobalt was higher than that for nickel in the pH range from 3.4 to 6.5. The data were plotted in Figs. 3–5. For the extraction of cobalt and nickel, the extraction percent of cobalt is higher for  $R_4N-SCN$  and  $R_4N-Cl$  compared to that obtained for  $(R_4N)_2-SO_4$  while the extraction percent for nickel is highest with  $(R_4N)_2-SO_4$  but lowest with  $R_4N-SCN$ .

From the data obtained in Fig. 3, it can be observed that in the pH ranging from 0.0 to 3.4 the extraction of either cobalt or nickel was negligible, but as pH increased above 3.4 the extraction of both metal ions started to increase with gradual increase in pH up to 5.6, the percentage extraction in case of cobalt increased up to 88.8%, 84.3% and 28% for  $R_4N-SCN$ ,  $R_4N-Cl$  and  $(R_4N)_2-SO_4$ , respectively.



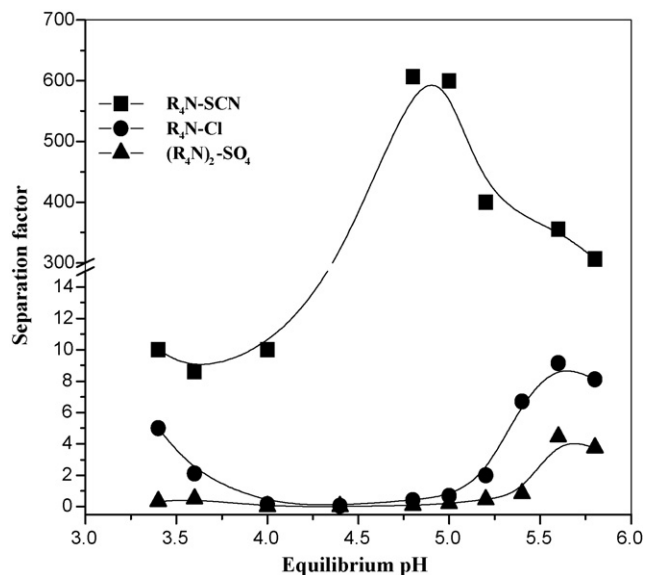
**Fig. 3.** Effect of pH on extraction percent of Co(II) and Ni(II) by 0.36 M  $R_4N-SCN$ ,  $R_4N-Cl$  and  $(R_4N)_2-SO_4$ . [Co(II)], [Ni(II)]: 0.01 M time: 20 min, [Aliquat 336]: 0.36 M in kerosene (O/A): 1, temp.: 25 °C.

While in case Ni(II), the extraction percent was slightly increased with increasing pH (pH 3.4–6.4) to 0.51%, 13.6% and to 16.7% for  $R_4N-SCN$ ,  $R_4N-Cl$  and  $(R_4N)_2-SO_4$ , respectively.

Fig. 3 shows the extraction increases with the increase in the pH of the aqueous phase. The difference of extraction values states that it is possible to separate Co(II) from Ni(II) in a suitable pH range by different forms of Aliquat 336.

Fig. 4 is a plot of  $\log D$  versus pH for extraction of cobalt with a slope of nearly 2.0 indicating the release of two moles of  $H^+$  from the aqueous phase which is responsible for extraction of Co(II) or Ni(II) from  $H_2SO_4$  solution.

As shown in Fig. 5, the separation factor,  $S_{(Co/Ni)}$ , increases for  $R_4N-SCN$  with the increase in pH to reach a maximum value of 606.7 at pH 4.8. Lower separation factors were obtained for the two other extraction systems studied within the pH range investigated. The value of separation factor obtained for the thiocyanate system in the work, 606.7, is higher than that reported by others in the literature for extraction of Co(II) and Ni(II) from sulfate solution [2,4,27].



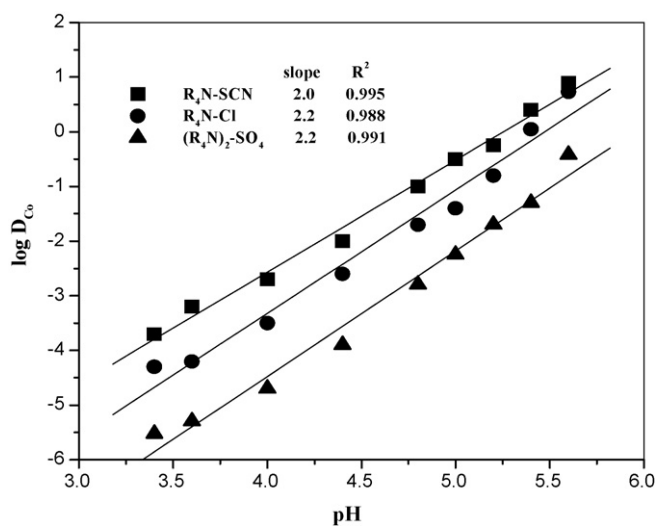
**Fig. 5.** Effect of equilibrium pH on separation factor of cobalt and nickel by 0.36 M  $R_4N-SCN$ ,  $R_4N-Cl$  and  $(R_4N)_2-SO_4$ . Co(II), [Ni(II)]: 0.01 M time: 20 min, [Aliquat 336]: 0.36 M in kerosene (O/A): 1, temp.: 25 °C.

### 3.1.3. Effect of sulfate concentration

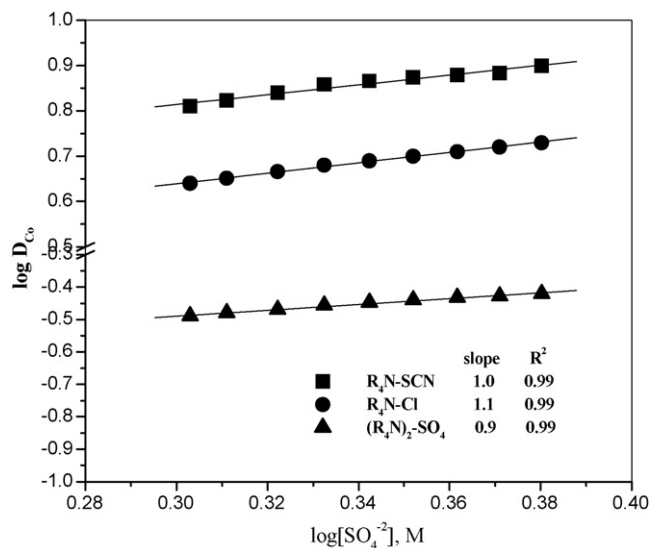
The effect of sulfate concentration on the extraction of cobalt and nickel was studied using 0.36 M of different  $R_4N$ -forms diluted in kerosene at constant  $H_2SO_4$  concentration (2.0 M) containing different sodium sulfate concentrations in the range from 0.01 to 0.4 M sulfate and shown as log–log relation in Fig. 6. The results obtained show that as the sulfate concentration increases the extraction of cobalt increases with a slope of unity. This means that one mole of sulfate from the aqueous sulfate solution is required for extraction of one mole of metal ion.

### 3.1.4. Effect of extractant concentration

The effect of Aliquat 336 in the different investigated forms, on the extraction of Co(II) from aqueous sulfate solution containing  $Na_2SO_4$  and  $H_2SO_4$  was studied with different extractant concentrations 0.018–0.36 M. The experimental data for  $\log D$  for Co(II) versus log different extractants concentrations were plotted in



**Fig. 4.** Plot of  $\log D$  for Co(II) vs. pH. [Co(II)], [Ni(II)]: 0.01 M time: 20 min, [Aliquat 336]: 0.36 M in kerosene (O/A): 1, temp.: 25 °C.



**Fig. 6.** Plot of  $\log D_{Co}$  vs.  $\log[SO_4^{2-}]$ . [Co(II)], [Ni(II)]: 0.01 M time: 20 min, [Aliquat 336]: 0.36 M in kerosene (O/A): 1, temp.: 25 °C, pH 4.8.



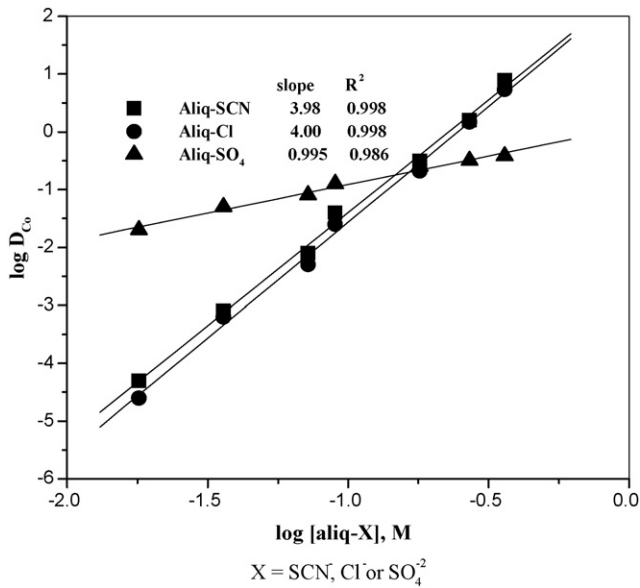
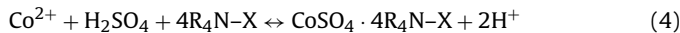


Fig. 7. Plot of  $\log D_{Co}$  vs.  $\log [\text{aliq-X}]$ ,  $[X = \text{SCN}^-, \text{Cl}^- \text{ or } \text{SO}_4^{2-}]$ .  $[\text{Co(II)}], [\text{Ni(II)}]: 0.01 \text{ M}$  time: 20 min, [Aliquat 336]: 0.36 M in kerosene (O/A): 1, temp.: 25 °C, pH 4.8.

Fig. 7. It was observed that the extraction of Co(II) increased with an increase in extractant concentration from 0.018 to 0.36 M. The plots, in Fig. 7, illustrates the slopes of nearly four for  $R_4N\text{-SCN}$  and  $R_4N\text{-Cl}$  and one for  $(R_4N)_2\text{-SO}_4$  form. These indicate the association of four moles of the  $R_4N\text{-SCN}$ ,  $R_4N\text{-Cl}$  and one moles for  $(R_4N)_2\text{-SO}_4$  for extraction of one mole of Co(II) into the organic phase. Some of these results agree with that reported before [21,22].

3.1.5. Extraction mechanism of cobalt

Quaternary ammonium extractants can extract metal ions by two mechanisms, namely by addition reactions or anion exchange [7,21]. Therefore and based on slope analysis of the experimental results, two different mechanisms are proposed for the extraction equilibrium of cobalt. Extraction of cobalt from sulfate medium by  $R_4N\text{-SCN}$  and  $R_4N\text{-Cl}$  can be given by the following equilibrium;



where, X is SCN or Cl.

In this reaction, cobalt is extracted by addition, where cobalt expanded its coordination numbers and coordinated to SCN or Cl attached to Aliquat 336. In this case, the extraction constant is given by the following;

$$K_{ex} = [\text{CoSO}_4 \cdot 4R_4N\text{-X}][\text{H}^+]^2[\text{Co}^{2+}]^{-1}[\text{H}_2\text{SO}_4]^{-1}[R_4N\text{-X}]^{-4} \quad (5)$$

$$K_{ex} = D[\text{H}^+]^2[R_4N\text{-X}]^{-4} \quad (6)$$

Under the experimental conditions investigated, the slope of the relation given in Fig. 6 supports the presence of one mole of  $[\text{SO}_4^{2-}]$  with Co(II) in the extracted species. Further, the slopes of the relations given in Fig. 7 indicate that in case of  $R_4N\text{-SCN}$  and  $R_4N\text{-Cl}$  the presence of four moles of the extractant in the extracted species. In this reaction Co(II) is extracted by addition reaction with the quaternary amine Aliquat-336. Therefore, the main extracted species of Co(II) for the  $R_4N\text{-SCN}$  and  $R_4N\text{-Cl}$  systems are  $(R_4N\text{-SCN})_4 \text{CoSO}_4$  and  $(R_4N\text{-Cl})_4 \text{CoSO}_4$ , respectively, with respective average extraction constants equal to  $790.0 \pm 9.4$  and  $531.6 \pm 12.4$ .

For the extraction of cobalt from sulfate medium by  $(R_4N)_2\text{-SO}_4$  the extraction equilibrium can be represented by the following equation;

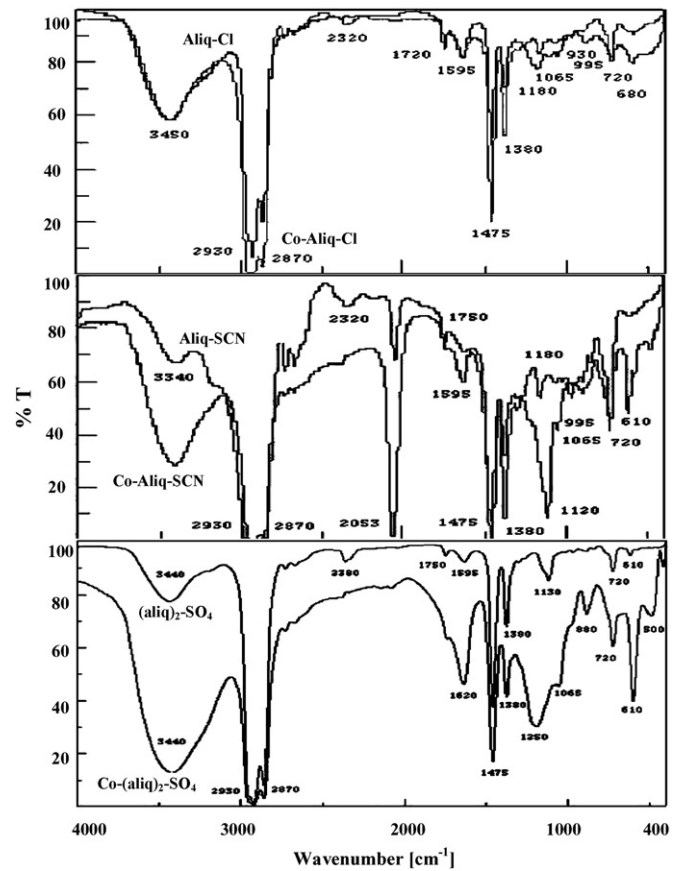
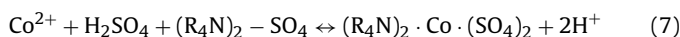


Fig. 8. FT-IR spectra of different  $R_4N$ -forms extractants and their complexes with cobalt.  $\text{Co(II)}: 0.01 \text{ M}$  time: 20 min, [Aliquat 336]: 0.36 M in kerosene (O/A): 1, temp.: 25 °C, pH 4.8.

In this reaction,  $[\text{Co}(\text{SO}_4)_2]^{2-}$  is extracted as ion pair with the quaternary amine Aliquat-336.

The extraction constant of this reaction is given by the following;

$$K_{ex} = [(R_4N)_2 \cdot \text{Co} \cdot (\text{SO}_4)_2][\text{H}^+]^2[(R_4N)_2\text{-SO}_4]^{-1}[\text{H}_2\text{SO}_4]^{-1}[\text{Co}^{2+}]^{-1} \quad (8)$$

Or

$$K_{ex} = D[\text{H}^+]^2[(R_4N)_2\text{-SO}_4]^{-1} \quad (9)$$

From the results obtained, the slope of the relation given in Fig. 6 supports the presence of one mole of  $[\text{SO}_4^{2-}]$  with Co(II) in the extracted species. Further, the slope of the relations given in Fig. 7 indicate that in case of  $(R_4N)_2\text{-SO}_4$ , the presence of one mole of  $(R_4N)_2\text{-SO}_4$  in the extracted species. Therefore, the main extracted species of Co(II) is  $(R_4N)_2 \cdot \text{Co} \cdot (\text{SO}_4)_2$  with respective average extraction constant equal to  $1.76 \pm 0.004$ .

To characterize the extracted metal ion-complexes, the FT-IR spectra of different Aliq-forms and their complexes with cobalt were carried out, Fig. 8. Comparing the spectra before and after the extraction for the three  $R_4N$ -forms studied, it is clear that after the extraction of Co(II) the absorption bands recorded before extraction remain, but new absorption bands at 1065 and 955  $\text{cm}^{-1}$  for cobalt(II) are resulted [28]. A band at 1130–1080  $\text{cm}^{-1}$  due to  $\text{SO}_4^{2-}$  stretching vibration were observed after the extraction process by the different extractant forms especially for  $R_4N\text{-SCN}$  and  $(R_4N)_2\text{-SO}_4$ . Additionally, the spectrum of the extractants–metal complexes exhibits a wide and strong

**Table 2**  
Effect of temperature on extraction percent of Co(II) and Ni(II) by 0.36 M R<sub>4</sub>N–SCN, R<sub>4</sub>N–Cl and (R<sub>4</sub>N)<sub>2</sub>–SO<sub>4</sub>.

T (°C)	Extraction percent (%)					
	R <sub>4</sub> N–SCN <sub>(Co)</sub>	R <sub>4</sub> N–Cl <sub>(Co)</sub>	(R <sub>4</sub> N) <sub>2</sub> –SO <sub>4</sub> (Co)	R <sub>4</sub> N–SCN <sub>(Ni)</sub>	R <sub>4</sub> N–Cl <sub>(Ni)</sub>	(R <sub>4</sub> N) <sub>2</sub> –SO <sub>4</sub> (Co)
25	88.8	84.3	28	0.25	9.2	6.3
35	91.6	84.3	34	0.24	9.1	6.2
40	91.5	84.4	34	0.2	8.6	6
45	91.5	84.4	34	0.18	8.4	5.7
60	91.4	84.3	33.9	0.15	8.2	5.3
70	91.4	84.3	34	0.11	7.6	4.7

absorption band 3500–3300 cm<sup>-1</sup> indicating the presence of H<sub>2</sub>O molecules in the extracted species [25].

### 3.1.6. Effect of temperature

To study the effect of temperature on extraction of cobalt and nickel, different experiments were carried out in the range 20–70 °C with a mechanical stirring for 20 min. It can be observed from Table 2 that in case of cobalt, the extraction rises up to 35 °C and the values of extraction percent remained nearly constant when the temperature is higher than 35 °C. While for nickel, extraction decreases with the increase of temperature throughout the temperature range studied.

### 3.2. Stripping investigations

Stripping studies were carried out on organic solution consisting of 0.36 M R<sub>4</sub>N–SCN in kerosene after extraction of 0.01 M Co(II) and Ni(II) from sulfate solution of pH 5.6. The effect of water temperature, 25–60 °C, HCl as well as H<sub>2</sub>SO<sub>4</sub> concentrations on the stripping of metals ion from the loaded organic extractant was investigated and the results are given in Table 3. The data obtained show that hot water, 60 °C, and dilute H<sub>2</sub>SO<sub>4</sub> can be considered as good stripping agents as it could lead to good recovery and separation of Co(II) from the loaded R<sub>4</sub>N–SCN. The stripped cobalt recovered in solution was further precipitated as a cobalt oxalate precipitate, by the addition of 10 g oxalic acid. Then, the subsequently roasting cobalt oxide is obtained by the calcination solids at 500 °C. The results obtained show that the percentage precipitation of cobalt was up to 98% with less than 2% of nickel.

**Table 3**  
Stripping of Co(II) and Ni(II) with water at different temperatures and different concentrations of H<sub>2</sub>SO<sub>4</sub> and HCl from loaded 0.36 M R<sub>4</sub>N–SCN solutions at O/A ratio of unity.

Stripping agent	Stripping % Co(II)	Stripping % Ni(II)
Water (°C)		
25	10.5	2.3
35	28.6	8.7
45	81.6	11.6
50	96.7	13.7
60	98.9	16.9
70	>99.9	18.7
HCl, M (at 25 °C)		
0.1	18.6	1.3
0.5	47.4	6.9
1.0	67.6	35.6
2.0	98.7	96.1
3.0	>99.9	>99.9
H <sub>2</sub> SO <sub>4</sub> , M (at 25 °C)		
0.01	23.5	8.4
0.05	45.8	9.8
0.1	59.8	11.3
0.2	76.5	28.4
0.5	88.9	29.8
0.6	91.7	34.8
0.8	94.6	77.8
1.0	99.8	99.1
2.0	>99.9	>99.9

### 3.3. Recovery of Co, Ni and lanthanides from spent Ni–MH batteries leach solution

Based on the results obtained, a flow sheet for separation of Co, Ni and Ln was developed and tested. In this concern, R<sub>4</sub>N–SCN has been chosen in preference to the other two R<sub>4</sub>N-forms for extraction of Co(II) from leaching solution and R<sub>4</sub>N–Cl has been used for the extraction of Ni(II). After leaching one cell of the batteries electrodes by 2 M sulfuric acid, the resulted leaching solution was found to contain 0.425 g cobalt, 5.28 g nickel, 0.7 g iron and 1.41 g lanthanides with 0.49 g of other impurities.

The extraction process for Co(II) was carried out by using 0.36 M R<sub>4</sub>N–SCN in kerosene at 25 °C with O/A ratio of unity for 20 min. Under these conditions, the organic phase was separated and the aqueous phase was analyzed. The results obtained indicated that the extraction percentages are 87.5% cobalt, 3.5% nickel, 89% iron, and 7.3% lanthanides together with less than 22% of other metal impurities. The organic phase was scrubbed with equal volume of 0.1 M HCl to remove iron and other impurities (except Ln) this was followed by scrubbing with 0.4 M HNO<sub>3</sub> to strip lanthanides. Stripping of pure cobalt from the organic phase was carried out using water at 50 °C. The stripped solution contained >0.34 g cobalt, <0.01 g nickel, <<0.01 g iron and <<0.01 g lanthanides, Table 4. Cobalt was further removed from the stripper solution as a cobalt oxalate precipitate by addition of 10 g oxalic acid. Then, the subsequently roasting cobalt oxide was obtained by the calcination solids at 500 °C for 3 h. The resulted oily green powder obtained showed that the percentage precipitation of Co was >99.5% (0.34 g), <0.02% (<0.006 g) of nickel and <0.1% (<0.01 g) lanthanides, Fig. 9, route A. The X-ray diffraction pattern of the product CoO is shown in Fig. 10.

The aqueous phase produced from cobalt extraction R<sub>4</sub>N–SCN containing mainly nickel and lanthanides was subjected to extrac-

**Table 4**  
Stripping of Co(II) and other metals leached from Ni–MH battery from loaded 0.36 M R<sub>4</sub>N–SCN solution in kerosene by water at different temperatures at A/O = 1 and A/O = 2.

Stripping agent	Stripping percent (%)						
	Co	Ni	Fe	Zn	Al	Mn	Ln
H <sub>2</sub> O, T (°C)							
A/O = 1							
25	10.2	–	–	–	–	–	0.8
35	25.2	1.2	–	–	–	–	1.0
40	77.6	4.9	–	–	–	–	1.0
50	92.4	6.7	1.3	–	–	–	1.0
60	97.4	11.2	9.9	1.2	0.6	0.1	2.1
70	>99.9	13.7	14.6	2.7	2.2	2.1	8.6
80	>99.9	28.9	46.9	12.8	3.4	2.8	14.
A/O = 2							
25	19.4	0.2	–	–	–	–	0.9
35	36.8	1.9	–	–	–	–	1.2
40	86.8	6.2	2.8	0.8	0.4	–	1.3
50	98.6	9.3	1.7	1.6	0.7	–	1.5
60	>99.9	28.6	21.4	4.5	2.7	2.2	4.6
70	>99.9	39.7	36.8	9.9	10.4	3.6	14.9
80	>99.9	57.8	67.8	18.2	12.6	3.9	16.8

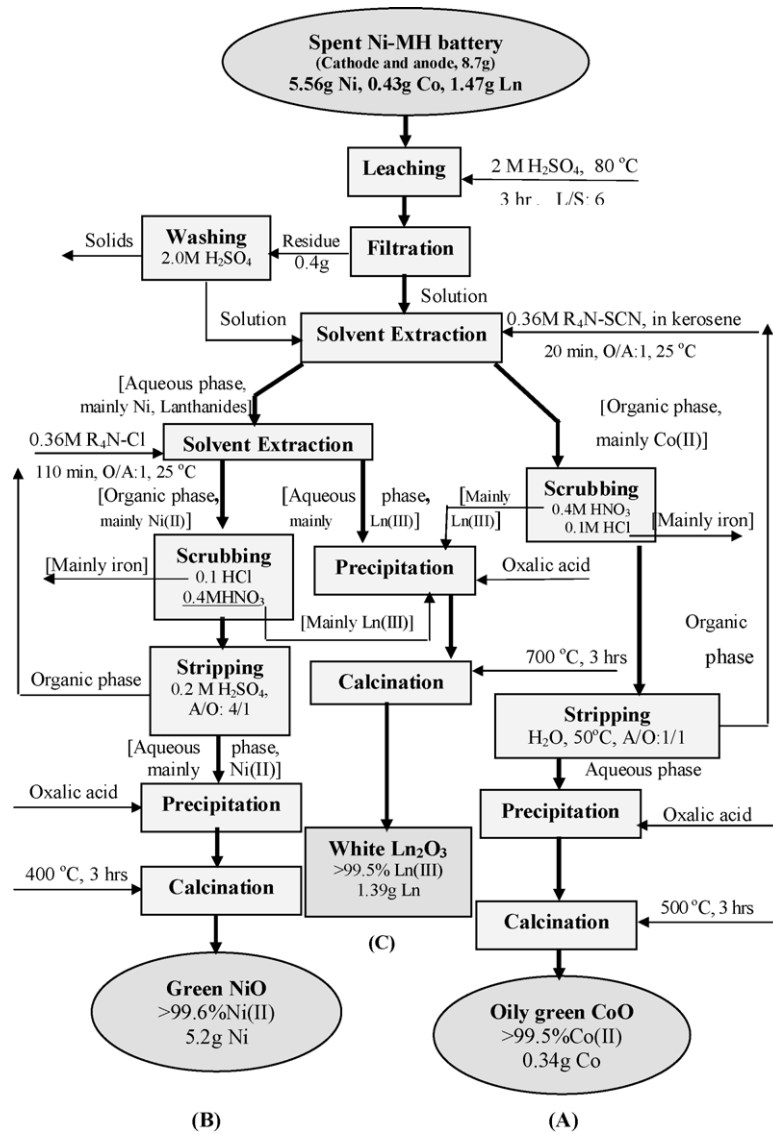


Fig. 9. Flow sheet for the recovery of Co(II), Ni(II) and Ln(III) from spent Ni–MH battery.

tion with 0.36 M  $R_4N-Cl$  for 110 min mixing with phase ratio of 1.0 at 25 °C. The organic phase was scrubbed with 0.1 M HCl to remove iron and other impurities except Ln(III). This was followed by scrubbing with 0.4M  $HNO_3$  to strip lanthanides. Stripping of pure Ni from the organic phase was achieved by 0.02 M  $H_2SO_4$  solu-

tion using organic/aqueous ratio of 1/4 at room temperature. The resulted organic phase was reused again in further solvent extraction process and the metals ions in the resulted aqueous phase were precipitated by 25 g oxalic acid and calcinated at 400 °C for 3 h. The resulted green powder obtained show that the percentage of nickel was >99.6% (5.2 g),  $\ll 0.3\%$  ( $\leq 0.001$  g) of iron and  $\ll 0.1\%$  ( $\leq 0.01$  g)

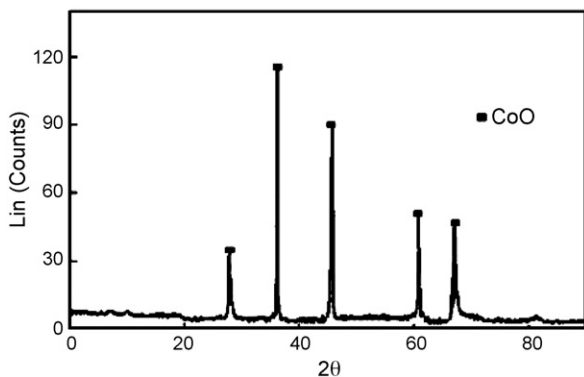


Fig. 10. XRD patterns of CoO.

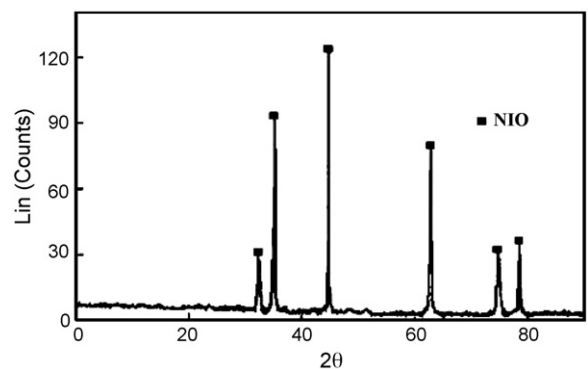


Fig. 11. XRD patterns of NiO.

lanthanides. The X-ray diffraction pattern of the product NiO is shown in Fig. 11.

Aqueous phase separated from extraction process by  $R_4N-Cl$  (route B) together with the scrubbing solution resulted from the same route (B), and the 0.4 M  $HNO_3$  scrubbing solution resulted from route (A), which contain mainly lanthanides(III), were collected. 15 g oxalic acid was added to this solution to precipitate the oxalate of the Ln ions. The resulted precipitate was calcinated at  $700^\circ C$  for 3 h. The resulted white powder obtained showed that the percentage of lanthanides was  $>99.7\%$  (1.39 g) and  $\ll 0.3\%$  ( $<0.001$  g) of iron (route C).

Chemical analyses of these products were found as the following:

- Cobalt was  $\gg 99.5\%$ ,  $\ll 0.02\%$  of nickel and  $\ll 0.1\%$  lanthanides, (route A).
- Nickel was  $\gg 99.6\%$ ,  $\ll 0.3\%$  of iron and  $\ll 0.1\%$  lanthanides, (route B).
- Lanthanides was  $\gg 99.7\%$  and  $\ll 0.3\%$  of iron (route C).

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