Spent NiMH batteries—The role of selective precipitation in the recovery of valuable metals

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ABSTRACT

The production of electronic equipment, such as computers and cell phones, and, consequently, batteries, has increased dramatically. One of the types of batteries whose production and consumption has increased in recent times is the nickel metal hydride (NiMH) battery. This study evaluated a hydrometallurgical method of recovery of rare earths and a simple method to obtain a solution rich in Ni–Co from spent NiMH batteries. The active materials from both electrodes were manually removed from the accumulators and leached. Several acid and basic solutions for the recovery of rare earths were evaluated. Results showed that more than 98 wt.% of the rare earths were recovered as sulfate salts by dissolution with sulfuric acid, followed by selective precipitation at pH 1.2 using sodium hydroxide. The complete process, precipitation at pH 1.2 followed by precipitation at pH 7, removed about 100 wt.% of iron and 70 wt.% of zinc from the leaching solution. Results were similar to those found in studies that used solvent extraction. This method is easy, economic, and does not pose environmental threats of solvent extraction.

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1. Introduction

The importance of information technology for the global economy has dramatically increased the demand for electronic equipment, such as computers and cell phones, and, consequently, batteries. Since the introduction of mobile telephony in Europe, the United States, and Japan in the early 1950s, the demand for this service has increased continuously, and the latent demand for mobile telecommunication services has been very strong for decades [1].

In Brazil, according to the Brazilian Electrical and Electronics Industry Association, a law that recently came into effect, known as the "Goods Law", reduced taxes on personal computers (PC) and notebook computers, created favorable conditions for the low-income population to avail finance for computers, and heated up sales. Telecommunications also grew significantly in the first quarter of 2008. The growth of the mobile telephony market contributed to this performance and pointed to good prospects for the next months, particularly due to the third-generation technology that increased the demand for new equipment. The number of mobile accesses reached 125.8 million at the end of March 2008 (65.9

accesses per 100 inhabitants). A comparison with the end of 2007, when mobile accesses totaled 121.0 million (63.6 accesses per 100 inhabitants), showed an increase of 3.8% [2].

Businesses in the sphere of computer sciences were still growing in the beginning of 2008. In the 1st quarter, PC sales were 26% greater than that in the same period of 2007 and reached 2510-thousand units: 1846-thousand desktop computers and 664-thousand notebook computers, with notebook sales increasing by a remarkable 165% in the same period [2].

All materials in a battery contribute to environmental pollution when discarded. Some of them, such as carbon, are not very detrimental to the environment and quickly merge into the ecosystem without noticeable impact. Other components, such as steel, plastics, and fabric, although not so actively toxic to the ecosystem, add to the volume of landfills because they decompose slowly. Of most concern, however, is the disposal of heavy-metal battery components, which, when discarded, can be toxic to plants, animals, and humans. Cadmium, lead, and mercury are the heavy metals most probable to raise environmental concerns [3].

Nickel metal hydride (NiMH) batteries are environmentally acceptable because they do not contain highly toxic metals, and they have replaced NiCd batteries in many devices because of their better performance [4]. The NiMH-operating system is similar to that of NiCd, but the Cd electrode is replaced with one of MH. Examples of M alloys are AB_2, which is an alloy of $TiNi_2$, and AB_5, which is a $LaNi_5$ alloy [5]. For economic reasons, La is often replaced with a rare-earth alloy [6].

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Table 1
X-ray fluorescence analysis of the negative and positive electrodes.

Metals	Electrodes	
	Negative	Positive
Ce	23.06	–
La	20.33	0.78
Nd	9.09	–
Pr	0.96	–
Ni	10.60	32.56
Co	20.31	26.20
Mn	11.05	3.12
K	2.14	15.27
Fe	1.25	0.57
Zn	0.66	19.60
Others	0.53	1.74

Large numbers of batteries are currently produced, and annual production volumes tend to grow. An example of this trend is the manufacture of electrical vehicles that do not generate environmental emissions. Their success will depend on the correct choice of an energy source, and NiMH batteries appear to be an excellent alternative [7–12]. On April 30, 2008, the Japanese company Toyota celebrated the first one-million mark of the sale of Prius cars in the world. This hybrid car uses NiMH batteries. Toyota plans to sell more than one-million hybrid cars a year by 2010 [13].

With the increase in the generation of spent NiMH batteries, recycling of their metal contents should be studied to avoid the disposal of tons of dangerous waste in the environment [14]. Because of the economic value of metals such as nickel, cobalt, and rare earths, efficient recycling processes should be developed to achieve the goals of waste minimization. Recycling this type of waste may bring environmental profits, in addition to economic benefits.

This study was divided into two phases. The purpose of the first phase was to evaluate the recovery of rare earths by selective precipitation and to determine the optimal pH range for precipitation. The second phase consisted of the purification of the solution obtained after recovery of rare earths to produce a solution rich in Ni–Co containing a low concentration of contaminants, such as Zn, Fe, and Mn. A review of literature showed that several studies suggest solvent extraction using different process parameters and different organic compounds for the recovery of rare earths and removal of contaminants [15,16].

The method described in this study is a simple alternative to the use of solvent extraction. Ni and Co can be recovered from the purified solution using an electrochemical process from which Ni–Co alloys of different compositions can be obtained [17–20].

2. Materials and methods

The active electrode material used in this study was a dark powder manually removed from the accumulators. Because the rare earths are sensitive to air, before removing the active electrode material from the accumulators, a small lateral gap was produced using a saw. This gap allows only a small amount of air to come in contact with the electrode material, thus reducing the rate of oxidation. If the entire electrode material is exposed to air, the material tends to ignite rapidly. In nonexperimental situations, this powder can be obtained using a mechanical process, which separates the active electrode materials from other materials, such as steel, plastics, and fabrics. Details about this mechanical process are described in a previous study [21]. The semiquantitative analysis of electrodes, presented in Table 1, shows that the resulting powder contains valuable metals, such as rare earths, nickel, and cobalt.

2.1. Rare-earth precipitation

The dark powder removed from the accumulators was dried and leached using different acid solutions: sulfuric, nitric, and hydrochloric acid solutions and aqua regia. The powder mass used in each experiment was 5 g. Leaching time was 30 min at room temperature. The concentration of the various solutions was 2 M.

NaOH and KOH solutions were used for the precipitation tests, both at 5 M concentrations. The initial pH values of all solutions that were obtained after leaching were approximately zero. In the precipitation tests, NaOH and KOH solutions were added to the different acid systems until the precipitate appeared. For the sulfuric acid solution, the final pH for precipitate formation was nearly 1. For the other systems, the precipitate only formed at a pH of approximately 7.

After the identification of precipitates in the different acid solutions, fresh tests were conducted using a 2 M sulfuric acid solution. The tests with sulfuric acid had the best results for the recovery of rare earths. Therefore, this new sequence of tests was used to define the ideal pH range for rare-earth precipitation.

The solid-to-liquid ratio used for leaching was about 1:20 (w/v). After 4 h at 90 °C, the unleached material was filtered. The solution obtained had a pH of approximately zero, and rare earths were precipitated by adding a 5 M NaOH solution. The pH values used for evaluations were 0.8, 1.0, 1.2, 1.4, and 1.6. This pH range was selected to avoid the precipitation of iron hydroxide, which usually begins at a pH of about 2.5–3.0. X-ray fluorescence (XRF) was used for the qualitative and semiquantitative chemical analyses of the precipitates obtained at different pH values and with different acid systems. All the precipitate samples were dried before each analysis. The precipitate obtained at pH 1.6 had its crystalline phases
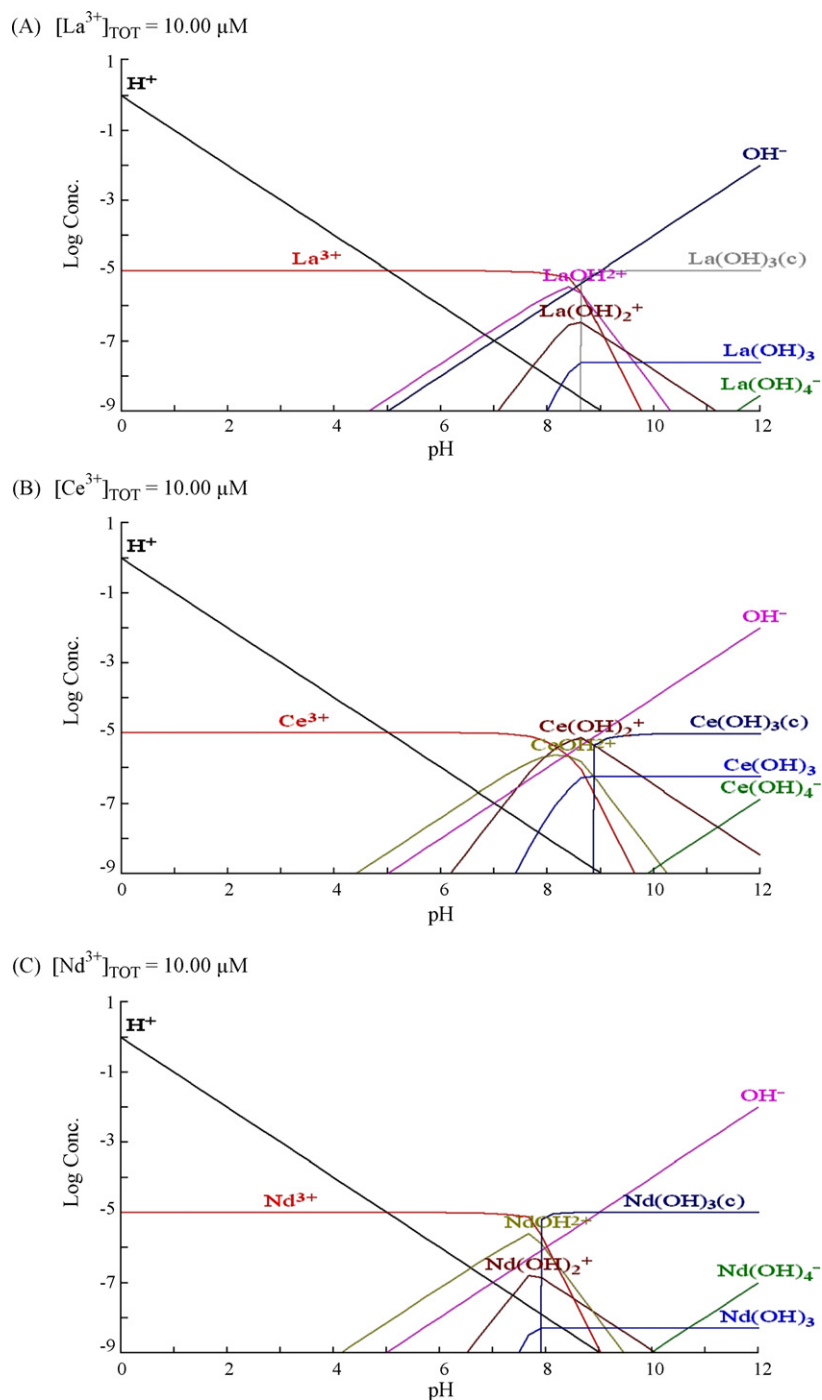
Table 2
Characteristics of the precipitates obtained.

	Solutions					Solutions			
	H_2SO_4	HNO_3	HCl	Aqua-regia		H_2SO_4	HNO_3	HCl	Aqua-regia
	pH ≈ 1	pH ≈ 7	pH ≈ 7	pH ≈ 7		pH ≈ 1	pH ≈ 7	pH ≈ 7	pH ≈ 7
Chemical analysis of precipitates obtained using KOH (%)					Chemical analysis of precipitates obtained using NaOH (%)				
Nd	32.27	3.90	2.09	3.64	Nd	34.74	4.27	4.50	2.43
La	30.88	1.81	0.84	1.80	La	36.00	2.73	1.63	1.65
Ce	14.15	–	–	–	Ce	21.53	–	–	–
Ni	10.80	36.54	47.86	34.77	Ni	3.22	56.39	76.21	74.46
K	7.87	30.78	27.44	25.08	K	0.70	0.26	–	–
Pr	4.02	1.69	–	0.23	Pr	3.82	0.50	0.32	0.01
Co	–	2.70	3.42	2.71	Co	–	5.31	7.93	3.99
Fe	–	22.58	18.36	31.76	Fe	–	29.28	8.92	17.16
					Mn	–	1.25	0.49	–

(A) $[La^{3+}]_{TOT} = 10.00\ \mu M$

(B) $[Ce^{3+}]_{TOT} = 10.00\ \mu M$

(C) $[Nd^{3+}]_{TOT} = 10.00\ \mu M$

Fig. 1. Elemental speciation diagram, according to the pH values, of lanthanum (A), cerium (B), and neodymium (C) [22].

identified by X-ray diffraction (XRD), recorded in the interval of $5° < 2\theta < 80°$.

2.2. Leaching efficiency using sulfuric acid

After the identification of sulfuric acid as the most efficient solution for the recovery of rare earths by precipitation, fresh tests were conducted to evaluate its efficiency in the dissolution of electrodes. In this phase, the active material from both positive and negative electrodes was manually homogenized and leached with $2\ M\ H_2SO_4$ solution at $90\,°C$ for 4 h under constant stirring. In this stage, a 1:20

solid-to-liquid ratio was used: in 1 l of solution, 50 g of powder were present. After leaching, the insoluble residue was filtered and rinsed with water.

The concentration of chemical elements in the electrodes was determined by complete dissolution in aqua regia at $90\,°C$ at a solid-to-liquid ratio of 1:20. Results of leaching with sulfuric acid were compared with those obtained using aqua regia. The concentration of rare earths was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The concentrations of Ni, Co, Fe, Mn, and Zn were determined by atomic absorption spectroscopy (AAS).
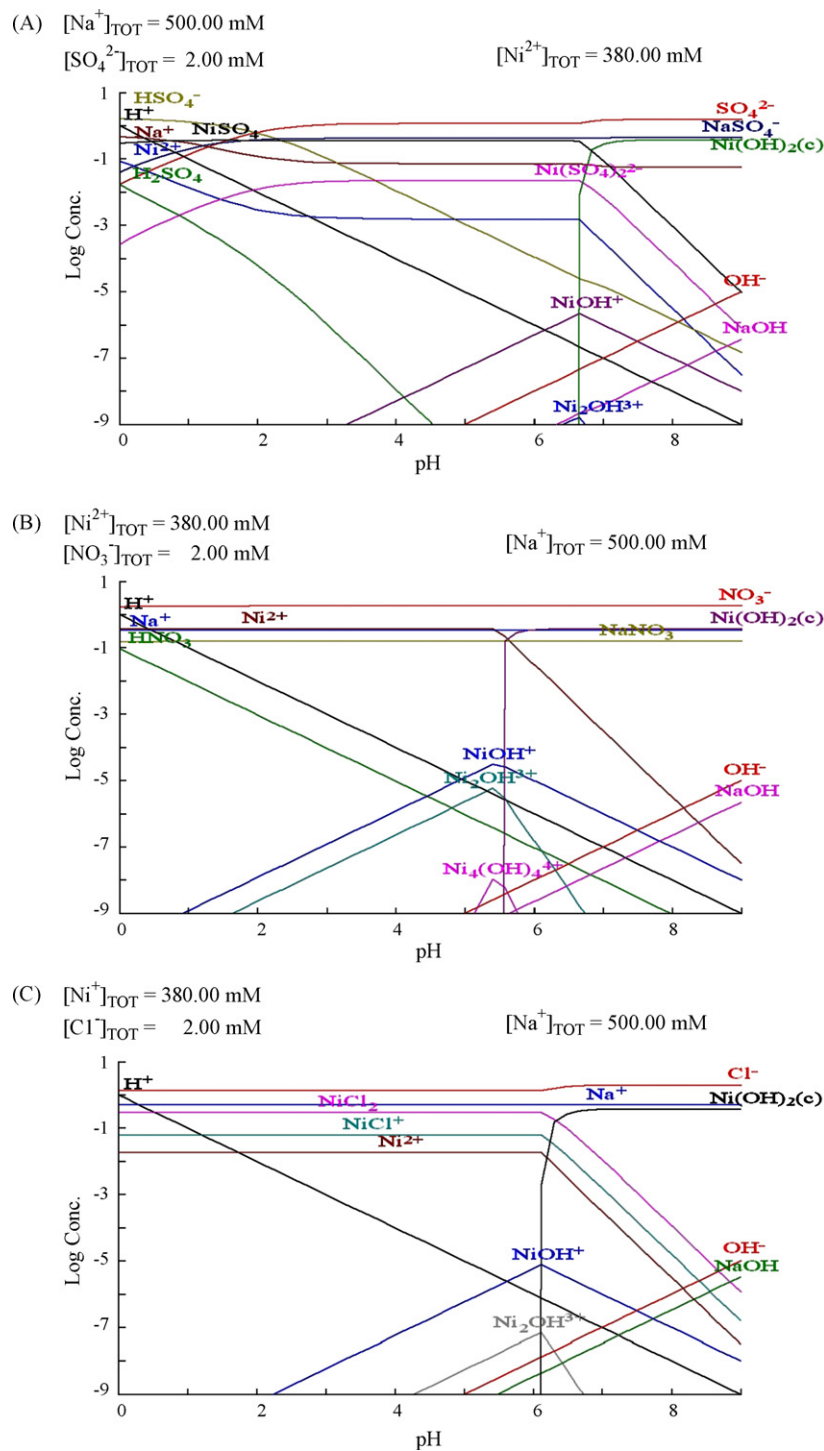
Fig. 2. Elemental speciation diagram, according to the pH values, of nickel in sulfuric (A), nitric (B) and hydrochloric (C) acids [22].

2.3. Contaminant precipitation

The solution obtained after separation of rare earths at pH 1.2 was used for other precipitation tests to evaluate the removal of contaminants, such as Zn, Fe, and Mn; Ni and Co were left unprecipitated in solution. The pH values of the solutions during the tests to evaluate the removal of contaminants were 5.0, 6.0, and 7.0. In all cases, the precipitates were obtained by adding NaOH. The concentration of rare earths was determined using ICP-AES and that of Ni, Co, Fe, Mn, and Zn, by AAS. The solution was filtered and analyzed after 4 h under constant stirring at room temperature in all tests.

3. Results and discussion

3.1. Rare-earth precipitation

Table 2 shows the results of the chemical analyses of the precipitates obtained in the selective precipitation tests. These tests were conducted using 5 M NaOH and KOH solutions and the 2 M solutions obtained with the different acid systems.

The results of the chemical analyses showed that the precipitates obtained with sulfuric acid solution yielded the best results in terms of the selective precipitation of rare earths using both NaOH and

KOH systems. For the other acid systems, high concentrations of Ni and low levels of rare earths were obtained. This may be explained by the fact that the pH had to be nearly 7 (higher than that necessary for precipitation of nickel) for precipitation to occur, except in the case of the sulfuric acid solution.

According to the elemental speciation diagrams of rare earths shown in Fig. 1, the precipitation of rare earths only occurs at pH values greater than 7, which may explain the high concentration of nickel and low concentration of rare earths. When the sulfuric acid system was used, rare earths precipitated at pH values close to 1. Of the different acid solutions used, only sulfuric acid yielded satisfactory results for the selective precipitation of rare earths, which may be the result of the decrease in solubility of rare earths caused by sulfuric acid. Furthermore, better results were obtained when NaOH, rather than KOH, was used.

Fig. 2 shows the elemental speciation curves, according to the pH, of nickel in sulfuric (A), nitric (B), and hydrochloric (C) acid solutions. These diagrams were constructed using concentrations close to actual concentrations that were estimated by the ICP chemical analysis.

The pH at which $Ni(OH)_2$ forms is about 6 and does not vary substantially, regardless of the type of acid solution used. However, the results in Table 2 show that nickel precipitated, although at a much smaller amount, at a pH of about 1 when sulfuric acid was used. This may be explained by a local increase in pH in the area where the NaOH drop fell into the solution; the hydroxide formed did not redissolve in spite of the low pH value.

3.2. Leaching efficiency using sulfuric acid

Because leaching was carried out to obtain complete extraction, the results of leaching with aqua regia showed the total concentration of elements in the electrodes. Table 3 shows the results of electrode leaching. The use of sulfuric acid resulted in low iron extraction. Low iron concentration was also attributed to the fact that the external cover and the perforated plates of the negative electrodes were removed during mechanical processing before leaching. The metal alloys used for making these parts have a high concentration of iron. In nonexperimental situations, these metal parts can be easily removed by magnetic separation [21].

During this phase of the study, although the experimental conditions were very similar to those found in the literature [15], a smaller amount of material was leached. For nickel, greater dissolution was not achieved probably because of the low level of dissolution of positive electrodes. Positive electrodes consist of a paste applied to a very thin nickel mesh. Fig. 3 depicts the morphology of this mesh. The material that did not undergo leaching, after filtration, was made up of this thin mesh. Nickel in its metallic form is more resistant to leaching, and more severe conditions, such as higher temperatures and acid concentrations, have to be used to achieve adequate conversions in reasonable time [23]. In practical situations, this material, which is made up of nickel alone, accord-
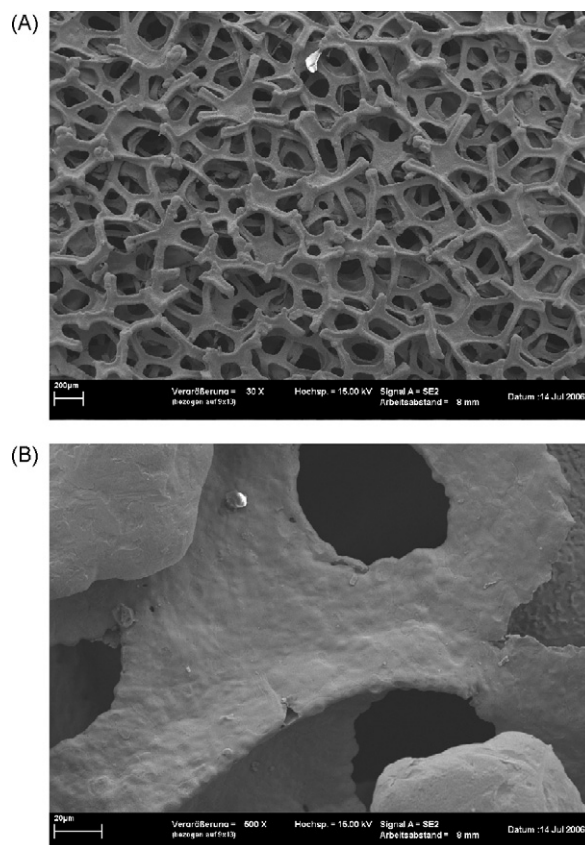
Fig. 3. (A) Micrograph of the positive electrode mesh and (B) surface detail.

ing to the energy dispersive spectroscopy (EDS) analysis shown in Fig. 4, may be directly sent for recycling.

3.3. Leaching mass balance

According to the semiquantitative analysis of electrodes shown in Table 1, other elements, apart from those analyzed in the leaching stage, constitute approximately 1.1% (electrode-weighted mean value) of the total electrode mass. The semiquantitative analysis also showed the presence of potassium at a total concentration of approximately 9.0% (electrode-weighted mean value). The pres-
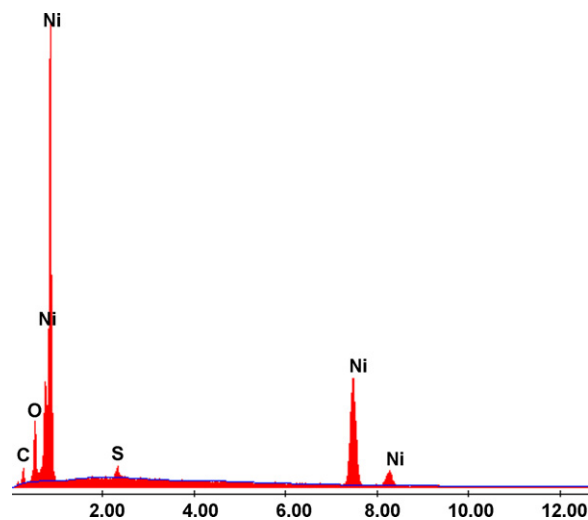
Table 3
Efficiency of leaching carried out using 2 M sulfuric acid solution at 90 °C for 4 h.

Element	Aqua regia (g l^{-1})	Sulfuric acid (g l^{-1})	Extraction (%)
Ce	3.6	3	83.33
La	2.5	2.1	84.00
Nd	0.88	0.76	86.36
Pr	0.79	0.63	79.75
Ni	27	22.3	82.59
Co	2.6	2.4	92.31
Zn	0.7963	0.7622	95.72
Fe	0.0872	0.0465	53.33
Mn	1.34	1.22	91.04
Total	39.59	33.22	–

Fig. 4. EDS analysis of the positive electrode mesh.
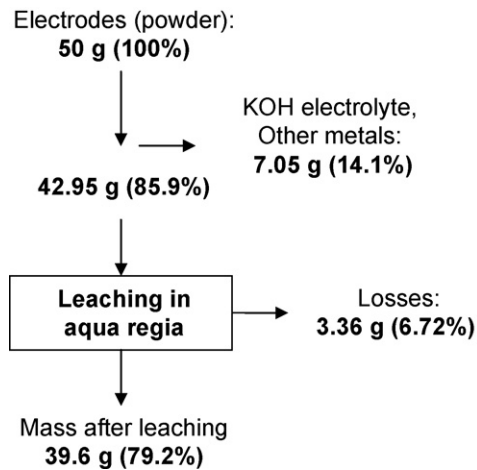
Fig. 5. Mass balance for the process of leaching with aqua regia.

Fig. 7. Chemical analysis of precipitates.

ence of potassium may be explained by the presence of KOH electrolytes. If K constitutes 9.0%, KOH is responsible for nearly 13% of the electrode mass. Therefore, 14.1% of the mass used in leaching was disregarded because it did not contain the metals under analysis. Of the 50 g of powder, 7.05 g correspond to the electrolytes and small amounts of other elements. Only 42.95 g of powder were actually found in the solution.

Fig. 5 shows the mass balance for leaching with aqua regia, in which the entire powder mass was leached. The amount of metals in the solution, even after leaching was carried out with aqua regia (39.50 g), was lower than that found in the semiquantitative analysis (42.95 g). This difference of 3.36 g corresponds to 6.57% of the initial powder mass.

This difference probably results from the type of semiquantitative analysis used to analyze the powder, ignoring the presence of other light elements, such as carbon, oxygen and nitrogen. Rare earths are oxidized in the presence of air and may even ignite when the accumulators are opened.

Fig. 6 shows the results of mass balance for leaching with sulfuric acid. Although leaching was not very effective, and only 66.45% of the initial mass was leached, almost all the material recovered after filtration was made up of the metal mesh, the EDS characteristics of which are shown in Fig. 4. This mesh, made up of nickel, is another product of the process. Therefore, if the losses inherent to the leaching process are disregarded, as established for leaching with aqua regia, which had a mass loss of 3.36 g (6.72%), then it may
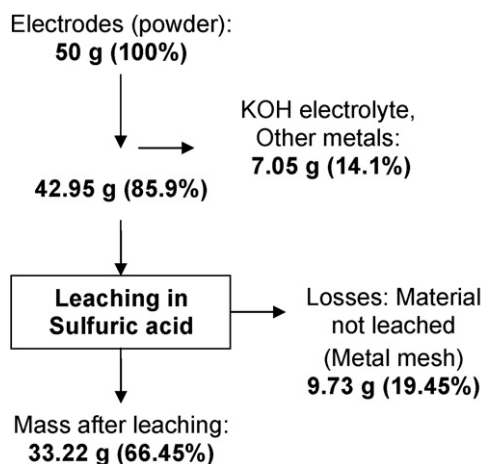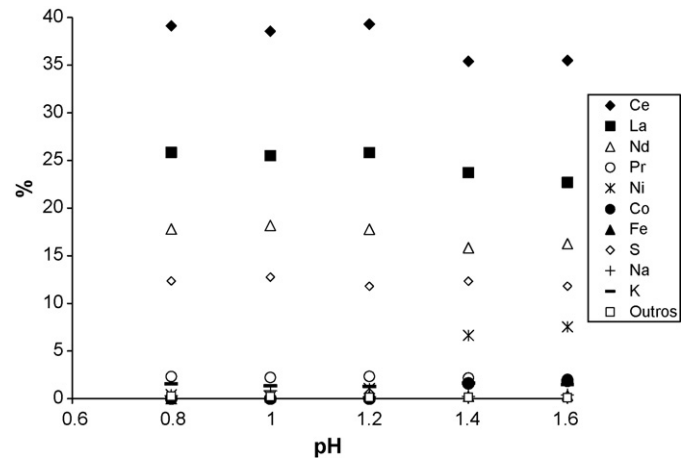
be estimated that 6.37 g or 12.73% of the initial mass corresponds to the metal mesh.

3.4. Characterization of rare-earth precipitates obtained with H_2SO_4 and NaOH at different pH values

Preliminary precipitation tests were conducted to find the optimal pH for the recovery of rare earths and to evaluate the amount of impurities in the precipitates. The pH value was strictly controlled, and NaOH was added slowly under constant stirring. If not, the pH may increase in the area where the NaOH drop falls, and $Ni(OH)_2$ may precipitate, which results in the loss of nickel.

The tests were conducted using 2 M H_2SO_4 and 5 M NaOH solutions, and different pH ranges were evaluated for rare-earth precipitation. Fig. 7 shows the results of the chemical analysis of precipitates obtained at pH 0.8, 1.0, 1.2, 1.4, and 1.6. This pH range was chosen to avoid iron precipitation, which usually occurs at a pH range of 2.5–3.

Precipitates were obtained with very high concentrations of elements in the form of a very thin white powder. The precipitate with the lowest relative concentration of rare earths was obtained at pH 1.6 (about 76%), and the one with the highest relative concentration was obtained at pH 1.2 (about 85%). However, rare-earth concentrations in the precipitates obtained at pH values between 0.6 and
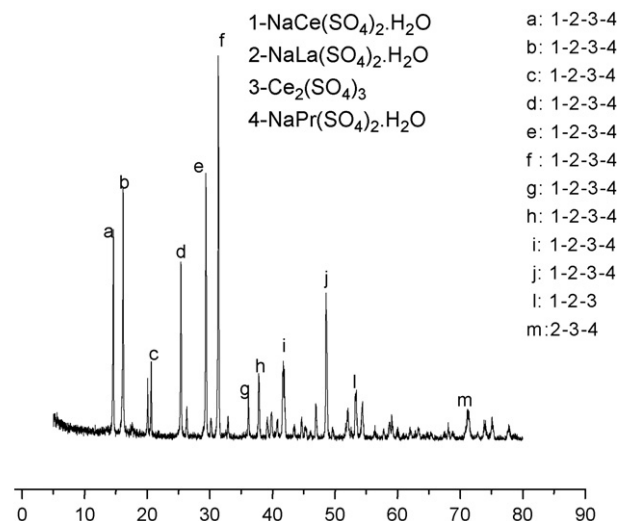

Fig. 6. Mass balance for leaching with sulfuric acid.

Fig. 8. X-ray diffraction analysis of precipitate obtained at pH 1.6.

Ce = 3,0 g/L	(100%)
La = 2,1 g/L	(100%)
Nd = 0,76 g/L	(100%)
Pr = 0,63 g/L	(100%)
Ni = 22,3 g/L	(100%)
Co = 2,4 g/L	(100%)
Zn = 0,7622 g/L	(100%)
Fe = 0,0465 g/L	(100%)
Mn = 1,22 g/L	(100%)

Precipitation pH 1,2   **Precipitate**

Ce = 2,96 g	**(98,6%)**
La = 2,04 g	**(97,2%)**
Nd = 0,74 g	**(97,8%)**
Pr = 0,62 g	**(99,0%)**
Ni = 0,41 g	(1,85%)
Co = 0,08 g	(3,3%)
Zn = 0,045 g	(5,9%)
Fe = 0,0046 g	(0,1%)
Mn = 0,0184 g	(1,5%)

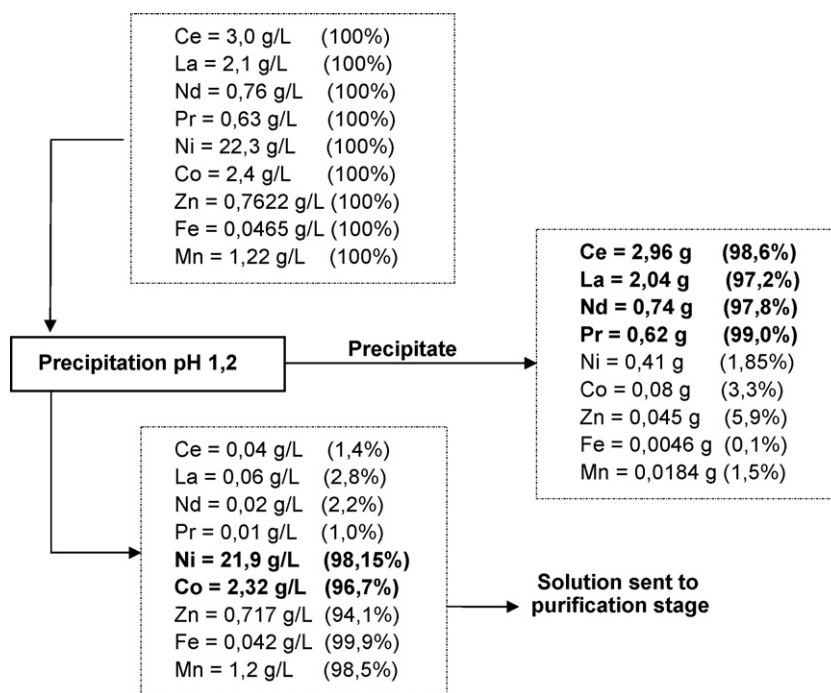| Ce = 0,04 g/L | (1,4%) |
La = 0,06 g/L	(2,8%)
Nd = 0,02 g/L	(2,2%)
Pr = 0,01 g/L	(1,0%)
Ni = 21,9 g/L	**(98,15%)**
Co = 2,32 g/L	**(96,7%)**
Zn = 0,717 g/L	(94,1%)
Fe = 0,042 g/L	(99,9%)
Mn = 1,2 g/L	(98,5%)

Solution sent to purification stage

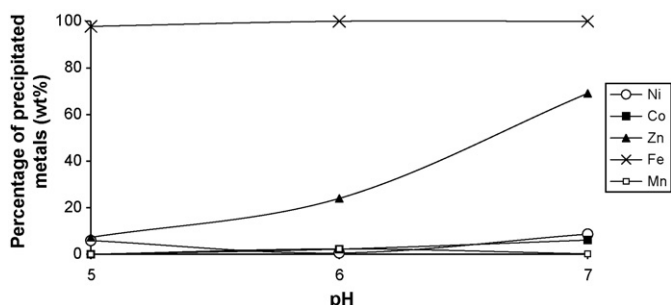Fig. 9. Mass balance for rare-earth precipitation.

Fig. 10. Contaminant-precipitation tests.

1.2 were similar. Therefore, rare earths may be effectively recovered using this pH range. In the precipitate obtained at pH 0.8, iron was not detected, but the iron concentration increased as pH increased. Nickel and cobalt concentrations in the precipitate increased as the pH values increased.

XRD analyses were carried out with the precipitate obtained at pH 1.6 to evaluate the phases that are found in the precipitates and to investigate whether minor elements, such as Ni and Co, form compounds with rare earths. This precipitate was chosen because it contains a higher concentration of the minor elements, as observed in Fig. 7. The XRD analysis, shown in Fig. 8, established that the precipitate is chiefly composed of the sulfate salts of rare earths. In most precipitates, sodium was part of the crystalline structure, which may explain the greater efficiency of NaOH, compared to KOH, in the precipitation stage.

The semiquantitative results shown in Fig. 7 suggest that precipitates obtained at pH 1.2 have the highest concentrations of rare earths and lowest concentration of other elements. For pH values higher than 1.2, the amounts of metals such as Ni and Co show an increase. Therefore, a quantitative analysis was further conducted in the solution obtained after the precipitation test at pH 1.2, and results were compared with the quantitative
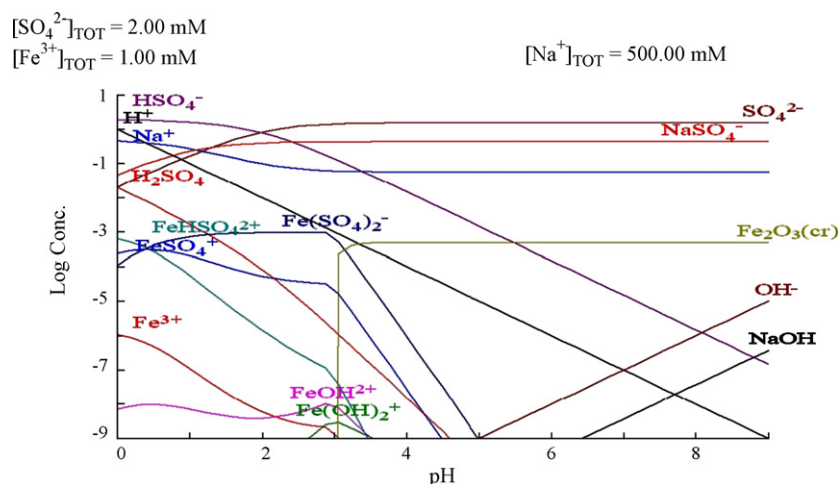
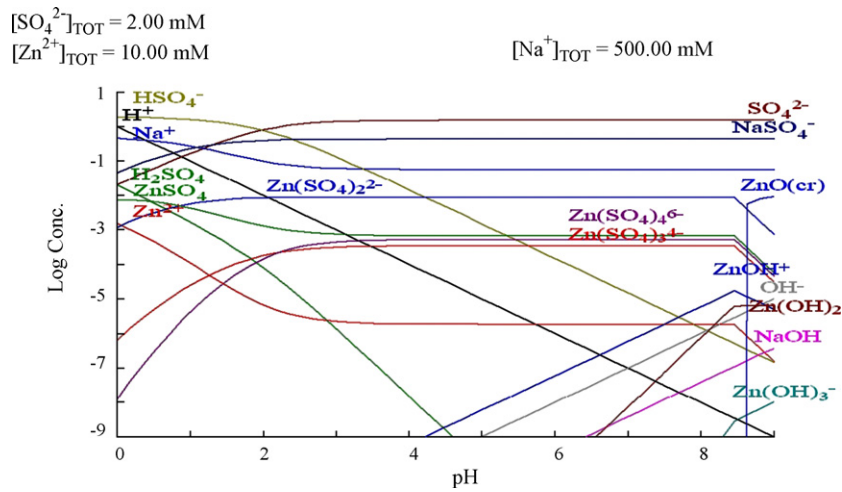Fig. 11. Elemental speciation diagram of Fe^{3+} in sulfuric acid according to the pH [22].

Fig. 12. Elemental speciation diagram of Zn^{2+} in sulfuric acid according to the pH [22].

results obtained for the solution after leaching, which are shown in Table 3.

The recovery of rare earths after precipitation at pH 1.2 was very high (Ce = 98.6%, La = 97.2%, Nd = 97.8%, Pr = 99.0%). The results were obtained by comparing the solution concentrations before and after precipitation. The contaminants with the greatest precipitation rates were Fe (9.9%) and Zn (5.9%), followed by Co (3.3%), Ni

(1.85%), and Mn (1.5%). This mixture of rare-earth metals can be reused in the production of new NiMH batteries.

3.5. Mass balance for rare-earth precipitation

The mass balance shown in Fig. 9 was calculated using 1 l of solution, with initial concentration for sulfuric acid as shown in
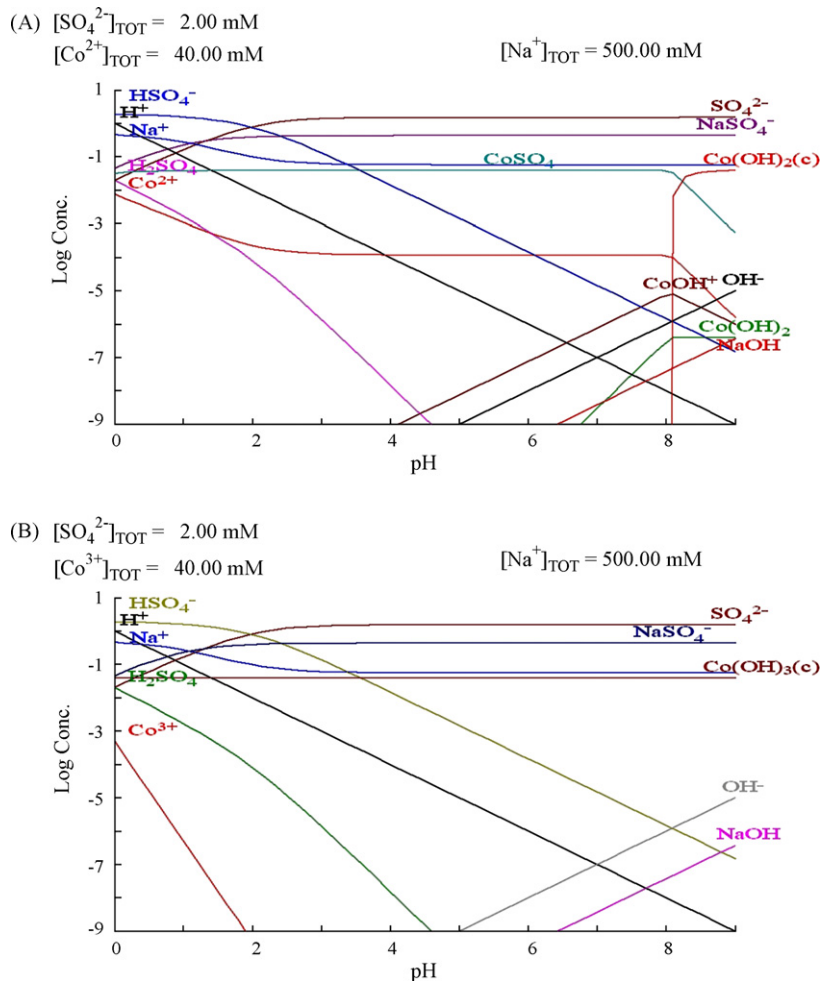

Fig. 13. Elemental speciation diagram of (A) Co^{2+} and (B) Co^{3+} in sulfuric acid according to the pH [22].
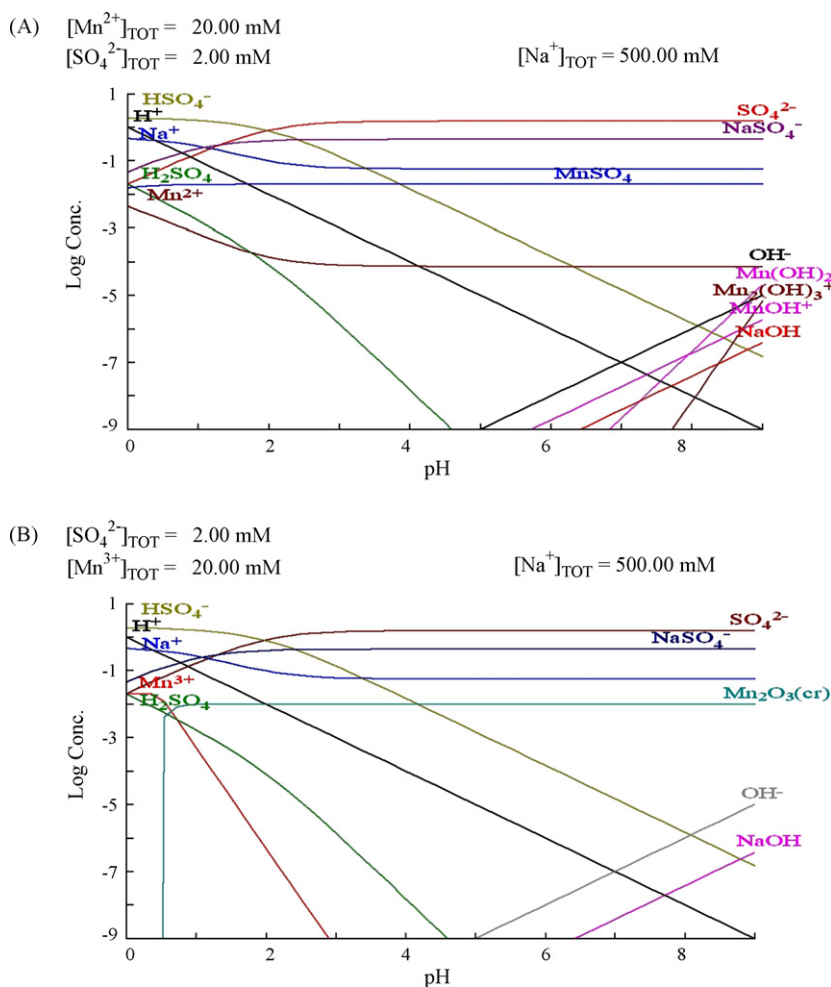
(A) $[Mn^{2+}]_{TOT} = 20.00$ mM
$[SO_4^{2-}]_{TOT} = 2.00$ mM
$[Na^+]_{TOT} = 500.00$ mM

(B) $[SO_4^{2-}]_{TOT} = 2.00$ mM
$[Mn^{3+}]_{TOT} = 20.00$ mM
$[Na^+]_{TOT} = 500.00$ mM

Fig. 14. Elemental speciation diagram of (A) Mn^{2+} and (B) Mn^{3+} in sulfuric acid according to the pH [22].

Table 3, and comparing these values with those obtained after rare-earth precipitation at pH 1.2.

3.6. Ni–Co solution purification

After the recovery of rare earths, other precipitation tests at pH values of 5–7 were conducted to evaluate the removal of Fe, Zn, and Mn, whereas Ni and Co were left behind in the solution. Fig. 10 shows the results of the precipitation tests. Fe is easily removed. At pH 5, practically all the Fe present in solution precipitated, which shows that a large part of the iron in solution is Fe^{3+}. According to the literature, Fe^{3+} precipitates as a hydroxide at pH 3.5, whereas Fe^{2+} hydroxides are only formed at pH 6 [24]. Fig. 11 shows the elemental speciation diagram according to the pH of Fe^{3+} in sulfuric acid. According to elemental speciation diagrams, calculated using concentrations close to those actually found in the solution, Fe_2O_3 forms at pH 3, which is in agreement with the current results.

The amount of precipitated Zn increased as pH increased. At pH 7, practically 70% of Zn is precipitated. However, a considerable amount of Ni (∼9%) also coprecipitated at this pH. The comparison of Zn results with the elemental speciation diagram according to pH shown in Fig. 12 showed that $Zn(OH)_2$ forms at a pH of about 6.5. Therefore, in theory, all zinc should have precipitated at pH 7, which did not occur maybe because the kinetics of precipitate formation was very slow.

The precipitation of Ni usually begins at about pH 6.5, which is in agreement with its elemental speciation diagram shown in Fig. 2(A). In this case, probably due to the higher concentration of Ni than that of other metals, Ni was coprecipitated at pH 5. This same phenomenon may be responsible for the precipitation of part of cobalt. Coprecipitation is associated with phenomena such as the mechanical imprisonment of solution in the precipitate itself, adsorption of foreign ions in the formation of the precipitated surface, etc. [25]. According to the diagrams shown in Fig. 13(A) and (B), if cobalt is present as Co^{2+}, its precipitation only occurs at a pH greater than 6.5; if Co^{3+} were present, it would be insoluble at all values within this pH range.

The efficiency of Mn removal was low, because only a small amount precipitated even at pH 7. These results indicate that manganese in solution may be Mn^{2+} because, as observed in Fig. 14(A) and (B), the elemental speciation diagrams of Mn^{2+} and Mn^{3+} according to the pH showed that Mn^{2+} is soluble at low concentrations, whereas Mn^{3+} precipitates at a very low pH range.

Ni and Co losses occur during purification, but a comparison of these values with those reported for solvent extraction in the literature, using a simple contact and a 1:1 ratio of the solution to be purified and the organic phase (composed of 25% extractor and 75% kerosene), shows that a very similar Ni amount is extracted together with impurities and that only 17% of Mn is removed from the solution. To increase Mn extraction, the ratio of organic-to-aqueous
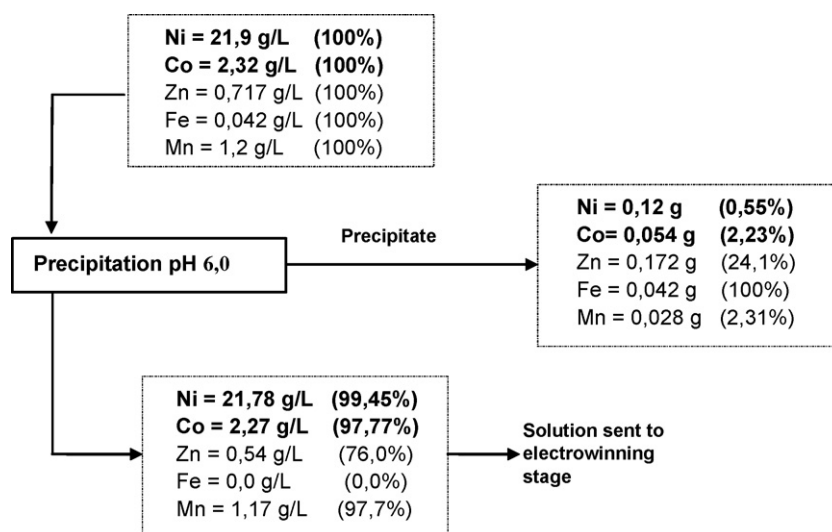
Fig. 15. Mass balance for the purification phase.

solutions should be increased and several extraction phases should be used [12].

3.7. Mass balance for contaminant precipitation

Fig. 15 shows the mass balance for contaminant precipitation. For this balance, the results of pH 6 were used. At this pH value, Ni and Co losses are small, although the results are not the best for zinc extraction.

Fig. 14 shows that the manganese found in solution is Mn^{2+}. Therefore, if the solution is aerated, a large amount of manganese might precipitate.

4. Conclusions

The results show that the recovery of rare earths, which constitute a large part of the negative electrode of AB-type NiMH batteries, is technically feasible. Rare earths are effectively recovered by solubilization of the electrodes in sulfuric acid, followed by precipitation using pH adjustments (addition of sodium hydroxide) at a pH range of 0.8–1.2. At pH 1.2, more than 98 wt.% of the rare earths in the solution, resulting from battery leaching, was recovered. XRD analysis showed that rare earths precipitated as sulfate salts. Chemical analysis showed that precipitates obtained at pH 0.8 had the greatest concentration of rare earths. Moreover, the use of higher pH values produced precipitates with greater concentrations of other metals, particularly nickel.

After the recovery of rare earths, at the second stage of precipitation at pH 7, practically all the iron and more than 70% of all zinc were removed by precipitation. However, manganese was not removed at the pH range under study. At both precipitation stages – rare-earth precipitation at pH 1.2, followed by precipitation at pH 7 – about 10% of nickel and 9% of cobalt were coprecipitated. These results are in agreement with previous studies that used solvent extraction. The process described in this study is easy to operate, economic, and does not pose environmental risks, in contrast to the processes that use solvents. The use of a purifying solution at pH 6 to obtain electrolytes was efficient. By combining both stages – precipitation at pH 1.2, followed by precipitation at pH 6 – about 2% of nickel and 6% of cobalt were coprecipitated. Therefore, the use of a purifying solution at pH 6 reduces both losses of Ni and Co and the use of reagents.

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