BRIEF COMMUNICATIONS

Determination of Nickel in the Solution Resulted from Sulfuric-Acid Leaching of the Active Mass of the Nickel-Oxide Electrode of the Nickel-Iron Battary

E. N. Volkova and A. I. Demidov

St. Petersburg State Polytechnical University, St. Petersburg, Russia

Abstract—A nickel content was determined in the solution resulted from sulfuric-acid leaching of the active mass of the nickel-oxide electrode of an exhausted nickel-iron battery by complexometric titration with visual indication of an equivalence point.

At present appreciable attention is given to secondary processing of wastage containing non-ferrous metals, the preference being given to hydrometallurgical methods, which are the most harmless and less energy-consuming.

A hydrometallurgical technology of secondary processing of nickel-iron batteries (NIB) was offered in [1]. One of its key points was the active mass (AM) leaching by a 200-300 g l^{-1} (17–26 wt %) sulfuric acid solution [2.]

Hydroxides of nickel(II) and (III) are the main components of the active mass of the nickel-oxide electrode of the exhausted nickel-iron battery. In addition a significant amount of iron and carbon compounds and a solid residue of the electrolyte (sodium hydroxide and carbonate) are present there. The active mass can be polluted by copper, sulfur, phosphorus, and tin in the form of trace admixtures with the contents of hundredths or thousandths shares of percent [3]. In most cases, the presence of trace contaminants does not essential by affect the determination of macrocomponents, however, certain analytical procedures require a careful selection of experimental conditions for obtaining reproducible results.

Depending on the quantitative nickel content in a sample under study the analysis is carried out by various methods: gravimetric, volumetric (titrimetric), or photometric [4, 5].

One of known volumetric methods of nickel determination is the complexometry. This method is based on the formation of complex compounds of sodium ethylene diamine tetraacetate (EDTA, Trilon B, or complexon III) with nickel ions in the presence of an indicator changing its color in an equivalence point (e.p.).

The values of the instability constants of nickel(II) complexes with EDTA p_{K1} HEdta^{3-} = 11.56 and HEdta^{4-} = 18.62 [6] suggest that a great number of cations of other metals will hinder the determination of nickel.

However, despite of it, the complexometric titration finds practical application for the determination of nickel in plating baths [7], alloys with copper and other non-ferrous metals [8], and in condensation polymers [9].

In this work it was of interest to determine the nickel content in a solution of complex composition, without its preliminary separation in the form of an organic complex and without masking iron, which is the main admixture that should be removed in the sulfate form at the secondary extraction of nickel from the nickel-oxide electrode active mass.

EXPERIMENTAL

Choice of an indicator and experimental conditions. The following indicators can be used in the complexometry of nickel [6, 10]: murexide, 1-(2-pyridylazo)-resorcinol

Table 1. Chemical composition of active mass of the nickel-oxide electrode of the exhausted nickel-iron battery

Element	Content, wt %	Analytical method
Ni	39.1	Atomic-adsorption according to the NSAM instruction no. 155 KhS
Cu	0.13	
Fe	1.22	
S	0.018	Titrimetric according to the NSAM instruction no. 352
C	16.5	Gas-volumetric
Sn	0.05	Atomic-emission with inductively bound plasma
P	0.12	Photometric according to the NSAM instruction no. 138 Kh(R)

Table 2. Data of the complexometric determination of nickel content in a solution resulted from the sulfate-acid leaching of an active mass of a nickel-oxide electrode of an exhausted nickel-iron battery

Sample no. 1		Sample no. 2		Sample no. 3	
V_{EDTA}, ml	m_{Ni}, g	V_{EDTA}, ml	m_{Ni}, g	V_{EDTA}, ml	m_{Ni}, g
6.8	0.3138	6.6	0.4062	6.8	0.4184
6.9	0.3185	6.8	0.4184	6.9	0.4247
6.9	0.3185	6.7	0.4123	6.8	0.4184
6.6	0.3046	6.7	0.4123	6.8	0.4184
6.6	0.3046	6.8	0.4184	7.0	0.4308
6.5	0.3000	6.7	0.4123	6.8	0.4184
6.4	0.2954	6.6	0.4062	6.8	0.4184

(PAR), azoxine, eriochrome black T, eriochrome blue SE, metoomegachrome blue BBL, omegachrome black PPV, pyrocatechin violet, 1-(2-pyridylazo)-2-naphthol (PAN), alizarin S, and acid chrome dark blue.

Chemical analysis was carried out on the basis of Joint-Stock Company "Mekhanobr Engineering Analit" Regional analytical center.

In the case when the reaction of nickel with EDTA at an ambient temperature is time consuming or nickel ions form stronger complexes with the indicator than with the conlexonate, the method of the back titration of the complexon (EDTA) excess by Mg, Zn, Cu, and Th salts was applied. Examples of such indicators are eriochrome black T, alizarin S, and acid chrome dark blue. The choice of the indicator, which is governed by the chemical composition of a sample under study and the presence of hindering ions, defines the experimental conditions and the technique of the equivalence point determination. As nickel-containing solutions are of a rather intensive green-blue color, this analytical method is applied to dilute solutions.

It this work we have selected the method of direct titration with the visual technique of the equivalence point determination in an ammonia buffer mixture with a 0.1% aqueous solution of pyrocatechin violet as an indicator [6].

The chemical composition of the nickel-oxide electrode active mass is shown in Table 1. As the procedure for its analysis with this indicator is not developed at present, we have carried out a series of experiments with pure solutions according to the method "taken-found" in the presence of the main admixture, iron(II) sulfate. For these experiments we used $NiSO_4 \cdot 7H_2O$ aqueous solution with an experimentally determined titre of 16.2 mg ml^{-1}. The pH of the medium (~8–10) was supported by adding a buffer mixture NH_3(aq) + NH_4Cl in the ratio 1:1 [11]. The volume of an aliquot was 10.0 ml. The determination of nickel by this method was carried out in the presence of iron(II) at the iron : nickel ratio of 1:32, which is characteristic for the solid active mass.

The presence of iron(II) in a solution under analysis leads to an overestimated result. However an addition of hydrogen peroxide (H_2O_2) reduces the error due to iron(II) oxidation to iron(III). The systematic error of the nickel determination in the solution is 2–3%.

Analysis of a solution resulted from sulfate-acid leaching of an active mass of a nickei-oxide electrode of a nickel-iron battery. A weighted sample of an AM powder (weight about 1 g) was dissolved in 50 ml of a 30% H_2SO_4 solutions with heating on a sand bath ($T \approx 80°C$). The volume of the solution after filtering was brought to 200 ml by distilled water.

A solution under analysis (10.0 ml) was placed in a 250 ml Erlenmeyer flask, 100 ml of a buffer mixture NH_3(aq) + NH_4Cl (1:1) and 15 ml of H_2O_2 were added. Several drops of an indicator (0.1% aqueous solution of pyrocatechin violet) were added and the sample was titrated with a 0.1 N solution of complexon III up to color change from blue-green to black-violet. The complexon solution was preliminarily standardized by a 0.1 N solution of zinc chloride.

The determination of nickel content was carried out in three probes taken from AM of the same plate of a nickel-oxide electrode of an exhausted NIB. The experimental results are given in Table 2.

It follows from our experimental data that nickel is distributed in the active mass inhomogeneously. The content of nickel in the solution resulted from sulfate-acid leaching of an active mass of a nickel-oxide electrode of an exhausted nickel-iron battery is (g): sample no. 1—0.3057 ± 0.0100, no. 2—0.4123 ± 0.0046, and no. 3 —0.4194 ± 0.0055 at a confidence probability $\alpha=0.95$. The error of the method is close to 3%.

On the basis of our experimental data and the results of the AM chemical analysis (Table 1) we have calculated the degree of nickel extraction into solution during the sulfate leaching. The corresponding average value is 90.6% at 80°C. The acid is consumed in the ratio of 50 ml per 1 g of a dry solid.

CONCLUSIONS

1. The content of nickel in a solid active mass of a nickel-oxide electrode of an exhausted nickel-iron accumulator is 39.1%.

2. The content of nickel in a solution after a sulfuric acid leaching is 0.304–0.421 g at a confidence probability of 95%.

3. The systematic error of the complexometric nickel determination in the active mass of the nickei-oxide electrode of an exhausted nickel-iron battery does not exceed 3%.

REFERENCES

1. Volynskii, V.V., Lopashev, A.V., and Kazarinov, I.A., *Elektrokhim. Energetika*, 2004, vol. 4, no. 3, pp. 165–167.
2. *Spravochnik khimika* (Handbook of the Chemist), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1968, vol. 3.
3. Khudyakov, I.F., Doroshkevich, A.P., and Karelov, S.V., *Metallurgiya vtorichnykh tyazhelykh tsvetnykh metallov* (Metallurgy of Secondary Heavy Non-Ferrous Metals), Moscow: Metallurgiya, 1987.
4. *Titrimetricheskii i gravimetricheskii analiz v metallurgii: Spravochnik* (Titrimetric and Gravimetric Analysis in Metallurgy: Handbook), Korostylev, P.P., Ed., Moscow: Metallurgiya, 1985.
5. Peshkova, V.M. and Savostina, V.M., *Analiticheskaya khimiya nikelya. Ser. "Analiticheskaya khimiya elementov"* (Analytical Chemistry of Nickel. Series "Analytical Chemistry of Elements"), Moscow: Nauka, 1966.
6. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook on Analytical Chemistry), Moscow: Khimiya, 1967.
7. Zhendareva, O.G. and Mukhina, Z.S., *Analiz gal'vanicheskikh vann* (Analysis of Galvanic Baths), Moscow: Khimiya, 1970.
8. *Sbornik nauchnykh trudov Ural'skogo instituta im. S.M.Kirova: Primenenie Trilona B v analizakh tsvetnykh splavov* (Transactions of Kirov Ural Polytechnic Institute: Application of Trilon B in Analysises of Non-Ferrous Alloys), Sverdlovsk: Izd. UPI, 1963, no. 130.
9. Kalinina, L.S., Motorina, M.A., Nikitina, N.I., et al., *Analiz kondensatsionnykh polimerov* (Analysis of Condensation Polymers), Moscow: Khimiya, 1984.
10. Mel'chakova, N.V. and Peshkova, V.M., *Assortiment reaktivov na nikel'. Ser. "Organicheskie reaktivy dlya opredeleniya neorganicheskikh ionov"* (Assortment of Reagents to Nickel. Series "Organic Reagents for Determination of inorganic Ions"), Moscow: IREA (NIITEKhKhIM), 1970.
11. Schwarzenbach, G. und Flaschka, H., *Die Komplexometrische Titration,* Stuttgart: Ferdinand Enke Verlag, 1965.