Conference Paper

Features of Nickel-Cadmium Batteries Recycling

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Abstract

The issue of operated-off alkaline nickel-cadmium batteries recycling is currently relevant due to a number of aspects: economic, environmental and social. It is most acute across the national corporation JSC Russian Railways. The article deals with some technological features of operated-off alkaline nickel-cadmium batteries recycling with valuable components being extracted (from the example of nickel-cadmium storage batteries of JSC "RZD" rolling equipment). The results of leaching in Trilon B synthetic oxides solution, the presence of which is possible in the raw material being processed, are presented in the study. Based on the study of leaching processes of CdO, NiO, FeO, Femet and Fe_2O_3 in Trilon B solution, the dependence of complexing on the pH of the solution was revealed. The experimental site of the hydrometallurgical processing of the research center (OCGP IC) in the GMO KhMC PJSC "Uralelectromed" was selected as the testing one for the technology proposed. As a raw material for the tests, a lot of negative lamellae packed in alkaline storage batteries of two different types were used. They were obtained as a result of preliminary drying and cutting at OOO Kursk factory "Accumulator". The particle size is 90% - 0.1 mm. The results obtained during the research allowed the author to formulate a hypothesis about the practical use of Trilon B for the processing of operated-off alkaline nickel-cadmium batteries with the extraction of valuable components having greater economic, environmental and social benefits compared to methods based on pyro metallurgy.

Keywords: nickel-cadmium batteries, recycling, Trilon B, Russian Railways, hydrometallurgical

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1. Introduction

JSC «Russian Railways» is experiencing a period of systemic reform, one of the most important goals of which is to establish the image of socially responsible, eco-oriented company. Environmental well-being and natural resources conservation are the priority objectives of the program for the development of the railway industry in Russia called "The Strategy for the Development of Railway Transport in the Russian Federation until 2030".

The technology offered by the authors can significantly contribute to the implementation of the environmental strategy adopted by Russian Railways in such key issues as resource saving, the environmental burden reduction, the environmental safety of the company's operations improvement, acting as a technological basis for generating additional revenue for the company.

The operated-off alkaline nickel-cadmium battery scrap belongs to the 1st hazard class (extremely hazardous) waste, but also contains nickel and cadmium metals, whose commercial reserves are very limited in nature, and the technology of extraction and processing is complex and expensive.

After the batteries are cut, two types of secondary raw materials are formed - positive nickel lamellae, processing of which is relatively simple and safe, and negative cadmium-containing recycling technologies this work are devoted to. Nowadays, in industrial practice, there is no environmentally friendly and cost-effective technology that would completely utilize this kind of raw materials to produce high quality products.

According to data provided on the official website of Russian Railways, to date, the fleet of the company's rolling stock includes about 20,000 locomotives, most of which use electric propulsion. Thus, taking into account that the average lifespan of alkaline nickel-cadmium batteries is 10 years, and radical modernization of the railway transport fleet by 2017 carried out by the corporation, the problem of the type of waste recycling mentioned above is very relevant.

2. Results and Discussion

Run down alkaline batteries are the complex multicomponent raw material of variable composition.

The cadmium-containing scrap produced by grinding the negative lamellae can include the following metal compounds: CdO, Cdmet, Femet, FeO, Fe_2O_3.

The aim of the work was to conduct studies on the leaching of synthetic oxides in a solution of Trilon B, the presence of which is possible in the feedstock. For this purpose, a 0.1 M Trilon B solution was prepared, the initial pH of which was 5.36.

A prepared sample of Trilon B with a volume of 50 cm^3 was filled with a sample of CdOreac. The leaching time was 60 minutes (Figure 1 curve 1).

By the form of curve 1, it can be said that complexation is stepwise. Presumably, this is due to the sequential deprotonation of the Trilon B molecule. In the pH range from 5.46 to 6.4 Trilon B is in the form of H_2edta^{2-}.

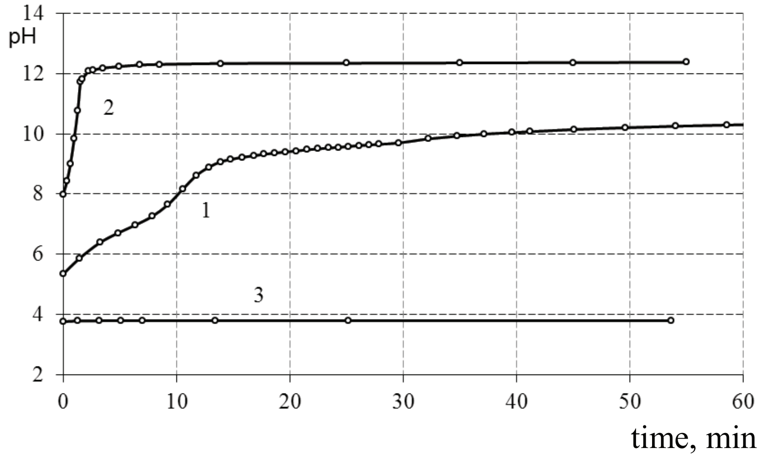

Figure 1: CdO leaching in Trilon B solution at different initial pH of the medium: 1-5.36; 2-8.0; 3.8.

With the increase in pH, which is due to the basic nature of cadmium oxide, the reaction of cadmium trilonate formation can be represented as follows:

$$CdO + H_2O + [H_2edta]^{2-} = CdH_2edta + 2OH^-$$

In the next region of pH (7-10), the anion $[Hedta]^{3-}$ predominates, actively dissociating in the alkaline medium with the formation of the anion $[edta]^{4-}$ and, consequently, the formation of a normal complex:

$$Cd^{2+} + [Hedta]^{3-} + OH^- = [Cdedta]^{2-} + H_2O$$

The pH of the medium remains unchanged. The experiment in an acid medium (curve 3) demonstrates the absence of complexation with cadmium at pH <4.

The next stage was a series of experiments on the leaching of iron, nickel oxide and iron oxide (Figure 2). The result obtained, the unchanged pH throughout the experiment, allows us to conclude that the formation of complexes does not occur in the entire pH range.

When carrying out experiments on the leaching of iron oxide (III), it was found that a small amount of iron-trilonate complex is possible to present in the acidic region (Figure 3 curves 1-2). In the alkaline region, where subsequent leaching of the raw material is planned, the formation of complexes with iron is not seen (curve 3).

To determine the influence of the initial pH of the solution on the rate of trilonate complexes formation, studies were carried out using the potentiometry method of 0.01 M cadmium sulfate solution and 0.01 M ferrous sulfate solution with a pH value of 0.1 M Trilon B solution (pH = 5.36) (Figure 4). The "Aquilon" titrator was used applying computer control system, data collection and processing.

The formation of trilonate cadmium complexes is accompanied by the increase in the acidity of the solution up to pH <3, which is connected with the transition of H^+

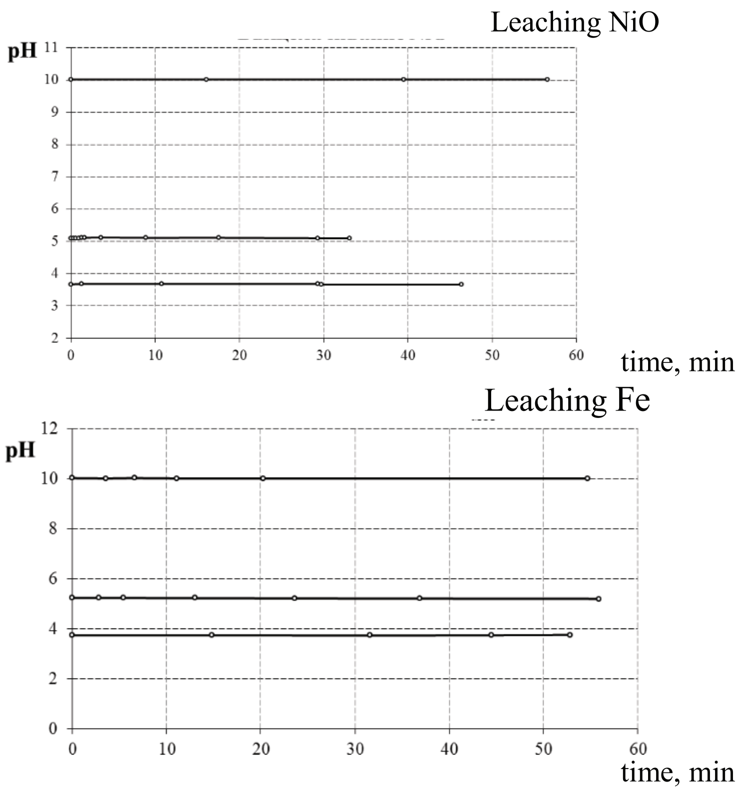

Figure 2: Leaching of NiO, FeO and Femet in a Trilon B solution.

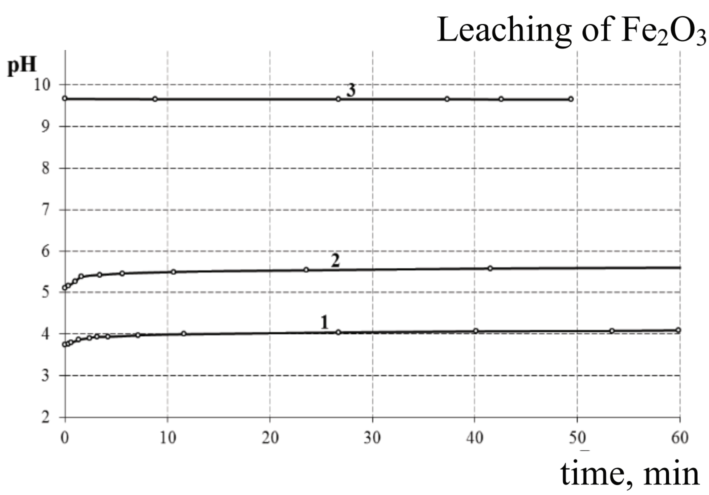

Figure 3: Leaching of Fe_2O_3 in a Trilon B solution.

ions from the carboxyl groups of ethylenediaminetetraacetate to the solution. The existence of disubstituted cadmium complexonates is most likely in the pH range 4-8 (curves 1-3), which is manifested in the investigated region. The course of curve 4 (pH <3) indicates a low probability of cadmium complexation in this region. The thermodynamic diagram of the ionized forms existence of the complexon shows that in the pH range of 4-8, H2edta^{2-} and Hedta^{3-} are predominated and form strong cadmium compounds in this region. At pH> 5, the hydrogen ion dissociates from betaine

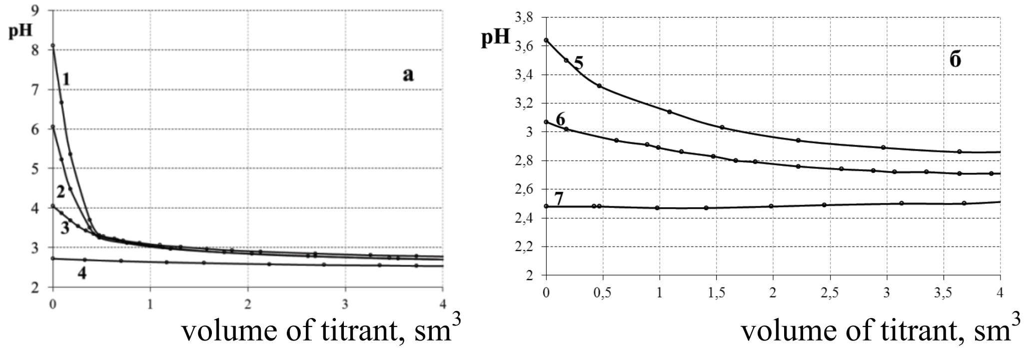

Figure 4: Curves of potentiometric titration: a - solution of $CdSO_4$;B - solution of $FeSO_4$.

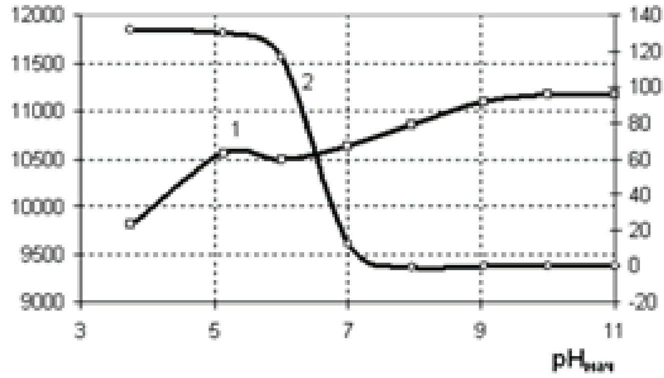

Figure 5: Dependence of cadmium (1) and iron (2) concentration in solution on pH at leaching of a mixture of cadmium and iron oxides.

nitrogen, which allows the covalent coordination of the metal-ligand to be organized. The titrant consumption during complexation in this pH range indicates the ratio of the metal: ligand = 1: 1 in the compound.

The decrease in the pH of the solution during titration of the iron (II) sulfate solution is not so obvious, however, the titration curves show the possibility of the trilonate complexes formation in the pH range of 2.65-3.65 (up to the point where hydrolytic precipitation of the basic sulfate and ferric hydroxide begins)). At pH <2.6, pH does not change with increasing ligand concentration, which indicates the absence of complexation between iron (II) and edta.

To eliminate the influence of random factors on the speed of the process, a series of experiments was conducted to leach a sample of a mixture of reactive cadmium and iron oxides at a ratio of 1: 4 for 10 min in a solution containing 100 g / dm^3 of edta at fixed pH values ranging from 4 to 11. The data obtained (Figure 5) indicate that in the pH range of the solution above 7.0, the existence of soluble trilonate iron complexes is not possible, whereas the rate of cadmium leaching increases significantly with an increase in pH.

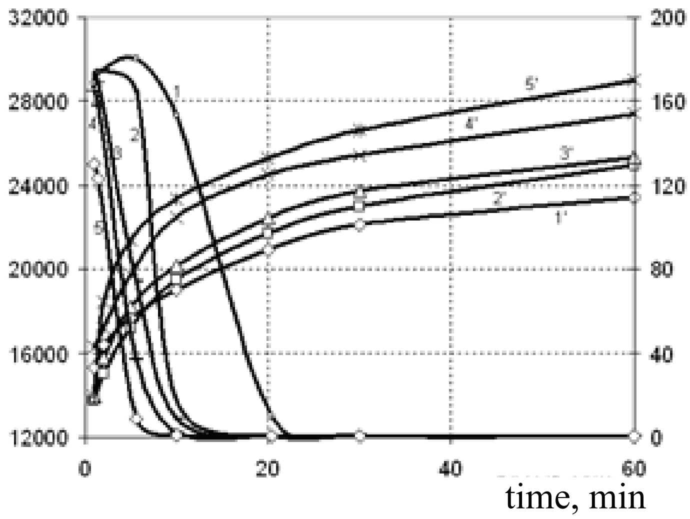

Figure 6: Change in the concentration of cadmium (1′-5 ′) and iron (1-5) in the leaching of the active mass of alkaline batteries. Temperature, °C: 1,1 ′- 20; 2.2 ′- 30; 3,3 ′- 40; 4.4 ′- 50; 5.5 ′- 60.

The change in the course of the pH-concentration curves in the pH range of 5-6 shows the competitiveness of cadmium and iron ions during complexation: at pH> 5, the concentration of cadmium in the leaching solution over the concentration of iron is clearly predominated (by a factor of 10), which in this region exists only in the form of hydroxy compounds. Consequently, carrying out the process in neutral and slightly alkaline medium will allow selectively to transfer cadmium into the solution, quantitatively leaving iron in the solid phase. Similar results were obtained by us in [7, 8] when studying the leaching of lead cakes of zinc production.

Laboratory studies of the active mass of alkaline batteries leaching were carried out in a thermostated (20-60 °C) glass reactor with a stirrer. A solution of 100 g / dm^3 Trilon B was used with an initial pH of 7; The ratio of G: T = 7: 1, which ensured the stoichiometric ratio Cd: edta = 1: 1 and the preparation of solutions with a maximum concentration of cadmium.

The obtained results (Fig. 6) confirm the assumptions about the features of complexation in the system "iron-cadmium-edta".

The presence of iron in the solution is noticeable in the first 7-10 minutes of the experiment, which is determined by the rate of transition of cadmium into the solution and by competitive complexation.

3. Conclusion

The authors presented the technological features of processing run-down alkaline nickel-cadmium batteries recycling with the extraction of valuable components (from the example of nickel-cadmium storage batteries of JSC ”RZD” rolling equipment). The following results were obtained during the study:

1. During the process of CdO leaching in Trilon B solution at different initial pH: 1-5.36; 2-8.0; 3, 3.8, the dependence of complexation on the pH values of Trilon B is found.

2. During the leaching of NiO, FeO and Femet in a Trilon B solution, it was found that complex formation does not occur over the entire pH range.

3. During experiments on leaching iron oxide (III), the traces of iron-trilonate complex can be possibly found in the acidic region (in Trilon B solution). In the alkaline region, in which it is subsequently planned to leach raw materials, the formation of complexes with iron has not been observed.

Thus, the presented technology of nickel-cadmium batteries recycling not only has the right to exist due to the real need on the part of JSC «Russian Railways», but also significantly surpasses from the point of view of ecological safety the existing methods of recycling based on pyrometallurgical methods.

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