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Kinetics of Leaching of Nickel Compounds from Spent Electrodes of Nickel–Iron Batteries in Ammonia Solutions

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Abstract—The extent of nickel recovery from spent electrodes of nickel–iron batteries in ammonia solutions was studied in relation to time and leaching temperature. The optimal time and the temperature at which the extent of nickel recovery in leaching solutions containing ammonium salts is the highest were determined and the dependence of the process efficiency on the anionic composition of the solution was analyzed. The apparent activation energies of nickel leaching from the active mass preliminarily extracted from lamellas are calculated, and the adequacy to the actual process of the model of leaching controlled by external diffusion is assessed.

The problems of utilization and recycling of raw materials containing non-ferrous metals, including nickel, are presently the matter of strong interest. The priority direction in this field is the development of hydrometallurgical processing techniques characterized by environmental safety and low energy consumption [1–4].

Complexation in ammonia solutions underlies nickel recovery from oxidized ores [5–7]. Previously, it has been shown that this approach is promising for processing of positive electrodes of nickel–iron batteries. Nickel is present in lamellas of spent batteries in the form of hydroxides, mainly $Ni(OH)_2$ dissolving in aqueous ammonia by the overall reaction

$$Ni(OH)_2(s) + 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 2OH^-(aq). \quad (1)$$

Ammonium salts added to aqueous solutions make higher the dissolution efficiency because of their buffer action preventing accumulation of OH^- ions by reaction (1), which takes the form

$$Ni(OH)_2(s) + 4NH_3(aq) + 2NH_4^+(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 2H_2O. \quad (2)$$

It was established that the extent of nickel recovery may be as high as 99% in some cases of leaching of lamella fragments in ammonia solutions containing ammonium salts [8]. However, revealing the possibility of such processing on industrial scale requires more detailed studies of the process kinetics.

The rate of leaching (generally dependent on reagent concentration, temperature, rate of stirring, extent to which the surface of the solid phase is developed, etc.) may vary in the course of the process. The heterogeneous process of leaching includes at least three main stages, namely, transport of reagents toward the reaction surface, chemical reactions proper, and removal of dissolved products into the solution bulk. Therefore, one of the basic tasks in studying the kinetics of a complex process consists in finding the apparent activation energy of the process and in determining its limiting stage.

In this study, we analyzed the efficiency of the process in relation to the time and temperature of leaching for several solution compositions. The leaching was performed from a spent active paste, both contained within lamella fragments and preliminarily extracted from it. The leaching solutions were prepared using the following reagents: aqueous ammonia NH_4OH (ultrapure grade) and ammonium salts (chemically pure grade) NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, and $(NH_4)_2CO_3$.

The extent of nickel recovery was calculated from the results of spectrophotometric analysis for nickel in the leaching solutions by the technique described in [8]. The leaching process was studied in solutions of the following compositions (M): 2 NH_4OH and 1 NH_4NO_3 (solution A), 2 NH_4OH and 1 NH_4Cl

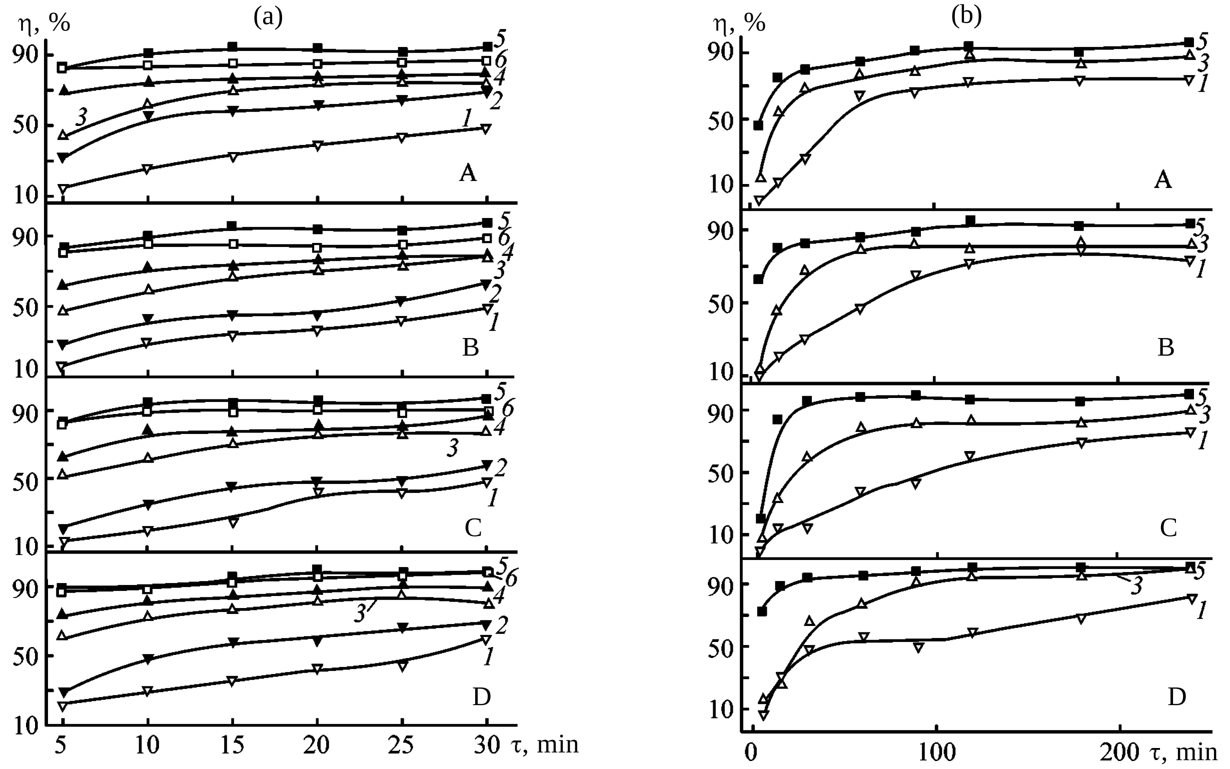

Fig. 1. Kinetics of nickel recovery from (a) active paste and (b) lamella fragments into ammonia solutions A–D at various temperatures. (η) Extent of nickel recovery and (τ) time; the same for Fig. 3. Leaching temperature (°C): (*1*) 30, (*2*) 40, (*3*) 50, (*4*) 60, (*5*) 70, and (*6*) 80.

(solution B), 1.5 NH_4OH and 1 $(NH_4)_2SO_4$ (solution C), and 1.5 NH_4OH and $(NH_4)_2CO_3$ (solution D).

The leaching was done from 1.0-g portions of spent active paste and also from closed lamella fragments containing approximately the same amount of the active paste. A sample was placed in a preliminarily thermostated flask with 50 ml of leaching solution, equipped with a magnetic stirrer. In this stage of the investigation, the rate of agitation was maintained constant. The duration of leaching was varied from 5 to 240 min for lamellas and from 5 to 30 min for the active paste without lamellas.

Figure 1a illustrates the progress in time of isothermal leaching of nickel from the active paste into solutions containing various ammonium salts. Several tentative conclusions follow from the presented plots: (1) the curve shapes are basically the same for all of the studied leaching solution compositions; (2) recovery of nickel is strongly temperature-dependent, especially in the initial stage of the process (first 10 min) and at temperatures lower than 50°C; the maximum extent of recovery is observed at 70°C and then, with temperature raised to 80°C, decreases somewhat; (3) above 50°C the rate of leaching tends to decrease with time, except for the initial stage; (4) at 70–80°C the optimal time of nickel recovery is 10–20 min and 1–2 h for leaching from, respectively, the active paste and lamellas in ammonia solutions, irrespective of their anionic composition.

This suggests that, in its initial stage, the leaching proceeds in a mixed diffusion-kinetic mode and then tends to pass into the predominantly diffusion region [9–11].

The results obtained in leaching of nickel compounds from lamella fragments (Fig. 1b) on the whole agree with the aforesaid, with correction made for the even more pronounced decrease in the leaching rate with time. The shapes of the curves obtained at 30°C differ from those of the curves taken at 50 and 70°C to a greater extent than these latter differ from each other. Comparison of the data in Figs. 1a and 1b shows that direct leaching through the lamella sheath at a given temperature imposes on the process obvious diffusion limitations, which is one more evidence in favor of the above tentative conclusions.

To confirm these conclusions quantitatively, the obtained kinetic dependences were processed to evaluate the apparent activation energy of the process. To construct a plot in the Arrhenius coordinates, the rate of leaching was determined from the initial portions of the curves. Figure 2 presents the results of mathematical processing of the kinetic curves obtained in leaching in ammonia solutions of the active paste not enclosed in a lamella. In the same coordinates are shown experimental points describing leaching from lamella fragments under similar conditions. The slope of the straight line presented in the figure was used to determine the activation energy of leaching of the active paste to be, on the average, 30 kJ mol^{-1}, which is a quantitative indication of the occurrence of the process in the transition diffusion-kinetic region [10, 11].

At the same time, the experimental dependence in Fig. 2, well described by a straight line in the Arrhenius coordinates (with correlation coefficients exceeding 0.95) at $1/T > 2.95 \times 10^{-3}$ K^{-1} ($T < 65°\text{C}$), shows an obvious tendency toward a decrease in its slope (and, consequently, in the apparent activation energy). These results confirm the assumption that the process tends to pass into the diffusion region with time and with increasing leaching temperature. In addition, the closeness of the experimental points in Fig. 2 indicates that the leaching parameters affect in about the same way the percentage of nickel recovery from the active paste and lamella fragments. It should be noted that no significant differences were revealed between the activation energies obtained for all of the four leaching solutions: 29.9, 32, 33, and 27.4 kJ mol^{-1} for, respectively, solutions A, B, C, and D.

Erofeev and Kolmogorov derived a generalized kinetic equation that can be used to derive, without composing differential equations, formulas of chemical kinetics for homogeneous and heterogeneous reactions. In particular, the equation for topochemical processes has the form

$$E = 1 - \exp(-k\tau^n), \tag{3}$$

where E is the fraction of substance reacted by the instant of time τ, having the meaning of the probability that a molecule has reacted by the time τ.

Bulanov *et al.* [13] used for describing the kinetics of leaching of iron-containing raw materials in obtaining ferrous chloride a similar equation

$$C_i = C_i^0[1 - \exp(\alpha_i\tau)], \tag{4}$$

where $\alpha_i < 0$ is a constant accounting for specific features of the reagent diffusion, C_i^0 is the concentration of ith leached substance in the starting concentrate, and C_i is its concentration in solution.

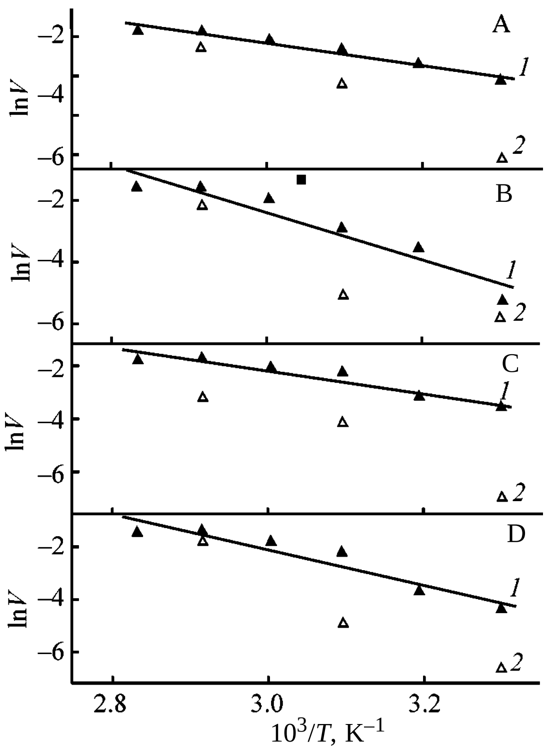

Fig. 2. Dependence of the leaching rate $\ln V$ (for explanation, see text) in ammonia leaching solutions A–D on temperature T. (*1*) Active paste and (*2*) lamella fragments.

The numerical values of the coefficients can be obtained by means of linear regression analysis of experimental data. Such a model of the leaching process requires some assumptions, which idealize somewhat the process in question, but are rather frequently used in modeling. At the same time, the validity of the following assumptions is the criterion for the possibility of regarding the process as an ideal mixing process [13]: (1) all solid particles have spherical shape which is preserved during the chemical reaction; (2) the average granulometric composition of particles is the same throughout the reaction volume; (3) the solid particles and the solution are homogeneously mixed in the reaction volume; (4) the active surface of the particles is proportional to the concentration of the substance being dissolved in the solid phase; (5) the sludge temperature is constant in time and the same throughout the reaction volume; (6) the leaching of the active paste is diffusion-controlled, the substance transfer within pores of a particle toward its boundary (internal diffusion) can be neglected and only external diffusion (substance transfer from the particle surface into the bulk of the liquid) be con-

Results of linear regression analysis of the kinetics of nickel leaching from the active paste and lamella fragments in ammonia solutions at 70°C

Solution	$G = \ln(1 - \eta)$	R
	Active paste	
A	$-1.540 - 7.61 \times 10^{-2}\tau$	0.840
B	$-1.927 - 3.931 \times 10^{-2}\tau$	0.746
C	$-2.119 - 4.945 \times 10^{-2}\tau$	0.764
D	$-1.467 - 1.113 \times 10^{-1}\tau$	0.865
	Lamella fragments	
A	$-1.229 - 8.344 \times 10^{-3}\tau$	0.869
B	$-1.504 - 6.131 \times 10^{-3}\tau$	0.796
C	$-1.888 - 1.307 \times 10^{-2}\tau$	0.704
D	$-2.047 - 1.776 \times 10^{-2}\tau$	0.836

sidered; (7) the concentration of the leached component at the surface of the solid phase is close to the saturation concentration; (8) surface adsorption can be neglected in considering heterogeneous chemical reactions and the rate at which the adsorption equilibrium is attained greatly exceeds the rate of the chemical reaction; (9) all reactions occur on the surface of the solid phase; (10) ammonia leaching solutions are in excess in the apparatus; (11) the diffusion surface can be taken to be proportional to the nickel hydroxide concentration in the solid phase in considering Ni^{2+} diffusion flows; (12) the leaching process can be considered under conditions excluding hydrolytic decomposition of ammonia solutions.

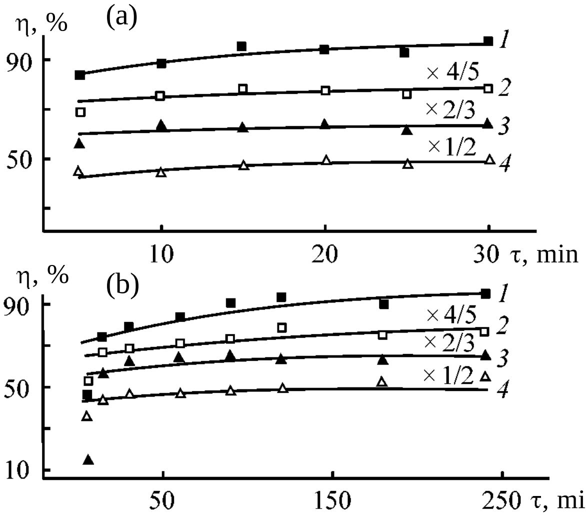

Fig. 3. Comparison of model kinetic curves with experimental data for nickel leaching from (a) active paste and (b) lamella fragments at 70°C. Solution: (*1*) A, (*2*) B, (*3*) C, and (*4*) D.

With account of the fact that the C_i/C_i^0 ratio is in the given case equivalent to the extent of recovery η, an attempt was made to describe the leaching process in terms of the model proposed in [13]. For this purpose, the experimental data were subjected to regression analysis in the coordinates G–τ, where $G = \ln(1 - \eta)$, with the slope of the straight line yielding in this case the coefficient α. The results of the analysis are presented in the table (R is the correlation coefficient).

Thus, the coefficients of the models are significant, since t (Student's test) gives significant correlation coefficients $R \geq 0.67$. Hence, we can obtain theoretical and experimental models describing how nickel passes into solution in the course of time. Model kinetic curves of nickel recovery, plotted using the equations (see table), are in good agreement with the experimental data for the active paste (Fig. 3a). Leaching from lamella fragments is also satisfactorily described by the equations of the model, except in the initial stage when, as shown above, the share of the kinetic component is still relatively high (Fig. 3b).

Analysis of the model suggests that the process of nickel passing into solution can indeed be considered an ideal mixing process with sufficient accuracy. The coincidence of the calculated and experimental data suggests that the process of nickel leaching in ammonia solutions from both the active paste itself and lamellas with active paste is diffusion-controlled.

CONCLUSIONS

(1) A study of the kinetics of nickel leaching from spent electrodes of nickel–iron batteries demonstrated that, in the initial stage (especially at temperatures below 50°C), the process occurs in a mixed diffusion-kinetic mode and then tends to pass into the diffusion region.

(2) The anionic composition of ammonia leaching solutions exerts no fundamental effect on the efficiency of nickel recovery from the active paste and lamella fragments.

(3) The optimal time of leaching at 70–80°C is about 10–20 min for the active paste and 1–2 h for lamella fragments.

(4) The model of outer-diffusion-controlled leaching satisfactorily describes the kinetics of nickel recovery from the active paste and lamella fragments taken from spent positive electrodes of nickel–iron batteries.

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