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BRIEF COMMUNICATIONS

Oxidation of Zinc Sulfide in the System HNO_3–$Fe(NO_3)_3$–H_2O

S. V. Ostanova, A. V. Chubarov, S. V. Drozdov, and V. V. Patrushev

Institute of Chemistry and Chemical Technology, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, Russia

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Abstract—The behavior of zinc sulfide in the system HNO_3–$Fe(NO_3)_3$–H_2O at 25, 55, and 80°C was studied using the simplex-lattice design method.

Data on reactions of certain metal sulfides with mineral acids are well known; however, the range of systems under study is rather narrow. The system HNO_3–$Fe(NO_3)_3$–H_2O has been studied insufficiently [1].

This system was studied to analyze reactions of zinc sulfide in the ternary system HNO_3–$Fe(NO_3)_3$–H_2O at various HNO_3 and $Fe(NO_3)_3$ concentrations and to obtain data on the composition of precipitates formed in redox reactions at 25, 55, and 80°C.

EXPERIMENTAL

Zinc sulfide was synthesized by the technique described in [2] and identified by X-ray phase analysis; its specific surface area S_{sp} = 4.1 $m^2\ g^{-1}$ was determined by BET. Chemically pure iron(III) nitrate and nitric acid, and also distilled water, were used in the study. The experiments were carried out in a temperature-controlled system (the accuracy of temperature measurements was ±0.1°C) in the course of 2 h (preliminary experiments showed that the concentration of Zn^{2+} ions in solution remains unchanged after 2-h contact of zinc sulfide with the solution) with permanent stirring and initial s : l ratio of 1 : 5.

The concentration of Zn^{2+} ions in the liquid phase was determined by titrimetry and atomic-absorption spectrophotometry [3, 4], and that of nitric acid, by titrimetry [4]. After filtration, the solid phase was washed with water and ethanol to remove the solution, dried, and subjected to X-ray phase analysis.

The results obtained were processed by means of the simplex-lattice design [5]. The following components were the vertices of the concentration triangle: X_1, H_2O (55.56 M); X_2, $Fe(NO_3)_3$ (1.8 M); and X_3, HNO_3 (3.2 M). As functions served the extents to which Zn^{2+} passes from ZnS into solution.

A simplex-lattice design for the incomplete cubic model used to describe the system under study is presented in the table. These data were used to calculate the regression equations for 25, 55, and 80°C:

$$Y_{25} = 0.05X_1 + 21.79X_2 = 49.44X_3 + 30.95X_1X_2 + 24.16X_1X_3 + 96.34X_2X_3 + 113.09X_1X_2X_3,$$

$$Y_{55} = 0.08X_1 + 12.46X_2 + 37.31X_3 + 74.42X_1X_2 + 37.16X_1X_3 + 49.70X_2X_3 - 176.91X_1X_2X_3,$$

$$Y_{80} = 0.07X_1 + 50.00X_2 + 55.22X_3 + 22.53X_1X_2 - 98.05X_1X_3 - 19.40X_2X_3 + 237.98X_1X_2X_3.$$

The root-mean-square error was 3%. It was found that these equations describe adequately the data obtained in control experiments nos. 8–10, with 97% probability. The equations were used to construct phase diagrams for the temperatures under study (Figs. 1a–1c).

The increase in the degree of Zn^{2+} leaching is directed toward the HNO_3–$Fe(NO_3)_3$ system in all the diagrams, with the most complete extraction of about 62% achieved at 25°C. The same behavior is observed at 55 and 80%, but the degree of leaching of zinc ions is lower (40 and 55%, respectively). Addition of nitric acid to the solution promotes the oxidation reaction, with an increase in acidity favoring sulfide break-

Simplex-lattice design for incomplete cubic model*

Experiment no.	X_1	X_2	X_3	Y_{e25}	Y_{c25}	Y_{e55}	Y_{c55}	Y_{e80}	Y_{c80}
	M			%					
1	1	–	–	0.05	0.05	0.08	0.08	0.07	0.07
2	–	1	–	21.79	21.79	12.46	12.46	50	50
3	–	–	1	49.44	49.44	37.31	37.31	55.22	55.22
4	0.5	0.5	–	18.66	18.66	24.85	24.85	19.40	19.40
5	0.5	–	0.5	30.78	30.78	27.99	27.99	3.13	3.14
6	–	0.5	0.5	59.70	59.70	37.31	37.31	47.76	47.76
7	0.33	0.33	0.33	44.78	44.78	27.99	27.99	28.36	28.36
8	0.15	0.15	0.7	53.01	53.01	36.01	36.01	37.10	37.07
9	0.15	0.7	0.15	38.36	38.37	25.41	25.41	40.43	40.43
10	0.7	0.15	0.15	20.43	20.45	17.57	17.57	6.47	6.48

* Y_{e25}, Y_{e55}, Y_{e80}, Y_{c25}, Y_{c55}, and Y_{c80} are the experimental and calculated degrees of zinc extraction at 25, 55, and 80°C.

down, as seen from the figures. At 80°C, the concentrations of Fe^{3+} and HNO_3 ions hardly affect the degree of leaching, which falls within the range 50–55%. When temperature is lowered, the oxidation process is shifted to higher nitric acid concentrations, although the highest degree of zinc extraction is observed in the concentration ranges 1.92–2.4 M of HNO_3 and 0.72–0.45 M of $Fe(NO_3)_3$.

According to X-ray phase analysis data, undecomposed ZnS and elementary sulfur are present in the solid phases. As shown by an analysis of the precipitates after breakdown, the content of elementary sulfur at 25°C is much lower than that at elevated temperatures. This suggests that S(–2) $\rightarrow$ S(0) $\rightarrow$ S(+6) conversion occurs in the course of the reaction of nitric acid and iron(III) nitrate with ZnS. Raising the temperature results in faster ZnS oxidation and evolution of gaseous reaction products (evolution of NO and NO_2). Such a behavior of the system under study seems to be related to the screening of the reaction surface of the material by elementary sulfur, which is the reason for the poorer extraction of zinc ions at elevated temperatures.

The reaction of ZnS with the oxidizing system $Fe(NO_3)_3$–H_2O depends only on the concentration of the reactants in virtually the entire temperature range under study. Such a behavior suggests that the presence of Fe^{3+} ions in solution promotes zinc sulfide oxidation, and further increase in the concentration of nitric acid results in faster oxidation of the sulfide sulfur to elementary sulfur and in the screening of the reaction surface. By varying the dispersity, one can pass from leaching to complete dissolution of zinc sulfide.

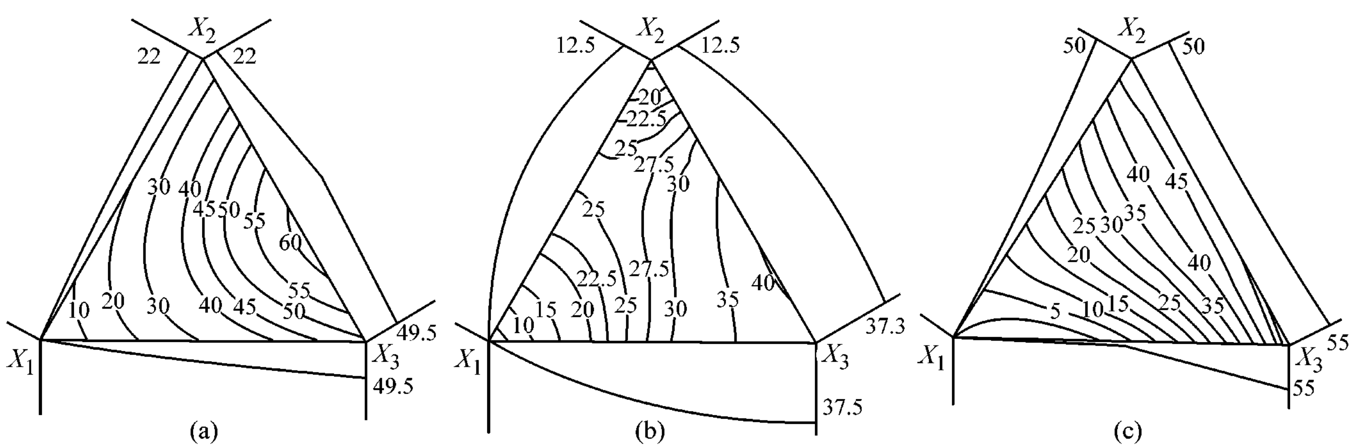

Fig. 1. Zn^{2+} extraction from ZnS (%) at (a) 25, (b) 55, and (c) 80°C.

CONCLUSIONS

(1) The degree of Zn^{2+} leaching grows with increasing concentrations of nitric acid and iron(III) nitrate, and an increase in temperature hardly affects the leaching.

(2) At 25°C the solid phase contains a lesser amount of elementary sulfur than that at elevated temperatures.

(3) In the course of the ZnS reaction with nitric acid and iron(III) nitrate a $S(-2) \rightarrow S(0) \rightarrow S(+6)$ conversion takes place.

(4) Equations describing the degree of Zn^{2+} extraction at 25, 55, and 80°C were obtained, and the corresponding diagrams were constructed on their basis.

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