ISSN 1070-4272, Russian Journal of Applied Chemistry, 2008, Vol. 81, No. 6, pp. 1074–1077. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.V. Patrushev, S.V. Ostanova, A.V. Chubarov, S.V. Drozdov, 2008, published in Zhurnal Prikladnoi Khimii, 2008, Vol. 81, No. 6, pp. 1036–1038.

BRIEF COMMUNICATIONS

Behavior of Silver Sulfide in the System $Ag_2S–Fe(NO_3)_3–HNO_3–H_2O$

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

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

Received November 2, 2007

Abstract—Behavior of silver sulfide in the system $Ag_2S–Fe(NO_3)_3–HNO_3–H_2O$ was studied at 25, 55, and 80°C using the method of the simplex-lattice experiment design. The quantitative dependences of Ag_2S oxidation on the concentrations of the acid and Fe^{3+} were determined. The isoconcentration diagrams were obtained.

DOI: 10.1134/S1070427208060311

The main amount of silver is extracted from complex ores and concentrates in which silver is in the form of silver sulfide, argentite, one of the most widespread minerals. Argentite is contained in gravitational and flotation concentrates produced in processing of gold- and silver-containing ores and, in particular, lead-zinc ores, and in secondary raw materials.

Hydrometallurgical procedures for recovery of silver, including that in the form of silver sulfide, employ cyanide [1, 2], thiocyanate [3], thiourea [4], and thiosulfate [5] solutions. However, it is necessary to use in such cases oxidizing agents, e.g., O_2 or Fe^{3+}, which involves additional expenditure.

A technology for processing of sulfide lead-zinc ores and concentrates and, in particular, those from the Gorevo deposit with the use of nitric acid and iron(III) nitrate solutions has been developed. The behavior of silver sulfide in systems of this kind has not been studied.

Nitric acid is a strong oxidant ($E^0_{NO_2/HNO_3}$ = 0.80 V) and, therefore, it oxidizes silver sulfide without introduction of any additional oxidizing agent into a system. However, it is of interest to study the effect of Fe^{3+} additives on the process of argentite oxidation. This is due to the composition of technological solutions, because, in most cases, the concentration of Fe^{3+} ions is appreciable when nitrate acid-salt solvents are used for processing of silver-containing ores and concentrates.

EXPERIMENTAL

To obtain information about the oxidation of silver sulfide in complex systems with various mineral forms in industrial processing of silver-containing ores and concentrates, we studied $Ag_2S–Fe(NO_3)_3–HNO_3–H_2O$ systems with a high content of silver. The silver sulfide synthesized was identified by X-ray phase analysis. The behavior of Ag_2S in the systems under study was judged from the variation of the total silver concentration in solution and from the composition of insoluble precipitates. The concentration of silver in solution was determined by titration analysis and atomic-absorption spectrophotometry [6, 7], and that of HNO_3, by titration analysis [7]. The mathematical data processing was carried out by the method of simplex-lattice experiment design [8].

The experiments were performed in thermostated cells at 25 ± 0.1, 55 ± 0.1, and 80 ± 0.1°C in the course of 2 h, with mechanical stirring at s : l = 1 : 5. Preliminary experiments demonstrated that making longer the time of contact of phases does not change the silver concentration in solution. After the completion of the experiments, the solution was analyzed for the content of silver and nitric acid. The solid phase was filtered and washed with water and ethanol to remove the solution, Design matrix for the incomplete cubic model*

Exper-iment no.	Volume fraction of a solution			Amounts of oxidized silver sulfide, %					
				Y_{exp}	Y_{calc}	Y_{exp}	Y_{calc}	Y_{exp}	Y_{calc}
	X_1	X_2	X_3	25°C		55°C		80°C	
1	1	0	0	ND	0	ND	0	0.922	0.922
2	0	1	0	0.618	0.618	11.538	11.538	36.896	36.896
3	0	0	1	26.815	26.815	100.000	100.000	100.000	100.000
4	0.5	0.5	0	0.249	0.249	2.769	2.769	14.989	14.989
5	0	0.5	0.5	11.885	11.885	64.846	64.846	100.000	100.000
6	0.5	0	0.5	5.192	5.192	43.154	43.154	86.474	86.474
7	0.33	0.33	0.33	4.455	4.458	35.963	35.960	66.938	66.938
8	0.15	0.15	0.7	2.538	2.539	72.040	72.041	100.000	100.951
9	0.15	0.7	0.15	11.238	11.238	24.655	24.657	52.999	53.066
10	0.7	0.15	0.15	1.568	1.569	12.882	12.883	34.755	34.753

* X_1 stands for H_2O (55.56 M); X_2, $Fe(NO_3)_3$ solution (1.8 M); X_3, HNO_3 solution (3.2 M); Y_{exp} and Y_{calc}, experimental and calculated amounts of oxidized silver sulfide; ND, not determined.

dried, and subjected to an X-ray phase analysis. The data obtained were processed by the method of simplex lattices, whose application to systems of this kind yielded good results in [9, 10]. The simplex-lattice design for an incomplete cubic model employed in the study is presented in the table.

Using the data obtained, we calculated the coefficients of polynomials of incomplete third order, which describe the dependence of the degree of silver sulfide oxidation on the reactant concentrations. The equations were used to construct composition–property diagrams (see Figs. 1a–1c).

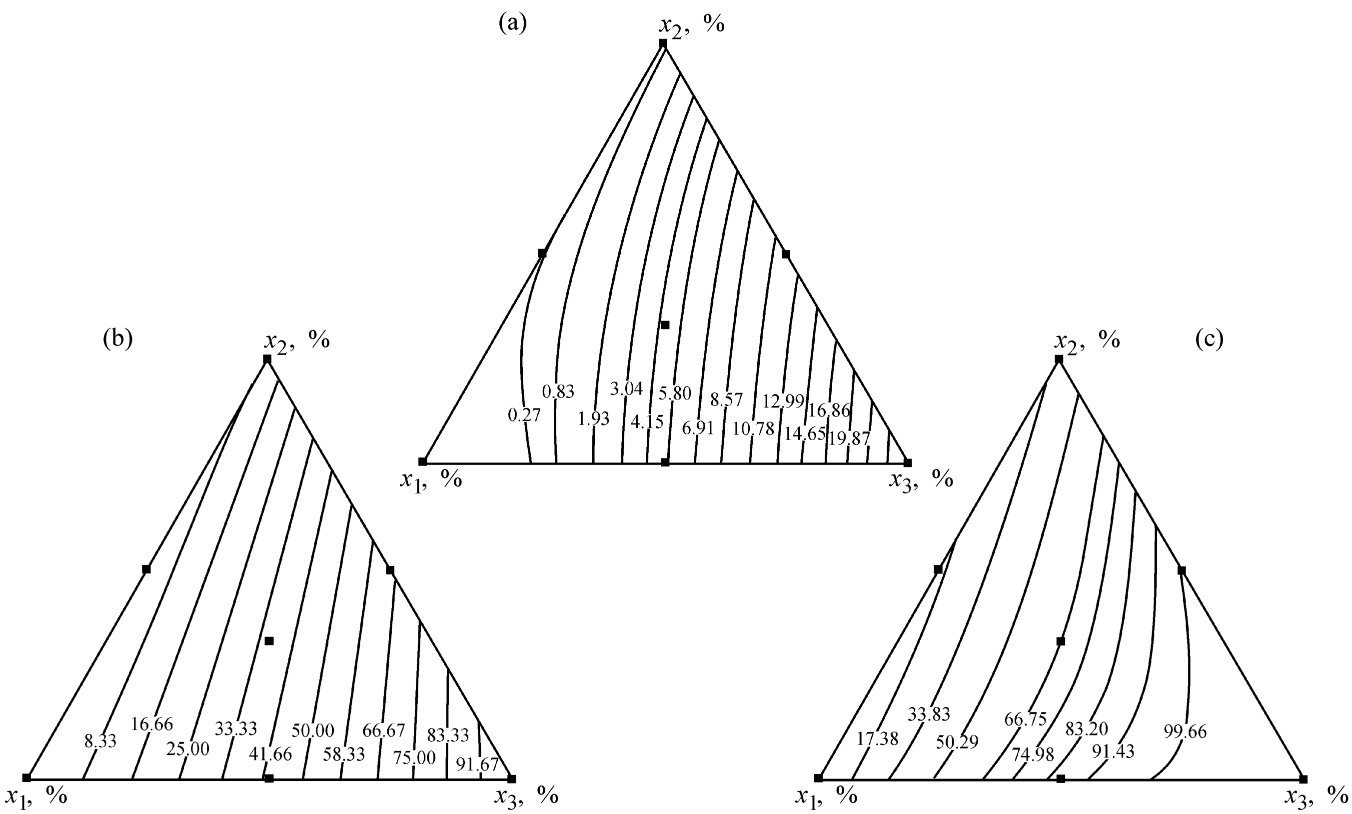

Fig. 1. Diagram of the Ag_2S oxidation (%) in the Ag_2S–$Fe(NO_3)_3$–HNO_3–H_2O system at different temperatures. Temperature (°C): (a) 25, (b) 55, (c) 80.

The oxidation of silver sulfide in the system Ag_2S–$Fe(NO_3)_3$–HNO_3–H_2O can be described by the following reaction equations:

$$Ag_2S + 4HNO_3 \rightarrow 2AgNO_3 + 2NO_2 + S^0 + 2H_2O, \quad (1)$$

$$Ag_2S + Fe(NO_3)_3 + H_2O \rightarrow 2AgNO_3 + Fe(OH)_2 + NO_2 + S^0, \quad (2)$$

$$Ag_2S + Fe(NO_3)_3 + 2HNO_3 \rightarrow 2AgNO_3 + Fe(NO_3)_2 + NO_2 + S^0 + H_2O, \quad (3)$$

$$Ag_2S + 2Fe(NO_3)_3 + 2HNO_3 \rightarrow Ag_2SO_4 + 2Fe(NO_3)_2 + 3NO_2 + NO + H_2O. \quad (4)$$

The experiments we performed demonstrated that the maximum transfer of silver into solution at 25°C (see Fig. 1a) reaches 26.8% at a HNO_3 concentration in solution of 3.0 M. Addition of iron(III) nitrate to the solution hardly affects the oxidation of silver sulfide.

The X-ray data show the presence of a significant amount of unoxidized sulfide. As the content of nitric acid in solution increases, the amount of elementary sulfur in the precipitate grows.

Based on the experimental data, we derived the regression equation relating the degree of Ag_2S oxidation to the concentrations of nitric acid and iron(III) nitrate at a temperature under consideration. A verification against the data of control run nos. 8–10 demonstrated that the equation adequately describes the process with a confidence probability of 97%. The root-mean-square error in the determination of Y values was 3%.

Raising the temperature to 55°C (see Fig. 1b) does not change the general pattern of silver sulfide oxidation in the acid–salt system under study, but only favors an increase in its transfer to solution. The maximal value (~100%) is reached at the point with the highest concentration of nitric acid. The X-ray data show the same trend toward formation of elementary sulfur in precipitates as that at 25°C. This suggests that reaction (3) predominates as the nitric acid concentration increases to 3.2 M.

For this temperature, we also derived a regression equation. To verify its adequacy, a series of control experiments were carried out. The root-mean-square deviation was 3% at a confidence probability of 97%.

At 80°C, the same behavior as that at 25 and 55°C is observed (see Fig. 1c). Only the quantitative characteristics of the process change: the whole amount of silver passes into solution even at an HNO_3 concentration of about 2.3 M.

The regression equation describing the behavior of silver sulfide in the system under consideration at 80°C was obtained. The results of control experiments show that this equation adequately describes the process with a confidence probability of 97%. The root-mean-square error in the determination of Y values was 3%.

It is necessary to note that temperature affects the possibility of occurrence of reactions (1)–(4). Reactions (1), (3), and (4) proceed in the whole temperature range under study, whereas reaction (2), only upon heating. For example, reaction (2) does not proceed at 25°C even at a Fe^{3+} concentration of 1.8 M; at 55°C, changes occur in solution beginning at a Fe^{3+} concentration of 0.744 M; and at 80°C, reaction (2) proceeds at even lower Fe^{3+} concentrations.

It was found that, in a mixture of silver and lead sulfides, produced by their coprecipitation from nitrate solutions with hydrogen sulfide, and also in mechanical mixtures of silver sulfide with elementary sulfur and lead sulfide, Ag_2S is oxidized in the same way as pure silver sulfide. An increase in HNO_3 and $Fe(NO_3)_3$ concentrations results in that the degree of silver recovery into solution becomes higher. Temperature strongly affects the process. For example, the fraction of oxidized silver sulfide was 20–30% at 25°C and 100% at 80°C. The nature of the starting solid mixtures has no effect on the degree of silver sulfide oxidation.

CONCLUSIONS

(1) A study of the effect of the concentration of nitric acid and iron(III) nitrate on the oxidation of silver sulfide in the systems Ag_2S–$Fe(NO_3)_3$–HNO_3–H_2O at various temperatures revealed that nitric acid strongly affects the oxidation of Ag_2S, which reaches the maximal value (100 %) at an HNO_3 concentration of 3.2 M.

(2) The chemical mechanism of the oxidation of Ag_2S in nitrate media to give elementary sulfur at 25 and 55°C and sulfate sulfur at 80°C was elucidated.

(3) Diagrams describing the dependence of the degree of silver sulfide oxidation on the HNO_3

and $Fe(NO_3)_3$ concentrations were constructed on the basis of the experimental data.

REFERENCES

1. Buketov, E.A. and Ugorets, M.Z., *Gidrokhimicheskoe okislenie khal'kogenov i khal'kogenidov* (Hydrochemical Oxidation of Chalcogens and Chalcogenides), Alma-Ata: Nauka, 1975.
2. Kakovskii, I.A. and Potashnikov, Yu.M., *Kinetika protsessov rastvoreniya* (Kinetics of Dissolution Processes), Moscow: Metallurgiya, 1975.
3. Chursanov, Yu.V., Potashnikov, Yu.M., and Gortsevich, S.L., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 7, pp. 1181–1184.
4. Maslenitskii, I.N., Chugaev, L.V., Borbat, V.F., et al., *Metallurgiya Blagorodnykh Metallov* (Metallurgy of Noble Metals), Moscow: Metallurgiya, 1987.
5. Potashnikov, Yu.M., Chursanov, Yu.V., and Gortsevich, S.L., *Zh. Fiz. Khim.*, 2000, vol. 74, no. 9, pp. 1593–1596.
6. Fainberg, S.Yu. and Filippova, R.A., *Analiz rud tsvetnykh metallov* (Analysis of Ores of Nonferrous Metals), Moscow: Metallurgizdat, 1963.
7. Alekseev, V.I., *Kolichstvennyi analiz* (Quantitative Analysis), Moscow: Khimiya, 1972.
8. Akhnazarova, S.L. and Kafarov, V.V., *Optimizatsiya eksperimenta v khimii i khimicheskoi tekhnologii* (Optimization of the Experiment in Chemistry and Chemical Engineering), Moscow: Vysshaya Shkola, 1978.
9. Ostanova, S.V., Chubarov, A.V., Drozdov, S.V., and Patrushev, V.V., *Zh. Prikl. Khim.*, 2002, vol. 75, no. 8, pp. 1381–1383.
10. Ostanova, S.V., Chubarov A.V., Drozdov, S.V., and Patrushev, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2003, vol. 46, no. 3, pp. 90–92.