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Regularities of Oxidative Autoclave Leaching of Pyrite Concentrates

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ABSTRACT: As a result of laboratory studies, the optimal combination of independent variable factors was revealed during the autoclave leaching of pyrite concentrate with up to 63% recovery of elemental sulfur (S^0): temperature range 383-388K, leaching duration 83-90 min, HNO_3 concentration 21-22 wt. % and ratio W: T = 3.0-3.4; in this case, up to 90% of the iron is deposited in cake in the form of oxide. It was shown that the process of interaction of sulfide iron feed with nitric acid largely depends on the temperature and concentration of the chemical reagent.

KEY WORDS: pyrite concentrate, autoclave, leaching, nitric acid, experiment planning.

I.INTRODUCTION

Previous work [1] presented the results of physicochemical studies of the autoclave leaching process in various technological modes of opening up the pyrite concentrate in a hydrochemical environment. An assessment of the completeness of processes flow was carried out according to the calculated values of the isobaric-isothermal potential at constant pressure, Gibbs energy (ΔG_T^0, kJ / mol) and the values of equilibrium constants (Kp). This work is devoted to the establishment of optimal conditions for this process, depending on the most significant technological factors, influencing the chemical mechanism of the process and its performance. The optimal leaching option was chosen taking into consideration of the chemical mechanism that ensures the oxidation of sulfide sulfur of the raw material to the elementary oxidation state with the simultaneous production of iron in the form of hematite. The task of this work is development of conditions for the implementation of this mechanism, determined by the optimal combination of technological factors.

II. OBJECT AND METHODS OF RESEARCH

The research was carried out on a sample of pyrite concentrate containing the main elements: Fe 25.6%, S 26.7%, Ag 12.3 g / t, Au 4.5 g / t, as well as impurities ∑ non-ferrous metals 4, 17% (including: Al 3.35%, Zn 0.55%, Ni 0.13%, Cu 0.075%, Co 0.065%), As 3.6%, Sb 0.53%, Si 21%. The assessment of the technological factors influence on the indicators of the studied complex oxidative hydrochemical process was carried out by the method of mathematical planning of experiments [2, 3].

III. RESULTS OF THE INVESTIGATIONS AND DISCUSSION

Laboratory experiments have established that the process of leaching of pyrite concentrate is regulated mainly by temperature and time factors, as well as, by the consumption of the oxidizing agent in various combinations. Thus, leaching of pyrite concentrate with nitric acid with a concentration of 1.63-3.70 M (≈102-233 g / l), at S: L = 1: 4-5, temperature 363-383K (90-100^{0}C) and the duration of the process of 5- 8 hours at atmospheric pressure is characterized by slow kinetics and low extraction of elemental sulfur (5-10%). At the same time, due to the formation of amorphous forms of hydrolyzed iron, it becomes difficult not only to open up the raw material in time, but also to filter the pulp. Therefore, further studies were carried out using autoclave technology at elevated temperatures and pressures which ensures complete and rapid decomposition of raw materials. As a result, relatively easily filterable solid residue was obtained, that is containing mainly elemental sulfur and hematite, as well as, productive solutions with water-soluble forms of non-ferrous metals from ligature impurity in the form of chemical compounds.

According to the purpose of the study, the maximum output S0 (Y) was chosen as the optimization parameter. The area of the factorial technological space was provided on the basis of the preliminary experiments results with the following levels (Table 1):

a) temperatures (X_1) from 358 to 388K;

b) process time (X_2) 60-90 min;

c) the concentration of HNO_3 (X3) 15-25 wt.%; d) L: S (X4) 2-4.

The calculations used the coded (+ and -) factors values, which were obtained by dividing the difference between the boundary and average values of "X" by the interval of their variation.

Table 1. Planning matrix 24-1IV and results of experiments on nitric acid autoclave leaching of pyrite concentrate for the purpose of the S^0 recovery

No	Level	Factors			
		X_1	X_2	X_3	X_4
1	Basic - average level (X_0)	373	75	20	3
2	Variation interval	15	15	5	1
3	Upper	388	90	25	4
4	Lower	358	60	15	2

No	Factor's coded values								$φ_{final}$	pH_{final}	S^0, % - S_{total} in concentrate			$Š^2_i$
	X_0	X_1	X_2	X_3	X_4	$X_1X_2=X_3X_4$	$X_1X_3=X_2X_4$	$X_1X_4=X_2X_3$			Y´	Y´´	Ý	
1	+	-	-	-	-	+	+	+	0,421	1,32	21.6	19.8	20.7	0,810
2	+	+	-	+	-	-	+	-	0,440	1,22	49.0	48.2	48.6	0,160
3	+	-	-	+	+	+	-	-	0,451	1,21	31.9	30.9	31.4	0,250
4	+	-	+	-	+	-	+	-	0,430	1,28	44.4	43.2	43.8	0,360
5	+	+	+	-	-	+	-	-	0,390	1,36	64.5	62.3	63.4	1,300
6	+	+	-	-	+	-	-	+	0,420	1,34	48.2	47.6	47.9	0,090
7	+	-	+	+	-	-	-	+	0,373	1,26	44.3	42.7	43.5	0,640
8	+	+	+	+	+	+	+	+	0.320	1,31	74,9	73,5	74,2	0,490

Notes: Y´ and Y´´ are the results of parallel experiments, Ý is the mean; $Š^2_i$ –values of variances of the arithmetic mean of each experiment, calculated by the formula: $Š^2_i = {}_i\sum^k(Y´- Ý)^2/n(n-1)$; initial values of redox potential and pH for 15% HNO_3 $φ^0$=0.78V and pH_0 =-1.31; for 25% HNO_3 $φ^0$ =0.89V and pH^0 =-1.59.

It is shown that in the selected factor space area, the parameter "Y" takes on its extreme value and depends on "X" according to an equation that has polynomial form: $Y = b_0 + {}_{i=1}\sum^k b_iX_i + {}_{j=1}\sum^k b_ib_jX_iX_j + \dots$ [4], where k is the number of factors; b_0, b_i and b_j are the regression coefficients characterizing the strength of the influence of technological factors on the extraction of elemental sulfur. The experiment planning matrix was selected to calculate the regression coefficients values which are a semi-replica of the full factorial experiment of $\mathbf{2^4}$ with a resolution of IV and with a generating relation of $X_4 = X_1X_2X_3$[5]. The experiments on the nitric acid leaching of pyrite concentrate were carried out by varying the technological factors X_i. The results of calculations carried out using experimental data and presented in Table 1. It was defined:

- regression coefficients: b_0 =46,69; b_1 =11,84; b_2 = 9,54; b_3 = 2,74; b_4 = 2,64; b_{12} = 0,74; b_{13} = 0,14; b_{14} = -0,11;

- variances: $S^2_{[bj]} = S^2_{[Ý]}/N^2 = 4{,}1/8^2 = 0{,}0641$, where $S^2_{[Ý]} = {}_{i=1}\sum^N S^2_i/N$; where N is the number of the dispersion degrees of freedom equal to 8.

Taking into account the calculated regression coefficients, the polynomial equation takes the form of a mathematical statistical model for the extraction of elemental sulfur from pyrite concentrate, depending on the above factors X_i: $Y_S = 46{,}69 + 11{,}84X_1 + 9{,}54X_2 + 2{,}74X_3 + 2{,}64\,X_4$(1).

The model is adequate, since the calculated criteria for testing the adequacy hypothesis (F_{exp} = 1.723) turned out to be less than the tabular one [4], corresponding to the number of degrees of freedom of the adequacy variance f = 3

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and N = 8. At the same time, all the regression coefficients significantly affect the achievement of the optimization parameter, since the confidence interval has a value of 0.1482 [5], which is less than the calculated coefficients.

Analysis of the mathematical model shows that during the oxidation of pyrite concentrate with nitric acid, both temperature (b_1 = 11.84) and concentration factors (b_3 = 2.74) have a significant effect on the extraction of elemental sulfur. Similar model of iron extraction into solution was derived depending on the above factors during leaching of pyrite concentrate: $Y_{Fe} = 59,34 + 9,05X_1 + 1,44X_2 + 2,74X_3 + 2,64X_4$.As can be established, the behavior of iron is also determined by concentration and temperature factors in the studied process,.

The experimental data of autoclave leaching of pyrite concentrate by nitric acid (Table 2) allows to conclude depending on these factors:

Table 2.Results of nitric acid autoclave leaching of pyrite concentrate; S: L = 49g: 1 dm^3 (initial sample - Fe 25.6% -12.5 g; S 26.7% - 13.0 g)

No	τ, min	$φ_{final}$,V	pH_{final}	Extraction,%			Concentration in solution, g/l	
				solution		cake		
				Fe^{+3}	S^{+6}	S^0	SO_4^{-2}	NO_3^-
105 g/l HNO_3, 383K								
-	0	0.766	-1.25	0	0	0	0	0
1	5	0.741	-0.89	12.3	10.6	23.8	6.3	65.8
2	10	0.732	-0.92	19.4	16.7	28.9	10.0	57.9
3	20	0.724	1.13	50.1	31.9	39.0	19.1	63.7
4	40	0.719	1.34	68.6	44.2	41.1	26.0	64.6
5	60	0.712	1.62	71.7	58.8	40.6	26.7	79.0
223 g/l HNO_3, 383K								
-	0	0.884	-1.45	0	0	0	0	0
6	5	0.765	-0.70	27.3	19.9	44.0	25.0	117.5
7	10	0.756	-0.98	46.5	31.9	42.0	40.0	67.5
8	20	0.740	1.04	79.9	44.6	41.5	56.0	50.0
9	40	0.728	1.32	90.3	55.4	36.6	64.4	52.2
10	60	0.720	1.56	81.6	60.5	36.8	75.7	79.9
354 g/l HNO_3, 383K								
-	0	0.955	-1.80	0	0	0	0	0
11	5	0.748	-0.51	27.8	25.8	45.2	51.1	126.9
12	10	0.740	-0.94	65.5	47.0	39.8	93.0	70.0
13	20	0.736	-0.95	76.5	61.5	25.4	122.5	58.3
14	40	0.729	1.12	87.4	62.2	18.3	123.8	56.6
15	60	0.724	1.14	91.0	62.6	12.1	124.4	91.8
105 g/l HNO_3, 433K								
-	0	0.766	-1.25	0	0	0	0	0
16	5	0.718	-0.98	41.9	14.7	54.7	9.0	66.2
17	10	0.708	1.16	77.8	22.0	41.5	17.8	46.7
18	20	0.698	1.35	83.8	47.7	39.2	28.3	31.7
19	40	0.689	1.74	52.8	60.9	26.6	36.1	36.6
20	60	0.679	2.15	25.4	71.5	13.3	42.3	49.7
223 g/l HNO_3, 433K								
-	0	0.884	-1.45	0	0	0	0	0
21	5	0.742	-0.99	54.5	42.2	18.0	53.0	43.9
22	10	0.731	1.23	82.6	48.0	26.2	68.0	25.1
23	20	0.718	1.25	66.1	51.8	31.1	65.0	25.1

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24	40	0.716	170	47.9	48.0	34.1	60.1	25.9
25	60	0.710	1.98	18.9	42.5	38.8	53.3	42.3
354 g/l HNO_3, 433K								
-	0	0.955	-1.80	0	0	0	0	0
26	5	0.740	-0,90	88.5	35.3	25.0	70.0	53.3
27	10	0.732	1,00	87.7	48.1	32.8	95.5	40.8
28	20	0.717	1,10	84.8	59.1	30.5	117.5	31.7
29	40	0.708	1,60	62.8	60.6	28.6	120.6	49.0
30	60	0.689	1,81	51.4	54.5	24.8	108.3	68.7

1) The use of nitric acid with a concentration of 105-223 g / dm^3 at 383K leads to increase the oxidation state of sulfide sulfur to sulfate with an increase in the acidity of the solution and keeping time of the pulp in autoclave. At the same time, the oxidizing potential of the solutions is quite high after leaching: φ_{final} = 0.71-0.76V.

2) In more acidic solutions with the HNO_3 concentration of 354 g / dm^3, this pattern is not preserved: the degree of formation of sulfate sulfur practically does not change from 61.5 to 62.6% over time from 20 to 60 minutes, consequently.

3) With an increase in the process temperature to 433K, the oxidation of sulfur to sulfate within the acidity range of 105-223 g / dm^3 HNO_3only increases when the pulp is kept in an autoclave for up to 20 minutes. With a longer exposure time and increased initial concentrations of nitric acid (354 g / dm^3), a slight decrease in the content of sulfate sulfur in solutions is observed with simultaneous pH change and decrease of$\varphi_{final}$to 0.69 V. It can be assumed that process is accompanied by the release of sulfur as less water-soluble inorganic salts and compounds.

4) The process of formation of elemental sulfur during nitric acid autoclave processing of pyrite concentrates is characterized by:

- an increase of the S^0 formation with the increase in the acidity of the pulp at 383K at the initial stage of the process with further gradual decrease over time;
- a significant decrease of the S^0 formation at 433K in the beginning of the process with increasing of the HNO_3concentration from 105 to 354 g/dm^3, as well as, with an increase of the process duration at acid concentration which is not exceeding 105 g / dm^3;
- change the acidity of the HNO_3medium up to 223-354 g/dm^3 at 433K possibly slightly increases the extraction of elemental sulfur over time.

The study of the oxidation reaction of sulfide sulfur to elementary in the described process shows the possibility of controlling this reaction by regulating φ_{fin} at 0.26-0.38V and pH = 2.0-2.2 (Fig. 1)depending on the final oxidation potential of the solutions. In this case, the initial factors are: φ_0 = 0.60-0.74V and pH_0 = -1.5 ÷ -1.0.

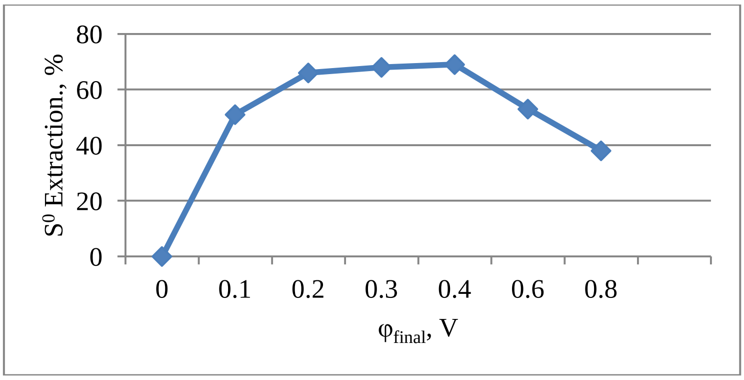

Fig. 1: Extraction of S^0 from pyrite concentrate: HNO_3 20-354 g/dm^3,383K, S: L = 1: 4, 60 min.

The use of a mathematical statistical model to optimize a process with a complex chemical mechanism, it should be noted, has a rather formal character. Indeed, such model is practically impossible to take into account all the interactions of optimization factors in a hydrochemical system, which is complex by its physicochemical nature with a variety of occurring chemical processes under increased temperatures and pressures. Therefore, further we searched the

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optimal conditions of the S^0maximum extraction by the steep ascent method [6] which is the known method of mathematical planning of experiments using previously calculated regression coefficients from equation (1) for Y_S.

In this regard, additional experiments were carried out with the preparation of a pulp with a calculated amount of nitric acid, providing $\varphi^0 = 0.60 \div 0.74$V and $pH^0 = -1.5 \div -1.0$ as an initial mode φ^0-pH^0, and the final values of φ up to 0.38V and pH up to 1.8 during leaching (Fig. 1). According proposed method, the movement on the response surface in the direction of steep ascent lead to change the independent variable factors X_i in proportion to the value of the corresponding regression coefficients according the sign and the size of the movement step - in proportion to the product of these values and variation unit (Table 3).

Table 3. Calculation of the optimal conditions for the maximum S^0recovery in cake during autoclave leaching of pyrite concentrate with HNO_3 solution without oxygen supply $\varphi^0 = 0.60 \div 0.74$V and $pH^0 = -1.2 \div -1.4$.

Indicators and calculated experiments	Factors				φ final	pH final	Extraction of S^0 to cake
	X_1	X_2	X_3	X_4			
Regression coefficient	11.84	9.54	2.74	2.64	-	-	-
Variation interval	177.6	143.1	13.7	2.64	-	-	-
Rounded step	5.0	4.0	0.5	0.1	-	-	-
Average experiment (basic)	373	75	20.0	3.0	0.428	1.42	49.6
Designed experiment No. 9	378	79	20.5	3.1	0.416	1.46	50.1
No 10	383	83	21.0	3.2	0.410	1.48	60.4
No 11	388	87	21.5	3.3	0.401	1.49	62.6
No 12	393	91	22.0	3.4	0.390	1.52	38.1

When choosing the step of changing the variable factors, we proceeded from the expedient step of the most significant factor, which is the temperature of the process as seen from (1). In this regard, theX_1changing step was adopted equal to 5K for technological reasons. This step is 35.5 times less than the variation interval (Table 3), therefore, the changing steps of the other variables X_{2-4} should also decrease by 35.5 times.

IV. CONCLUSION

1. Applied laboratory studies have revealed the optimal combination of independent variable factors in the studied process with reaching up to 63% S^0 recovery: 383-388K, leaching duration 83-90 min, HNO_3 concentration 21-22 wt% and ratio S: L = 3 0-3.4; in this case, up to 90% of iron is deposited in the cake in the oxide form.

2. Fundamental research has established that:

- the process of interaction of iron sulfide raw materials with nitric acid highly dependent on temperature and concentration of the chemical reagent;
- the initial period of the process is characterized by the intensive formation of water-soluble forms of iron and sulfur, as well as, gaseous nitrogen oxide, solid elemental sulfur and hematite;
- secondary chemical reactions of the oxidation of sulfur S^0 to sulfate, etc. occur with the development of the process in time.

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