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Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty, Kazakhstan

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Gladyshev Sergey Vladilenovich

Institute of Metallurgy and Ore Beneficiation,

Satbayev University Almaty, Kazakhstan

Email: s.gladyshev@satbayev.university

ORCID ID: 0000-0002-4939-7323

Azlan M.N.

Sultan Idris Education University, Perak, Malaysia

Email: azlanmn@fsmt.upsi.edu.my

ORCID ID: 0000-0002-2792-4145

Production of non-ferrous metal concentrate in the processing of pyrite slags

Abstract: The method of preliminary chemical activation of mineral raw materials was used in the conducted studies for the complex processing of pyritic slags. The influence of preliminary chemical activation of kaolinite clays of Alexeevsky deposit in the solution of sodium hydrogen carbonate on the separation of kaolinite and quartz fractions was studied. The temperature of 150 °C, the duration of 120 minutes, and the concentration of sodium bicarbonate solution of 120 g/dm³ should be considered the optimum mode of activation. As a result of activation, the phase composition of the kaolinite fraction changed: the percentage of kaolinite fraction decreased; new phases of muscovite and sodium aluminosilicate appeared; the amount of quartz increased.

Keywords: pyritic slags, chemical activation, leaching, phase composition, non-ferrous metals, neutralization, concentrate.

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Introduction

One of the ways to produce sulfuric acid is roasting pyrite concentrate to produce sulfurous gas [12]. The resulting pyrite slag is stored, which creates a real threat of pollution of the water and air environment, while at the same time they are a valuable source of ferrous, non-ferrous, and noble metals, not used to date due to the lack of economically viable technologies. In this regard, the development of effective, integrated technology intended to process pyrite slag is **relevant**.

Pyritic pellets are equal to good iron ores in terms of iron content (50-60%), but their use for smelting pig iron is prevented by the presence of base metals and sulfur in them. Therefore, the technological scheme of processing should provide a sufficiently complete extraction of non-ferrous metals and obtain a product suitable for blast-furnace smelting.

The main method of processing pyritic slags introduced in some countries is chlorination roasting followed by leaching of nonferrous metal compounds [2, 6, 12, 13]. However, the high-energy consumption and the need to leach excessively large volumes is a disadvantage of the method, which reduces its practical significance.

Based on the available information [3, 7-10], the predominant direction of research is hydrometallurgical methods, which require improvement for complete utilization with the extraction of useful components - non-ferrous, precious metals, and iron.

The method of preliminary chemical activation of mineral raw materials was used in the conducted studies for the complex processing of pyritic slags. It promotes disintegration and phase changes [1, 4, 5, 11]. The method consists of thermal treatment with a solution of sodium bicarbonate. Due to the conditions of chemical activation, the hard-to-recover phases are modified and the mineral structure is disclosed by separating the non-metallic materials.

The optimal conditions for the preliminary chemical activation corresponding to the peculiarities of the mineral structure of pyritic slags were determined. The positive effect of activation is confirmed by the results of the leaching of non-ferrous metals from pyritic slags in sulfuric acid solution.

Methods

X-ray fluorescence analysis was performed with a Venus 200 wave dispersion spectrometer (PANalytical B.V., The Netherlands).

Chemical analysis of the samples was performed on an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, Perkin Elmer).

Semi-quantitative X-ray phase analysis was performed on a D8 Advance diffractometer (BRUKER) using copper Cu-K α radiation at an accelerating voltage of 36 kV, current 25 mA.

Chemical activation of pyritic slags was carried out in a solution containing 40 - 120 g/dm³ NaHCO₃ at S:L=2-10.0 and a temperature of 90 - 230° using a thermostatic unit with 6 autoclaves rotating through the head, with a working volume of 250 cm³. The duration of activation ranged from 30 to 300 minutes. The maximum content of sodium hydrogen carbonate 120 g/dm³ in the solution is chosen to take into account its solubility limit

Results, discussion

A representative sample of pyrite slag from the sulfuric acid production of the **Tselinny Mining and Chemical Combine** of Kazakhstan was used in this work.

According to the results of sieve analysis, it was found that in the class +2.5 mm content of useful components - noble, nonferrous metals, and iron is much lower (Table 1).

Table 1. Chemical composition of classes of pyritic slags

Content, %	Size class, mm					
	+2.5	-2.5+1.0	-1.0+0.25	-0.25+0.1	-0.1+0.056	-0.056
Na ₂ O	2.44	1.43	1.19	0.959	0.75	0.71
MgO	3.29	0.65	0.67	0.483	0.41	0.39
Al ₂ O ₃	10.96	6.92	6.37	4.163	3.11	3.03
SiO ₂	39.73	27.09	25.18	16.13	11.89	11.44
P ₂ O ₅	0.26	1.26	1.1	0.956	0.84	0.82
SO ₃	0.51	7.33	8.1	7.725	6.35	6.1
CaO	9.72	2.84	2.62	1.949	1.41	1.2
TiO ₂	1.26	0.42	0.37	0.25	0.178	0.16
Fe ₂ O ₃	7.63	41.63	45.63	60.94	70.187	71.16
CuO	0.02	0.2	0.22	0.26	0.261	0.28
ZnO	0.04	0.4	0.4	0.61	0.604	0.66
As ₂ O ₃	0.06	0.19	0.25	0.26	0.258	0.26
SeO ₂	0.003	0.51	1.01	0.57	0.23	0.19
BaO	0.186	2.07	2.33	2.81	2.866	3.01
HgO	-	0.09	0.19	0.14	0.055	0.04
PbO	0.005	0.15	0.17	0.2	0.185	0.21
No	22.266	6.29	3.61	1.237	0.146	0.08
Au, g/t	0.021	1.58	2.68	2.69	2.24	2.88
Ag, g/t	0.1	11.2	16.2	19.3	21.4	22.3
Output, %	31.0	6.2	5.5	20.8	34.3	2.2

Magnetic separation determined that the + 2.5 mm class is the non-magnetic fraction and the - 2.5 mm + 0 class is the strongly magnetic fraction; it was separated at a magnetic field strength of 200 - 400 oersted.

Chemical composition of the magnetic fraction of pyritic slags of size class - 2.5 mm + 0 wt. %: Na₂O 1.4; MgO 0.74; Al₂O₃ 5.69; SiO₂ 23.22; P₂O₅ 1.1; SO₃ 6.24; Cl 0.01; K₂O 0.44; CaO 2.52; TiO₂ 0.32; Fe₂O₃ 52.84; CuO 0.25; ZnO 0.53; As₂O₃ 0.24; SeO₂ 0.3; BaO 2.4; HgO 0.08; PbO 0.16; p.p. 1.82; precious metal content, g/t: Au 2,69; Ag 19,3.

The phase composition of the magnetic fraction of pyritic slags is represented, wt. %: magemite 24.1, hematite 18.1, quartz 17.2, albite 10.2, trisodium phosphate zinc oxide hydrate 9.5, sodium aluminosilicate 6.7, barium ferrite 4.7, nitrozarosite 4.2, sodium thiorphosphate 2.8 and dolomite 2.5 (Figure 1).

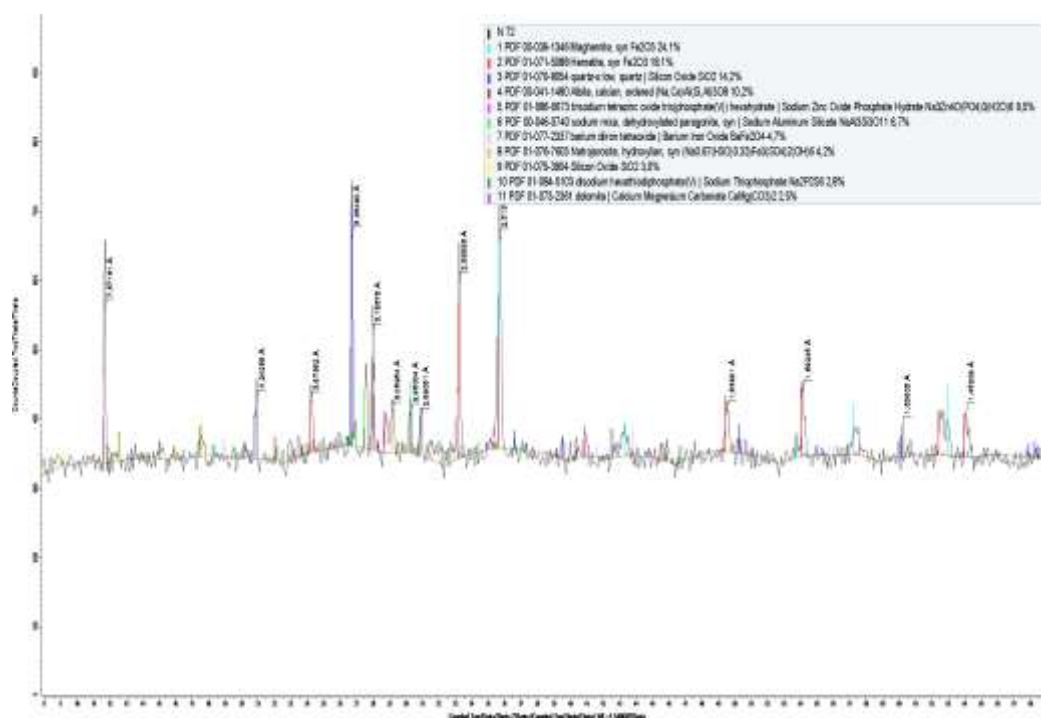


Figure 1. X-ray phase analysis of pyrite slag after chemical activation under optimal conditions

Chemical composition of the magnetic fraction of pyritic slags of size class -- + 2.5 mm wt. %: Na₂O 2.44; MgO 29; Al₂O₃ 10.96; SiO₂ 39.73; P₂O₅ 0.26; SO₃ 0.51; Cl 0.01; K₂O 0.8; CaO 2.72; TiO₂ 1.26; Fe₂O₃ 7.63; CuO 0.02; ZnO 0.04; As₂O₃ 0.06; SeO₂ 0.003; BaO 0.186; HgO 0.08; PbO 0.005; p.p. 23.076; noble metal content, g/t: Au 0,021; Ag 0,1.

The phase composition of the non-magnetic fraction of pyritic slags is represented, wt. %: magemite 2.1; hematite 1.4; quartz 29.9; albite 18.2; dolomite 18.2; calcite 17.3; clinocllore 7.7; muscovite 3.5 and gibbsite 1.4.

The poor fraction of size +2.5 mm, the amount of which is more than 30%, was not used in further studies.

To determine the main technological parameters of the preliminary chemical activation, the pellets of class - 2.5 mm + 0 were crushed in a ball mill to a coarseness of - 0.056 mm.

The dependence of the chemical activation of pyritic slags in sodium bicarbonate solution on temperature, duration, S:L ratio, and NaHCO₃ concentration was investigated. It has been determined that the optimum conditions of chemical activation are temperature 120 °C, duration 30 - 60 min, the S:L ratio = 4:1, and the concentration of NaHCO₃ solution 60 g/dm³ at which the maximum changes in the phase and chemical composition are obtained.

Chemical composition of pyritic slags after activation under optimal conditions, weight %: Na₂O 1.59; MgO 0.73; Al₂O₃ 5.63; SiO₂ 22.3; P₂O₅ 0.59; SO₃ 3.45; Cl 0.01; K₂O 0.43; CaO 2.64; TiO₂ 0.31; Fe₂O₃ 51.89; CuO 0.24; ZnO 0.52; As₂O₃ 0.16; SeO₂ 0.25; BaO 2.32; HgO 0.09; PbO 0.16; p.p 6.69.

Analysis of the chemical composition showed that after activation the content of P_2O_5 , SO_3 , and As_2O_3 in pyrite slag decreased by 46.36 %, 44.31 %, and 33.3 % respectively.

The phase composition of pyritic slags after chemical activation under optimal conditions is represented by wt%: maghemite, 28.4; hematite, 21.8; quartz, 14.7; albite, 8.7; sodium aluminosilicate, 6.0; barium ferrite, 6.2; natrojarosite, 4.3; sodium thiophosphate, 5.7; magnesium aluminosilicate, 2.5 and calcium silicate, 1.7. (Figure 2).

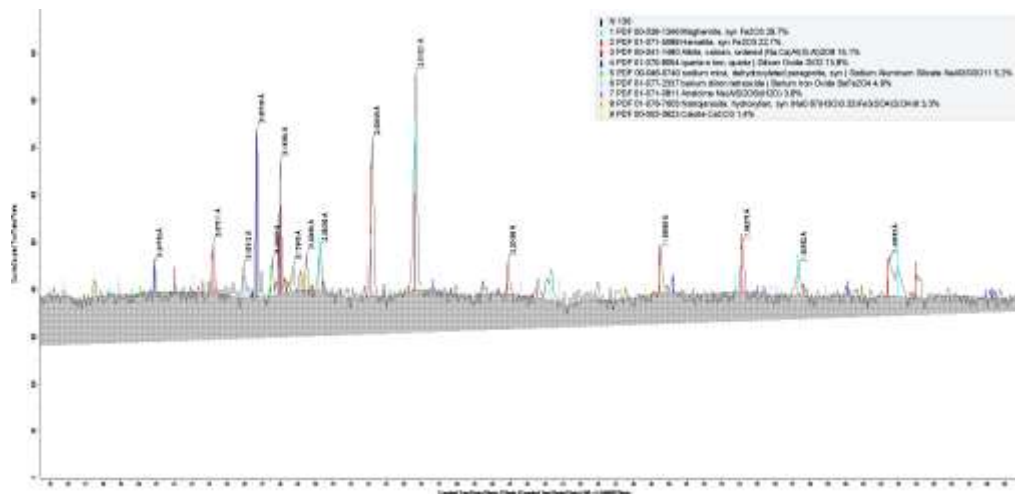


Figure 2 X-ray phase analysis of pyritic slag after chemical activation under optimal conditions

As a result of chemical activation of pyritic slags in optimal conditions, the phases of zinc phosphate trisodium hydrate oxide $Na_3Zn_4O(PO_4)_3(H_2O)_6$ and dolomite $CaMg(CO_3)_2$ disappeared; the amount of sodium thiophosphate phase $Na_2P_2S_6$ increased from 2.8% to 5.7%; the amount of albite phase $Na(AlSi_3O_8)$ decreased from 10.2% to 8.7% and that of natrojarosite $(Na_{0.67}(H_3O)_{0.33})Fe_3(SO_4)_2(OH)_6$ $(Na_{0.67}(H_3O)_{0.33})Fe_3(SO_4)_2(OH)_6$ 4.2% to 3.4%; the magnesium aluminosilicate phase $(MgAl_2Si_3O_{10})_{0.6}$, calcium silicate $CaSiO_3$ appeared.

Changes in the phase composition of pyritic slags as a result of chemical activation can be associated with the course of reactions of the interaction of sodium hydrogen carbonate with trisodium phosphate zinc oxide hydrate and natrojarosite with the formation of sodium thiophosphate and an increase in the content of iron-bearing phases, and also with dolomite with the formation of calcium silicate and magnesium aluminosilicate.

Studies were carried out to determine the effect of the chemical activation of pyritic slags on the extraction of non-ferrous metals and iron during leaching in sulfuric acid solutions.

Leaching of pyritic slags after preliminary chemical activation was carried out in H_2SO_4 solutions containing 5-20% at a temperature of 60 °C and a duration of 30 minutes.

The results of the leaching of pyritic slags in sulfuric acid solutions are shown in Figure 3.

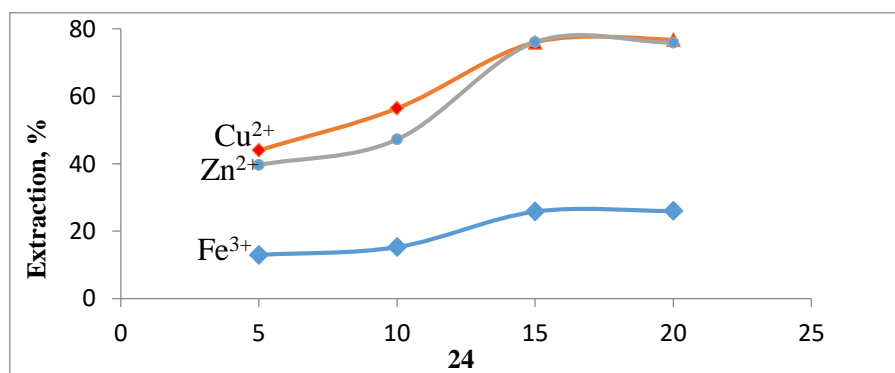


Figure 3. Dependence of non-ferrous metal and iron extraction from pyritic slags after activation in solution on the concentration of H_2SO_4

According to the data obtained, it is optimal to use a sulfuric acid solution with a concentration of 15% H₂SO₄ for leaching pyritic slags after chemical activation. Under these conditions, the recovery into sulfuric acid solution was, %: Cu²⁺ 76.8; Zn²⁺ 75.9, and Fe³⁺ 26.0.

The sulfuric acid leaching solution was neutralized with potash in several stages to obtain a non-ferrous metal concentrate (Table 2)

Table 2. Chemical composition of neutralization precipitation depending on solution pH

Content, %	pH		
	3.7	5.46	9.7
K ₂ O	0.11	0.08	13.8
MgO	-	-	1.2
Al ₂ O ₃	0.12	3.0	7.5
SiO ₂	0.12	1.2	2.9
P ₂ O ₅	25.27	3.5	0.02
SO ₃	8.3	11.08	15.9
Fe ₂ O ₃	53.37	19.3	3.8
CuO	-	0.04	6.4
ZnO	-	0.01	12.54
As ₂ O ₃	3.08	0.39	-
SeO ₂	0.1	0.01	-

Neutralization to pH 3.7 was performed to precipitate trivalent iron from the solution. Under these conditions, phosphorus, arsenic, and selenium partially precipitated from the solution together with iron.

At pH 5.46, iron, phosphorus, and arsenic residues were released into the neutralization precipitate from the solution.

Neutralization to pH 9.7 was carried out taking into account the pH of complete precipitation of zinc and copper. As a result, the non-ferrous metal concentrate was obtained with the content, weight. %: CuO 6.4; ZnO 12.55. The concentrate yield was 8.5 % of the total amount of neutralization sludge or 1.5 % of the initial mass of pyrite sludge. The yield of neutralization precipitation at pH 5.46 was 2.1 %, at pH 9.7 - 14.2 %.

The obtained results indicate that neutralization for impurity extraction of Fe₂O₃, P₂O₅, and As₂O₃ and obtaining concentrate of non-ferrous metals should be carried out in two stages to pH 5.46 and 9.7.

Conclusions

The influence of preliminary chemical activation of kaolinite clays of Alexeevsky deposit in the solution of sodium hydrogen carbonate on the separation of kaolinite and quartz fractions was studied. The temperature of 150 °C, the duration of 120 minutes, and the concentration of sodium bicarbonate solution of 120 g/dm³ should be considered the optimum mode of activation.

As a result of activation, the phase composition of the kaolinite fraction changed: the percentage of kaolinite fraction decreased; new phases of muscovite and sodium aluminosilicate appeared; the amount of quartz increased.

The main technological scheme of the complex processing of kaolinite ore was developed.

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