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Development of Technology for Processing Pyrite Cinder to Produce Non-Ferrous Metal Concentrate

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ABSTRACT

The existing technologies for processing of pyrite cinder require improvement for complex extraction of non-ferrous, precious metals and iron. The novelty of the technology used in the work for the processing of pyrite cinders is the preliminary chemical activation in a solution of sodium bicarbonate. The optimal activation modes were determined according to temperature, duration, L:S ratio and $NaHCO_3$ concentration. It has been established that activation of pyrite cinder results in changes in phase composition and a reduction in the content of the impurity components P_2O_5, SO_3 and As_2O_3. The leaching of pyrite cinder after pre-activation in 15 % H2SO4 solution resulted in an extraction into solution, wt. %: CuO 76, 8; ZnO 75, 9 and Fe_2O_3 26, 0. The degree of extraction of non-ferrous metals in sulphuric acid solution without chemical activation is lower by 15 - 20 %.

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1. INTRODUCTION

Since the last century, the main method of obtaining sulfuric acid has been the firing of pyrite concentrate [1]. Pyrite is an iron mineral of the sulfide class, which often contains impurities of gold, cobalt, copper and other non-ferrous metals. The resulting pyrite cinder is stored, which creates a real threat of pollution of the water and air environment, at the same time, they are a valuable source of ferrous, non-ferrous and precious metals, which have not been used until now due to the lack of economically viable technologies. In this context, the development of a rational technology for the processing of pyrite cinder is relevant. Pyrite cinder is equivalent to good iron ores in terms of iron content (50-60%), but their use for smelting pig iron is hindered by the presence of non-ferrous metals and sulphur in them. The process flow diagram should therefore ensure that the non-ferrous metals are extracted sufficiently and that the product is suitable for blast furnace smelting.

The main method of processing pyrite cinder introduced in a number of countries is chlorination roasting followed by leaching of non-ferrous metal compounds [1-4]. However, the high energy consumption and the need to leach excessively large volumes is a disadvantage of the method, reducing its practical relevance. The method [1] provides for low-temperature (550-600ºC) chlorinating roasting of a cinder with table salt (or calcium chloride) was introduced at the Duisburg plant in the Federal Republic of Germany, However, the need to leach excessively large volumes of chlorinated cinder in order to extract non-ferrous metals is one of the bottlenecks that reduces its practical significance.

In Finland and Zambia, the initial concentrate is subjected to sulfating or dissociating firing followed by hydrometallurgical treatment of slags [2]. The residual concentration of cobalt in the waste is more than 0.4% in Zambia and about 0.2% in Finland. With an initial cobalt content of about 3% in Zambian concentrates and about 1.2% in pyrrhotite concentrates in Finland, cobalt recovery is 80-85%. The method developed by Outokumpu provides for the melting of pyrite concentrates in a neutral atmosphere with the sublimation of sulfur and the production of troilite matte, the removal of slag, granulation of matte in water and its oxidative firing. The method allows to obtain a product containing up to 67 % iron, but does not provide for the extraction of non-ferrous and precious metals [3]. From more recent developments, it should be noted a method that includes heating the stub and melting it in the presence of a reducing agent and mixtures of fluxes composed of CaO and Al_2O_3 - containing materials, processing the iron-based alloy obtained in this case with solid

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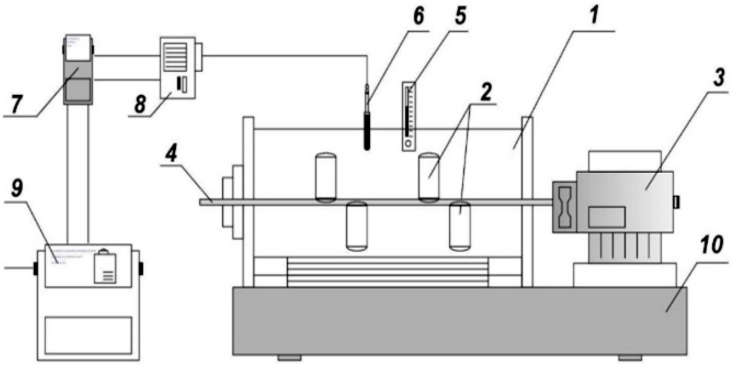
oxidizers containing calcium sulfate [4], in some cases SiO_2 is used as a flux [5]. The disadvantage of these methods is the low extraction of precious metals.

All the described methods are pyrometallurgical and are energy-intensive. Recently, much attention has been paid to hydrometallurgical methods of processing pyrite stubs [6-12], which require improvement for complete utilization with the extraction of useful components – non-ferrous, precious metals and iron. The method [13] includes a preliminary four-stage leaching of non-ferrous metals with water and a solution of sulfuric acid and subsequent leaching of noble metals with a hydrochloric acid solution of thiocarbamide. The method allows you to isolate black copper, iron oxide pigment, zinc oxide into separate products and extract noble metals from a thiocarbamide hydrochloric acid solution. The disadvantages of the method are the low extraction of iron and precious metals from the stub, as well as contamination of the resulting iron oxide pigments with impurities of non-ferrous metals.

A method of deep processing of pyrite stubs is known, including leaching of non-ferrous metals with a bacterial complex [14]. The disadvantages of this method are the long duration of bacterial leaching and the complexity of the process of culturing acidophilic thion bacteria. In the studies conducted for the complex processing of pyrite cinder a method of preliminary chemical activation of mineral raw materials was used, which promotes disintegration and phase changes [15-18]. The method consists in thermal treatment with a solution of sodium hydrogen carbonate. The conditions of chemical activation modify the hard-to-recover phases and open up the mineral structure by separating the non-metallic materials. The research identifies the optimum conditions for chemical activation corresponding to the specific mineral structure of pyrite cinder. The positive effect of activation is confirmed by the results of leaching of non-ferrous metals from pyrite cinder.

2. METHODS

A representative sample of pyrite stubs obtained at the sulfuric acid production of the Tselinny Mining and Chemical Csomplex of the Republic of Kazakhstan was used as the raw material for the research. The studies used X-ray fluorescence, chemical, X-ray phase analyzes. X-ray fluorescence analysis was performed on a Venus 200 wave dispersion spectrometer (PANalyical B.V., Holland). The chemical analysis of the samples was performed on an optical emission spectrometer with inductively coupled plasma (Optima 8300 DV, Perkinelmer, Waltham, Massachusetts, USA). The random component of the error is 2.0 %. X-ray phase analysis was performed using a D8 Advance (Bruker, Billerica, MA, USA) with Cu Kα radiation produced at 40 kV and 40 mA. The processing of the diffraction patterns and calculation of interplanar spacings were performed using EVA software, while the identification of phases was performed using the Search/Match program and the PDF-2 powder diffraction database. Semi-quantitative X-ray phase analysis was performed on a D8 Advance (BRUKER) diffractometer using copper Cu – Kα radiation at an accelerating voltage of 36 kV, a current of 25 mA. Chemical activation of pyrite cinder was performed in a solution containing 40 - 120 g/dm^3 $NaHCO_3$ at W:S=2-10.0 and a temperature range of 90-2300, using a thermostatic installation with 4 autoclaves rotating through the head, with a working volume of 250 cm^3.



1. Thermostat;
2. Autoclaves;
3. Electric motor;
4. Shaft;
5. Control thermometer;
6. Thermocouple;
7. Temperature sensor;
8. Starter;
9. Gearbox;
10. Base

Figure 1: Thermostatic installation with autoclaves

3. RESULTS AND DISCUSSION

A representative sample of pyrite cinder obtained in Kazakhstan at the sulfuric acid production of the Tselinny Mining and Chemical Complex in Stepnogorsk was used in these studies. Based on the results of the sieve analysis, it was found that the content of useful components - precious metals, non-ferrous metals and iron - is significantly lower in the +2.5 mm class (table 1).

Table 1: Chemical composition of the pyrite cinder classes

Contents, %	Size class, mm					
	+2.5	-2.5+1.0	-1.0+0.25	-0.25+0.1	-0.1+0.056	-0.056
Na_2O	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_2O_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_2O_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_2O_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_2O_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
other products	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
Yield, %	31.0	6.2	5.5	20.8	34.3	2.2

It was determined by magnetic separation that the + 2.5 mm class is not a magnetic fraction, and the 2.5 mm + 0 class is a strongly magnetic fraction, it was separated at a magnetic field strength of 200 - 400. Chemical composition of magnetic fraction of pyrite cinder of size class - 2,5 mm + 0 wt.%: Na_2O 1.4; MgO 0.74; Al_2O_3 5.69; SiO_2 23.22; P_2O_5 1.1; SO_3 6.24; Cl 0.01; K_2O 0.44; CaO 2.52; TiO_2 0.32; Fe_2O_3 52.84; CuO 0.25; ZnO 0.53; As_2O_3 0.24; SeO_2 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 pyrite cinder is presented, wt.%: Maghemite 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; natrozharositis 4.2; sodium thiophosphate 2.8 and dolomite 2.5 (Figure 2).

The chemical composition of the non-magnetic fraction of pyrite cinder of the size class -+2.5 mm wt.%: Na_2O 2.44; MgO 0.3.29; Al_2O_3 10.96; SiO_2 39.73; P_2O_5 0.26; SO_3 0.51; Cl 0.01;K_2O 0.8; CaO 2.72; TiO_2 1.26; Fe_2O_3 7.63; CuO 0.02; ZnO 0.04; As_2O_3 0.06; SeO_2 0.003; BaO 0.186; PbO 0.005; p.p. 23.076; content of precious metals, g / t: Au 0.021; Ag 0,1. The phase composition of the non-magnetic fraction of pyrite cinder is presented, wt., %: Magnetite 2.1., Hematite 1.4; quartz 29.9; albite 18.2; dolomite 18.2; calcite 17.3; clinochlore 7.7; muscovite 3.5 and gibbsite 1, 4. The poorer fraction of +2.5 mm, which amounts to more than 30 %, was not used in further studies. Cinder of the class - 2.5 mm + 0 were ground in a ball mill to a particle size of - 0.056 mm. to determine the main technological parameters of preliminary chemical activation.

The dependence of the chemical activation of pyrite cinder in sodium hydrogen carbonate solution on temperature, duration, L:S ratio and concentration $NaHCO_3$ has been investigated. It has been found that the optimum conditions of chemical activation are temperature 120 ^{0}C, duration 30 - 60 min, L: S: ratio 4:1 and concentration of $NaHCO_3$ solution 60 g/dm^3 at which the maximum phase and chemical composition changes are obtained. Chemical composition of pyrite cinder after activation under optimal conditions, wt%: Na_2O 1,59; MgO 0,73; Al_2O_3 5,63; SiO_2 22,3; P_2O_5 0,59; SO_3 3,45; Cl 0,01; K_2O 0,43; CaO 2,64; TiO_2 0,31; Fe_2O_3 51,89; CuO 0,24; ZnO 0,52; As_2O_3 0,16; SeO_2 0,25; BaO 2,32; HgO 0.09; PbO 0,16; p.p 6,69.

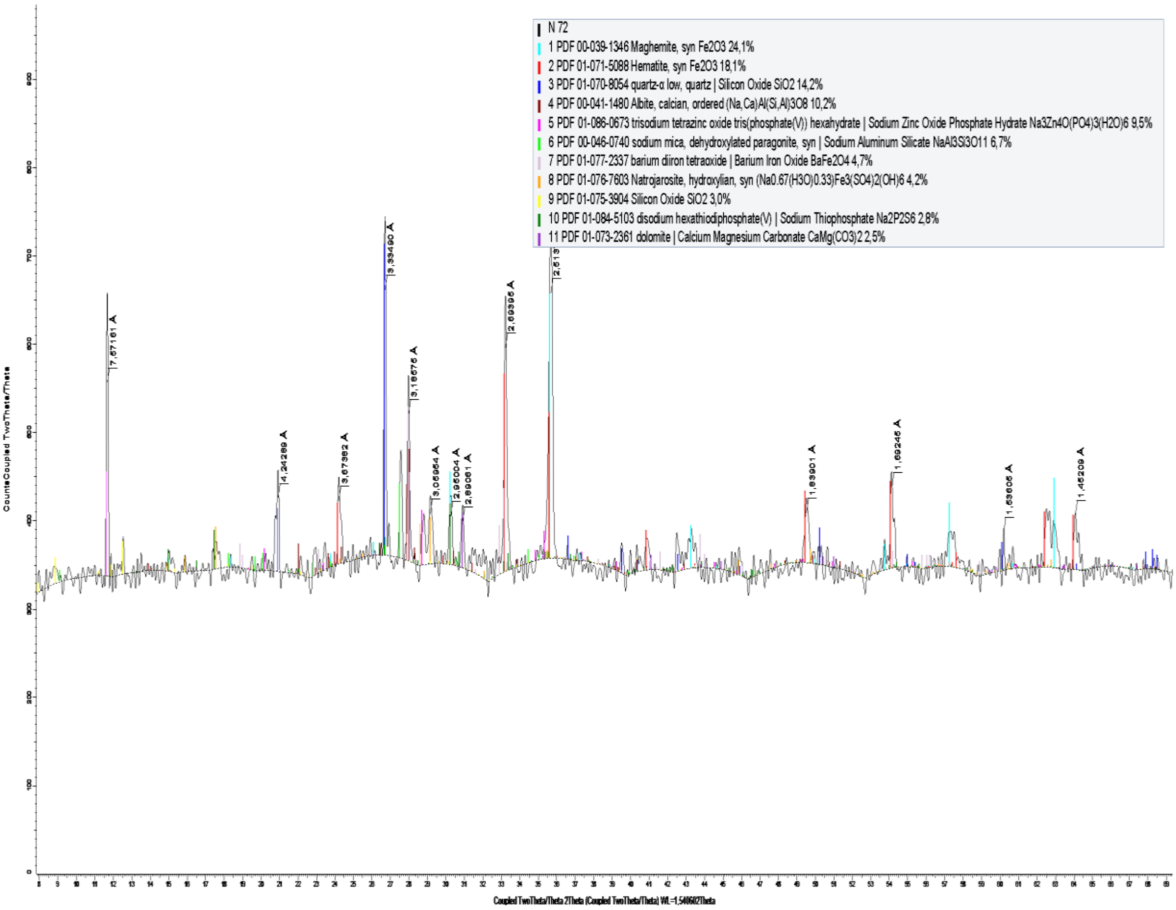


Figure 2: X-ray phase analysis of the magnetic fraction of pyrite cinder size class -2.5 mm + 0

Analysis of the chemical composition showed that after activation, the content of P_2O_5, SO_3 and As_2O_3 in pyrite cinder decreased by 46.36%, 44.31% and 33.3%, respectively. The phase composition of pyrite cinder 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; natrozarosit - 4.3; sodium thiophosphate - 5.7; magnesium aluminosilicate - 2.5 and calcium silicate - 1.7. (Figure 3).

According to the analysis of the phase composition of pyrite cinder, it was found that, as a result of chemical activation under optimal conditions, the phases disappeared; the phases of trisodium zinc phosphate, oxide hydrate and dolomite disappeared; the amount of sodium thiophosphate $Na_2P_2S_6$ phase increased from 2.8% to 5.7%; the amount of the phase of albite Na ($AlSi_3O_8$) decreased from 10.2% to 8.7% and natrozharosite $(Na_{0.67} (H_3O)_{0.33}) Fe_3 (SO_4)_2 (OH)_6$ from 4.2% to 3.4%; a phase of magnesium aluminosilicate $(MgAl_2Si_3O_{10})_{0.6}$, calcium silicate and sodium thiophosphate appeared. The analysis of changes in the phase composition of pyrite cinder as a result of chemical activation can be connected with the course of reactions of interaction of sodium hydrogen carbonate with trisodium phosphate zinc oxide hydrate and natrojarosite to form sodium thiophosphate and increase the content of iron-bearing phases, also with albite and sodium aluminosilicate to form magnesium aluminosilicate. The influence of preliminary chemical activation of pyrite cinders on extraction of non-ferrous metals and iron at leaching in sulfuric acid solutions was studied. Methods of hydrometallurgical processing of pyrite cinders using weakly acidic sulfuric acid solutions for leaching are known [18-22]. The disadvantage of the methods is the low extraction of non-ferrous metals. Leaching of pyrite cinder in H_2SO_4 solutions containing 5-20% at a temperature of 60°C and a duration of 30 minutes was performed to check the effect of chemical pre-activation on the extraction of non-ferrous metals and iron. The results of leaching pyrite cinder in sulfuric acid solutions are shown in Figure 4.

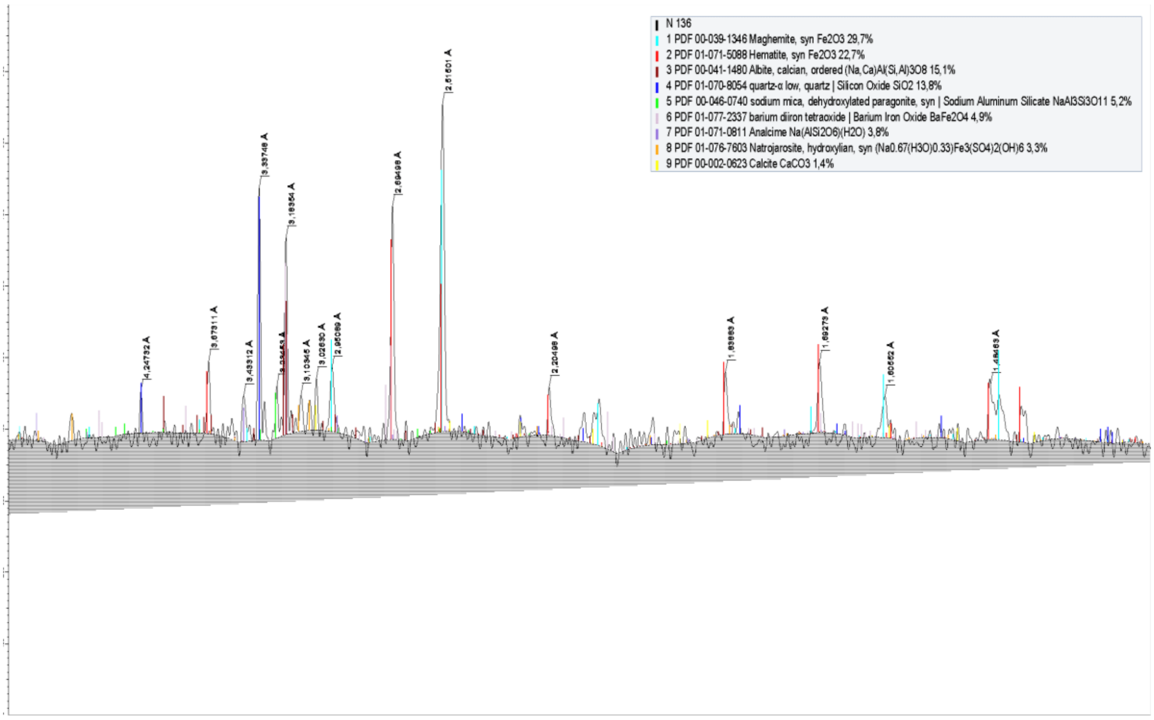


Figure 3: X-ray phase analysis of pyrite cinder after chemical activation under optimal conditions

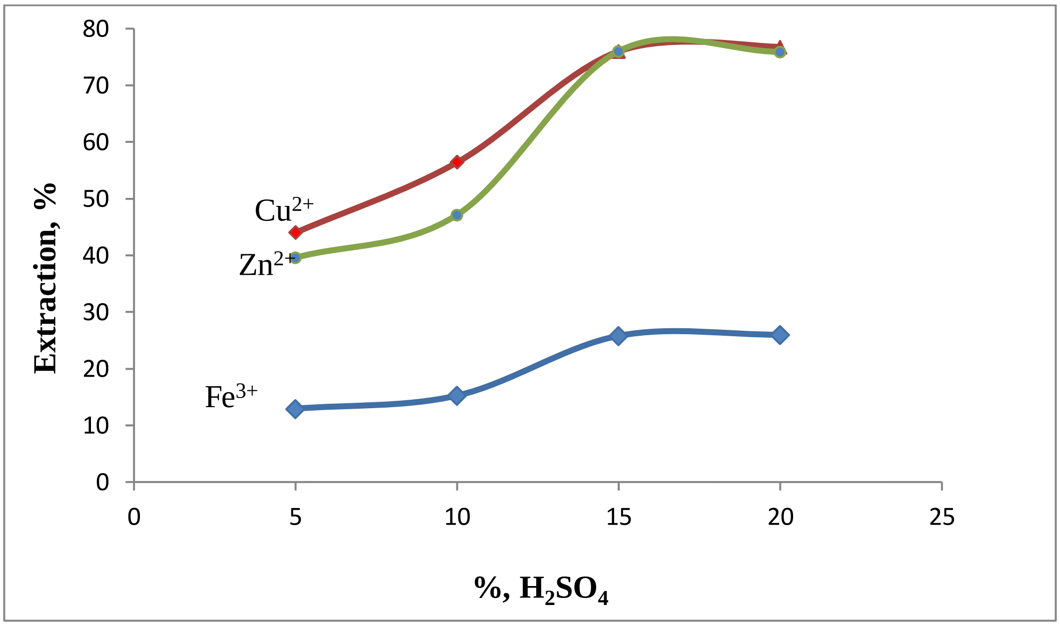


Figure 4: Dependence of the extraction of non-ferrous metals and iron from pyrite cinder after activation into solution on concentration H_2SO_4

According to the data obtained, it is optimal to use pyrite cinder for leaching after chemical activation of a sulfuric acid solution with a concentration of 15% H_2SO_4. The extraction into the sulfuric acid solution was, %: Cu^{2+} 76.8; Zn^{2+} 75.9 and Fe^{3+} 26.0 under these conditions. The degree of extraction of non-ferrous metals and iron into a solution of 15% H_2SO_4 is 15 - 20% lower without chemical activation. The sulphuric acid leaching solution was neutralized with potash in several stages to produce a base metal concentrate (Table 2).

Table 2: Chemical composition of neutralization precipitates depending on the pH of the solution

Contents, %	**pH**		
	3.7	5.46	9.7
K_2O	0.11	0.08	13.8
MgO	-	-	1.2
Al_2O_3	0.12	3.0	7.5
SiO_2	0.12	1.2	2.9
P_2O_5	25.27	3.5	0.02
SO_3	8.3	11.08	15.9
Fe_2O_3	53.37	19.3	3.8
CuO	-	0.04	6.4
ZnO	-	0.01	12.54
As_2O_3	3.08	0.39	-
SeO_2	0.1	0.01	-

Neutralization to pH 3.7 was performed to precipitate ferric iron from the solution. Phosphorus, arsenic and selenium partially passed into the precipitate from the solution under these conditions, together with iron. Iron, phosphorus and arsenic residues were precipitated from the solution into the neutralization precipitate at pH 5.46. Neutralization to pH 9.7 was performed taking into account the pH of complete precipitation of zinc and copper. The result is a concentrate of non-ferrous metals with a content, wt. %: CuO 6.4; ZnO 12.55. The concentrate yield was 8.5% of the total amount of neutralization precipitates or 1.5% of the initial mass of pyrite cinder before leaching. The neutralization precipitation yield at pH 5.46 was 2.1%, at pH 9.7 it was 14.2%. From the results obtained, it follows that neutralization to isolate impurities Fe_2O_3, P_2O_5 and As_2O_3 and obtain a concentrate of non-ferrous metals should be performed in two stages to pH 5.46 and 9.7.

4. CONCLUSION

Research has been performed on the processing of pyrite cinder, including preliminary chemical activation and leaching in a sulfuric acid solution to obtain a concentrate of non-ferrous metals. The phase composition changes and the content of impurity components P_2O_5, SO_3 and As_2O_3 decreases as a result of the chemical activation of pyrite cinder in a sodium hydrogen carbonate solution. The optimal activation mode has been selected according to temperature, duration, W: S ratio and $NaHCO_3$ concentration. Conditions for leaching of pyrite cinder after chemical activation in sulphuric acid solution are determined. A neutralization precipitate was obtained, as a result of staged neutralization of the pyrite cinder leaching solution at pH 9.7, - a concentrate of non-ferrous metals, wt. %: CuO 6.4; ZnO 12.55. The concentrate yield was 1.5 % of the initial weight of the pyrite cinder.

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REFERENCES

[1] Chernyshev A. K., Levin B. V., Tugolukov A.V. Sulfuric acid.1: properties, production, application. - M.: INFOCHIM, 2014. – 654 p.

[2] Güntner, J., Hammerschmidt, J., 2012. Sulphating roasting of copper-cobalt concentrates. J. South. Afr. Inst. Min. Metall, 112, 455–460. (in English)

[3] Vlasov O. A., Mechev V. V. *Method of processing pyrite stubs* Patent 2394924 RU. Publ. 20. 07. 10.

[4] Litvinenko L. G., Litvinenko V. G., Shchelkonogov M. A., Morozov A. A. *Method of complex processing of pyrite stubs*. Patent 2623948 RU. Publ. 12. 06. 2017.

[5] Shin S. N., Gulyaeva R. I. *Method of processing pyrite stubs*. Patent 2172788 RU. Publ. 27. 08. 2001.

[6] Mukhamedshin I.Kh., Bashlykova T.V., Fadina I.B., Zhivaeva A.B. *Method for deep processing of pyrite cinders*. Patent 2397260 RU. Published on 20.03.13.

[7] Binbin He, Xike Tian, Yan Sun, Chao Yang, Yanglin Zeng, Yanxin Wang, SuxinZhan, Zhenban Pi Recovery of iron oxide concentrate from high-sulfur and low-grade pyrite cinder using an innovative beneficiating process // Hydrometallurgy. 2010. Volume 104, Issue 2, – P 241-246.

[8] Bakov A.A., Arzhannikov G.I. *Method for processing pyrite cinders*. Patent 2149706 RU. Published on 03.19.2013.

[9] Gilmutdinova R.A., Michurin S.V., Kovtunenko S.V., Elizarieva E.N. On the issue of the use and processing of waste from mining and processing plants of the South Urals // Successes of modern natural science. - 2017. - No. 2. – P.68-73.

[10] Abdulvaliev RA, Gladyshev SV, Pozmogov VA, Imangalieva L.M. *Method of preparation of aluminosilicate raw materials before leaching.* Patent 32333 KZ. Published on 31.08.2017. Bul. No. 16

[11] Gladyshev S.V., Kenzhaliyev B.K., Abdulvaliev R.A., Dyusenova S.B., Imangalieva L.M. Development of technology for producing chromite concentrate from tailings tailings // Complex use of mineral raw materials.– 2018. - No. 1. – C.12-17.

[12] Kenzhaliyev B. K. (2019). Innovative technologies providing enhancement of nonferrous, precious, rare and rare earth metals extraction // Complex use of Mineral Resources/Mineraldik Shikisattardt Keshendi Paidalanu, 3.– P.64-75. https:// doi/org/10.31643/2019/6445.30

[13] Litvinenko L. G., Litvinenko V. G., Shchelkonogov M. A., Morozov A. A. *Method of complex processing of pyrite stubs.*Patent 2623948 RU. Publ. 12. 06. 2017.

[14] Abdulvaliev, R.A., Gladyshev, S.V., Kenzhaliev, B.K., Imangalieva, L.A. Complex processing of the iron-bearing fraction of bauxites with the manufacture of bloomery iron. Obogashchenie Rud, 2020, (2), pp. 41–45.

[15] Narkevich I.P., Pechkovsky V.V., Utilization and elimination of waste of inorganic substances technology, M. Chemistry, 1984, pp. 20-22.

[16] C. c. 1790230 USSR, MPC C 22 IN 7/00. Method for the complex processing of pyrite cinders / (USSR). - 4854117/02 stated 05.07.90. publ. 30.03.83, – P. 2.

[17] Dosmukhamedov N. K., Argyn A. A., Zholdasbay E. E., Kurmanseitov M. B. Converting of copper-lead matte: loss of gold and silver with slag // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu. - 2020. № 3 (314), pp. 5- 14. https://doi.org/10.31643/2020/6445.21

[18] Kazhikenova S. Sh. Monitoring kachestvennykh i kolichestvennykh pokazateley tekhnologicheskikh skhem proizvodstva medi na predpriyatiyakh Kazakhstana [Monitoring of qualitative and quantitative indicators technological schemes for the production of copper at the enterprises of Kazakhstan] // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources. No. 1 (312), 2020 pp. 79-86. (In Russian). https://doi.org/10.31643/2020/6445.10

[19] Kenzhaliyev B. K. (2019). Innovative technologies providing enhancement of nonferrous, precious, rare and rare earth metals extraction // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu, 3. – P.64-75. https:// doi/org/10.31643/2019/6445.30

[20] Dyussebekova, M.A., Kenzhaliyev, B.K., Kvyatkovskiy, S.A., Sit'ko, E.A., Nurkhadianto, D. The main reasons for increased copper losses with slags from vanyukov furnace. Metalurgija, 2021, 60(3-4), pp. 309-312

[21] Kenzhaliev, B.K., Kul'deev, E.I., Luganov, V.A., ...Motovilov, I.Y., Temirova, S.S. Production of Very Fine, Spherical, Particles of Ferriferous Pigments from the Diatomaceous Raw Material of Kazakhstan. Glass and Ceramics (English translation of Steklo i Keramika), 2019, 76(5-6), pp. 194-198. https://doi.org/10.1007/s10717-019-00163-w

[22] Dyussenova S.; El-Amir, Ahmed A. M. (2021). Research and development of a comprehensive technology for processing kaolinite clays in Kazakhstan. Challenges of Science. Issue IV, 2021, pp. 48-54. https://doi.org/10.31643/2021.07