RESEARCH OF TECHNOLOGY FOR EXTRACTION OF RARE AND NOBLE METALS FROM RESET CUES AND SLUDGE FIELD SOLUTIONS

Shodiyev Abbos Nematovich
assistant teacher of "Metallurgy"
department of Navoi state mining institute,
Navoi, Uzbekistan
Hasanov Abdurashid Saliyevich
deputy chief engineer in science of "Almalyk MMC" JSC,
Almalyk, Uzbekistan
Azimov Oybek Ahmadovich
Head of "Metallurgy"
department of Navoi state mining institute,
Navoi, Uzbekistan
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ABSTRACT

Currently, in world practice, standard molybdenum concentrates undergo oxidative firing to obtain technical molybdenum oxide, which is the starting material for the production of ferromolybdenum. For the production of high-purity products, technical oxide is subjected to chemical purification by dissolving it in a solution of ammonia water. Molybdenum salts are precipitated from ammonia solutions, and Fe, Si, Cu, Al impurities are introduced with waste solutions from the technological cycle.

Keywords: extraction, molybdenum, rare metals, ferromolybdenum, sorption, technogenic waste, molybdenum slurry, cementation, solutions, neutralization, polymolybdate.

The growing industry demand for molybdenum products requires the creation of new technologies for the extraction of molybdenum from secondary raw materials and molybdenum production wastes. The solution to this problem before the researcher is an initial study of the available molybdenum feedstock. As you know, the technology for the extraction of molybdenum from the concentrate used in the workshop No. 5 of the SPA RM&RA AMMC (Scientific Production Association Rare metals and refractory alloys of Almalyk mining and metallurgical combine)method of nitric acid decomposition does not provide high extraction of molybdenum into the finished product molybdenum oxide. Waste is removed from the technological process in the form of slurry pulps, they contain Mo, Re, Fe, Cu, Au, Ag and in the solid and soluble part of the pulp.

Analyzes of ICP - spectroscopy established that slurry cakes with the contents of non-ferrous and rare metals are valuable technogenic raw materials. The average cake samples by the content of the main components are, in (%): 4.8 Mo, (including 2.1 oxidized and 2.7 sulfide); 1.2 Cu; 0.03 Re; 0.24 W, as well as 9.5 Fe; 4.3 SiO_2; traces of As, P and 6.0 ion-exchange resins (used); industrial waste (pebbles, chips, etc.) and 42 (and above) moisture.

The results of x-ray phase analyzes determined the forms of the main components in the sludge cake: $Fe(OH)_3 \cdot 3H_2O$, MoO_2, MoO_3, MoS_2, $CuMoO_4$, $ZnMoO_4$, $CaMoO_4$, $PbMoO_4$, $Fe_2(MoO_4)_3$, as well as copper and molybdenum adsorbed on iron hydroxide tungsten. It is established that slurry cake has magnetic properties and its specific gravity is 1.33 t / m3. These properties are the scientific justification for the search and development of technology for extracting iron from sludge cakes using magnetic separation and gravitational enrichment.

In laboratory conditions, experiments were carried out on the magnetic separation of slurry cake containing 12.0–18.0% iron, which during the nitric acid decomposition of the sulfide concentrate was oxidized 95.0–98.0% to three valence forms of hydrated iron oxide. It was determined that the composition of the slurry cake also contains ferromolybdenum precipitates formed at the technological stage of purification of molybdate solutions from iron, they contain up to 30% iron oxide. By experiments of wet magnetic separation with the addition of magnetic particles and surfactants (polyacrylamide), 70% of iron was separated from the slurry cake in the magnetic fraction and a concentrate was obtained containing up to 29.6% of iron.

To extract molybdenum and other valuable components from the tailings of the magnetic separation of the slurry cake containing, (in%): 2.4 Mo; 0.011 Re, 2.5 Cu experiments were performed on leaching of cake. Soda ash was used as a leaching reagent; molybdenum and rhenium were extracted from the resulting productive solution by sorption on ion-exchange resins.

Two-stage countercurrent leaching of cake after magnetic separation and cementation of copper, with a solution of soda ash with a concentration of 120 g / l at a temperature of 80 ° C for 2 hours at each stage;

The main reactions occurring in leaching processes:

- transfer of molybdenum from slurry cake to solution:

$$MoO_3 + Na_2CO_3 \rightarrow Na_2MoO_4 + CO\uparrow \quad (1)$$

$$MoO_3 + 2Na_2CO_3 + H_2O \rightarrow Na_2MoO_4 + 2NaHCO_3 \quad (2)$$

- neutralization of the productive solution with nitric acid to pH-3

$$Na_2MoO_4 + HNO3 \rightarrow Na_nMo_mO_l + NaNO_3 \quad (3)$$

As a result of the neutralization of the solution, the molybdenum mono-ions are converted into a polymolybdate of variable composition and fed to sorption;

Selective two-stage sorption of molybdenum from solution onto sorbent A-100 (Mo) in NO3 form:

$$R\text{-}NO_3 + Na_nMo_mO_l \rightarrow R\text{-}Mo_mO_l + hNaNO_3 \quad (4)$$

In this case, polymolybdate ions are sorbed onto the sorbent A-100 (Mo), and sodium nitrate ($NaNO_3$) salts are concentrated in the solution. The molybdenum sorbent capacity reaches up to 150-180 g per 1 liter of sorbent. The residual molybdenum content in the solution after the 1st and 2nd stage of sorption is not more than 5.0 mg / l, this molybdenum concentration is considered to be a “breakthrough” and the mother liquors are sent to the disposal of effluents to produce $NaNO_3$. When the molybdenum content after the 1st stage of sorption to 3.0 g / l, the solution enters the column at the 2nd stage of sorption. Saturated sorbent is sent for washing;

Laboratory experiments and pilot industrial tests have determined that Purolite A100 (Mo) sorbent and Purolite A170 sorbent are more effective and selective for sorption of molybdenum. It was found that the extraction of molybdenum from solutions obtained after processing slurry cake is 95.0%, and rhenium is not less than 88.0%. The main test results of the sorption technology for the extraction of molybdenum and the qualitative characteristics of the obtained AMA are shown in the following table 1.

For the purpose of a deeper theoretical analysis and development of the technology for extracting rhenium from the slurry field effluent solutions (SPA RM&RA AMMC), the chemical and salt composition of the effluent solutions, as well as the ionic state of molybdenum, rhenium, and impurity elements in the solution, were separately studied. The composition of the solution from the sludge field are shown in table 1.

Table 1.

The composition of the solution from the sludge field.

	Content, mg/l	Connection elements	Content, mg/l
Molybdenum	7,43-86,9	Aluminium	13,63-100,44
Copper	14,67-1320	Titanium	5,0-30,0
Lead	2,71-5,20	Iron	67,33-599,54
Rhenium	1,87-9,18	Barium	6,15-35,8
Arsenic	0,4	Tin	0,33-3,64
Total sulfur	1,59	Zinc	60,5-752,74
Silica	28,2	Gallium	0,0001-0,0003
Calcium	962,4-4193,3	Gold, g/t	0,32-4,04
Magnesium	28,1-966,1	Silver, g/t	1,03-14,09

The possibility of extracting rhenium on activated carbon from nitric acid-sulfate solutions of a sludge field has been investigated. The experiments were carried out in a wide range of acidity (from pH = 2.0-3.0 to an acid concentration of 30-40%). It was found that the coal capacity is low 2.0-4.0% (at a rhenium concentration of 0.03-0.06 g / l), while molybdate ions are sorbed from the solution along with rhenium. This method requires preliminary cleaning of solutions from molybdenum to concentrations commensurate with the concentration of rhenium. For this purpose, a preliminary purification of the solution from molybdenum by sorption with a weakly basic resin AN-1 at pH = 2-5-3 is proposed. It was established that the proposed conditions from solutions of ReO4 ions are almost not adsorbed on AN-1 resin.

Desorption from the surface of the coal was carried out selectively: first, molybdenum was desorbed with a cold 1% solution of soda ash, and then rhenium heated to 90 ° C with a 1-3% solution of soda ash. Coal sorption is usually used to extract rhenium from poor solutions (0.01-0.05 g / l rhenium). In this case, the solutions obtained after desorption contain 0.2-0.6 g / l of rhenium. To obtain more concentrated solutions of rhenium, the operation of sorption on coal is repeated or a more effective ion-exchange concentration is used.

Considering that in recent years, Purolite sorbents have been widely used in practice in the technology of extracting molybdenum and rhenium from various solutions in practice, therefore, the sorption characteristics of the sorbents of Purolite A100 (Mo) and Purolite A170 anion exchangers have been studied.

Table 2.

The chemical composition of the obtained TMA prototypes

Name of indicator	Norm						
	Ts 00193950-083:2018		GOST 2677-78				
Mass fraction	Grade 1	Grade 2		Exp. №1	Exp. №2	Exp. №3	Exp. №4
1. Molybdenum anhydride (MoO_3), % no less	*76*	*74*	**78**	*67,33*	*83,66*	*92,87*	*91,17*
2. Iron (Fe)%, no more	*0,03*	*0,2*	**0,007**	*0,0025*	*0,004*	*0,017*	*0,007*
3. Aluminum (Al)%, no more	*0,005*	*0,04*	**0,005**	*0,0014*	*0,0014*	*0,0018*	*0,0017*
4. Nickel (Ni)%, no more	*0,001*	*0,001*	**0,005**	*0,001*	*0,001*	*0,011*	*0,0037*
5. Manganese (Mn)%, no more			**0,01**	*0,001*	*0,001*	*0,001*	*0,001*
6. Silicon (Si)%, no more	*0,05*	*0,3*	**0,01**	*0,006*	*0,005*	*0,008*	*0,004*
7. Calcium (Ca)%, no more			**0,004**	*0,006*	*0,003*	*0,005*	*0,005*
8. Magnesium (Mg)%, no more	*0,001*	*0,001*	**0,0015**	*0,004*	*0,002*	*0,0036*	*0,0026*
9. Arsenic (As)%, no more	*0,003*	*0,003*	**0,003**	*0,002*	*0,002*	*0,002*	*0,002*
10. Phosphorus (P)%, no more	*0,002*	*0,002*	**0,002**	*0,002*	*0,003*		

It was found that the extraction of molybdenum from the combined solutions is 95.0%, rhenium is not less than 88.0%. The main test results and technical characteristics of the obtained TMA and AMA sorption method shown in table 2.

Based on the conducted research, laboratory experiments and pilot industrial tests, a technology has been developed for the integrated processing of solid waste and waste solutions of the sludge field of molybdenum production by SPA RM&RA AMMC (Figure 5).

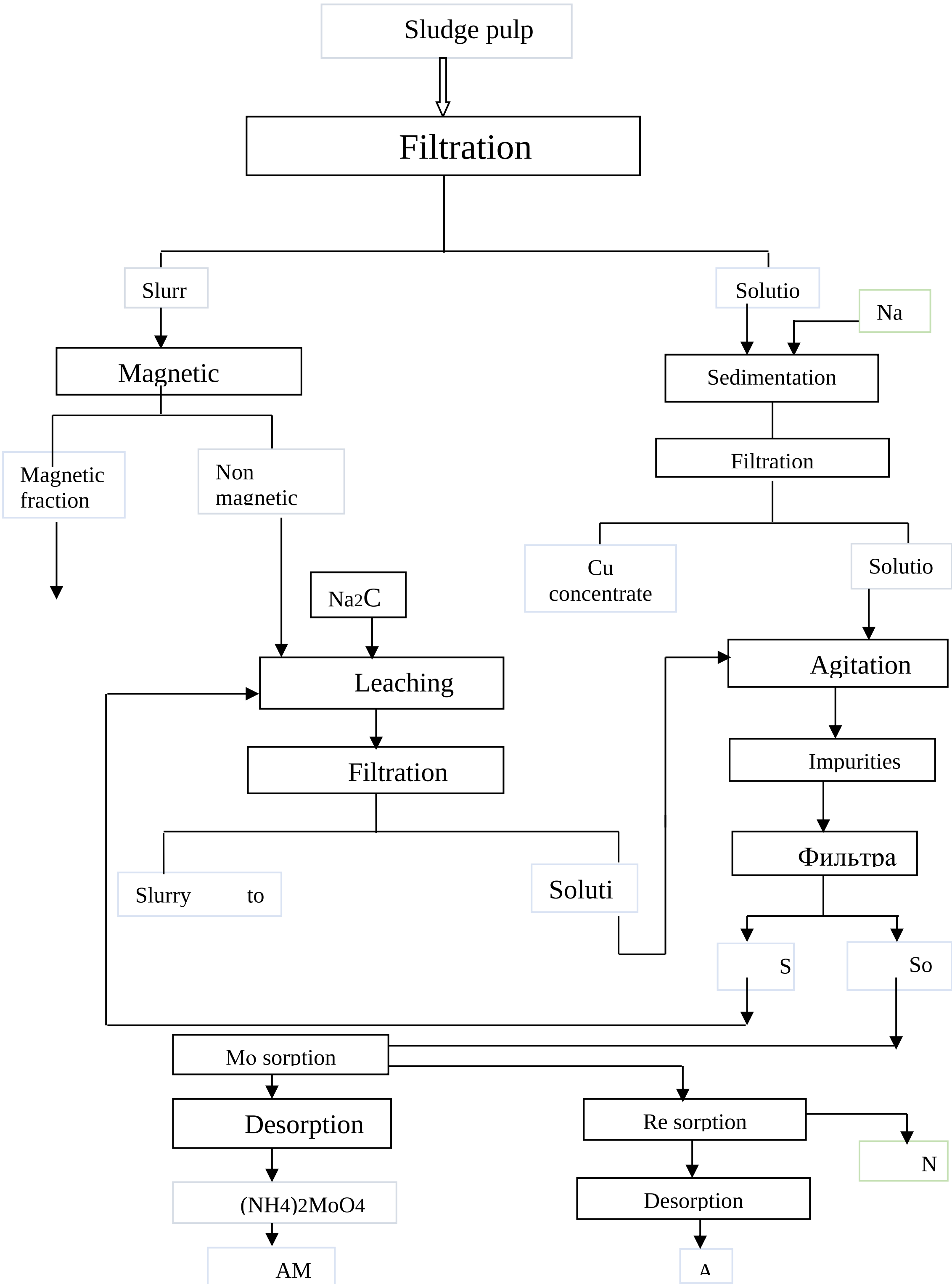

Fig. 5. The proposed technological scheme for the processing of waste from the sludge field of SPA RM&RA AMMC.

The developed technology is a complete research work, it is recommended for the implementation of SPA RM&RA AMMC in industrial conditions. For the development of technological regulations and the issuance of baseline data for the design of production, it is necessary to make technical and economic calculations, what the authors of the development will do in the future.

According to the result of this work, we can draw the following conclusions:

• Studies have established that for the processing of molybdenum concentrate, it is important to take into account the composition of the concentrate and the firing temperature when choosing a production technology;

• It was established that the problem of extracting rare metals from waste solutions by soda-sorption technology followed by precipitation of PMA and TMA, and purification methods, are one of the most important areas that emphasize the relevance and relevance of the work.

• Methods have been developed for obtaining a cleaner commercial product of molybdenum soda by sorption methods and by the method of precipitation and ion-exchange sorption.

• The possibility of additional obtaining a marketable product of noble metals and copper in the form of copper hydroxide by developed methods has been established.

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