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The Choice of Colloid Binder for Pelleting of Molybdenite Concentrate

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Abstract: Technology of production of the pyrite cinders of molybdenum middlings includes: mixture granulation (composition 1: Mo-concentrate 90%, kaolin 10%; composition 2: Mo-concentrate, 97.3-97.0%, kaolin 2%, SK polymer 0.7%), their firing at 600°C to oxidize sulfide minerals and to recover rhenium oxide. As a result of Mo concentrate mixing with kaolin, a "dilution" of the pyrite cinders with Mo takes place in the case of composition 1. The search of pellet-forming scheme based on alternative to existing compositions binding agents that minimize this rate is of actual importance. A composition for the charge granulation providing light duty of the extraction of Re and Mo from the cinder is created. Its disadvantage is an increased alkalinity of the polymer solution, which leads to adhesion of granules and metal corrosion of the hearth furnace. Objective is to develop organic polymer, devoid of this shortcoming. The approach bases on a comparison of strength and technological characteristics of binders: kaolin and alternative to it of organic nature, being in the composition of pellets and cinder of Mo concentrate is applied. The SK-N product is proposed which is formed when the molar ratio of polyacrylonitrile: NaOH = 1.0: 0.6, in contrast to SK (1.0: 1.0), neutralized to pH 7 with H_2SO_4. The alternative ashless organic binders are selected for the same purpose: polyacrylamide-GS (PAA-GS) and NH_4-CMC. Basing on the PAA-GS a new composition of the charge has been developed, % wt.: Mo concentrate 97.5%, kaolin 2%, polymer PAA-GS 0.5%, devoid of lack of charge with the SK.

Keywords: Cinder, Mo Concentrate, Binding, Kaolin, Organic Polymer

1. Introduction

Molybdenite concentrates used in the production of molybdenum, alloys (ligatures), including tungsten alloys, ferromolybdenum, salts, technical molybdenum trioxide. However, in the world, recently, molybdenum sulfides attract the attention of investigators in connection with the unconventional use of photocatalysts as advanced operating under visible light [1]. Such studies have been developed in Australia, the USA, Japan, and they are connected with the interest either directly to their photocatalytic activity and the behavior under the influence of the polymeric additives added to enhance their photocatalytic and performance properties due to granulation and composite materials obtain, etc. [1-3].

Study of photocatalytic materials in Uzbekistan was held in the framework of JSPS-Ronpaku (ID No. UZB10909): by the Institute of General and Inorganic Chemistry of the Academy of sciences of Uzbekistan together with the Tokyo Institute of Technology.

In this context, an important issue was the selection of the composition of the batch granulation of commercial molybdenite concentrate. Traditional batch composition includes up to 10% of kaolin, thereby reducing the Mo content in the calcine. An alternative composition on the basis of SK polymer is developed (0.7% in the charge, when the residual concentration of 2% kaolin), devoid of disadvantage [4].

The organic binder in the industry, according to our information, up to this point have been used with magnetite ore with colemanite [5]. Binders role as in Mo-concentrate [6] and in Fe-ore [7] was common: colloidal agent (kaolin) provides cohesive coupling of mineral particles in the pellet, allowing its strength while a synthetic polymer acts as a dispersing agent [8]. The practice of the SK has revealed its flaws: corrosive effect on a metal parts of an oven and granules' sticking.

Objective: rheology and viscosity modification of the polymer binder - a component of the charge of Mo concentrate pelletizing, to eliminate these shortcomings.

2. Experimental

Kinematic viscosity of the solutions was measured (VPG-2 viscometer). The pellets were calcined at 600°C. Their strength was assessed under load to failure. For elements analysis the spectrometers PE 3030V and 7500 Aligent ICP MS were used.

3. Results and Discussion

In accordance with the objective of the study, the reason of pellet blocking and high temperature corrosion effect on corrosion-resistant steel from the charge based on SK-polymer was revealed. The reason of metal's corrosion was excessive alkali content in the SK polymer, being the product of alkaline hydrolysis of the polyacrylonitrile (PAN), according to the scheme: PAN → polyacrylamide (PAA) → polyacrylic acid-Na, with the conversion of the amide groups in the carboxylic acid by means of hydrating the nitrile groups. The neutralization of excess alkalinity therein was conducted with sulfuric acid to pH 7 (Table 1).

Table 1. *Consumption of sulfuric acid to neutralize the SK.*

The hydrolysis of PAN in a solution of sodium hydroxide				Density,	Flow H_2SO_4
Product	**molar relation PAN: NaOH**	**The Mass of PAN fibers, g**	**H_2O, g**	**g/cm^3**	**(d = 1.655 g /cm^3), ml**
SK	1.0:1.0	10	80	1.1	1.2
SK-M	1.0:0.8	10	82	1.1	0.55
SK-N	1.0:0.6	10	84	1.3	0.45

The water content of the solution obtained with a molar ratio of PAN: NaOH = 1,0: 0,6 (SK-N product) was found to be 80%. During firing of the dry residue at 600°C, the residual ash weight was 10% of the original weight of the polymer. By dispersing 0.1 g of ash in 10 ml water pH value of the solution reached pH 10.5. The degree of hydrolysis of PAN, increasing the molar ratio of PAN: NaOH, in the range of 1: 0.6; 1: 1.3, rises from 60 to 80% in 51 hours (Figure 1).

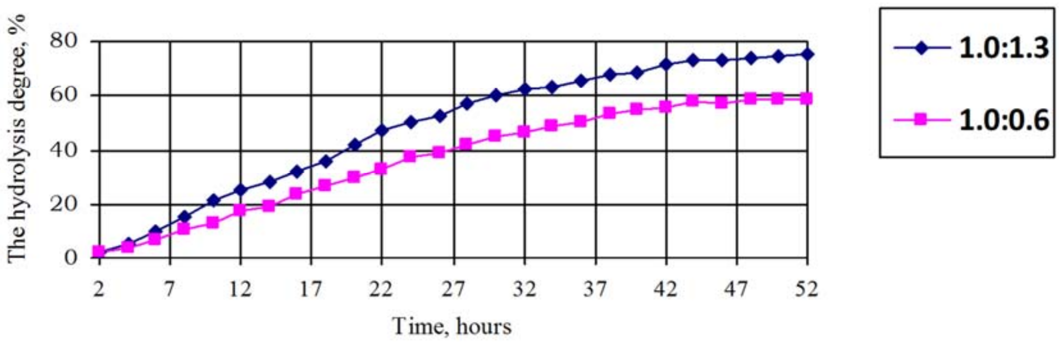

Figure 1. *Hydrolysis of the PAN, depending on the layout and the molar ratio [PAN]: [NaOH].*

An important parameter of the polymers SK and SK-N application is the achievement of a stable visco-current state. SK solution's viscosity was studied, depending on the temperature and dilution with water (Table 2).

Its stable fluid state was set at a dilution of 1: 5 and 1: 6. Characteristically that measured solution's viscosity reached maximum value at pH 7-9, at cooling. Based on the data of table 2, instruction was compiled for the neutralization of the polymer SK solution, from initial pH 12 down to pH 7 by means of solution of sulfuric acid. The calculation showed the need to put 120 l of H_2SO_4 (1,655 g/cm^3) in 1 cubic meter of SK polymer solution.

The criterion for selection of alternative organic binder for granulation molybdenite concentrate, instead of polymers of SC series, became an ash-free during firing of Mo concentrate at 600°C. On the role of alternative organic binder the following polymers are selected: 1) Na-carboxymethyl cellulose (Na-CMC); derivative thereof NH_4-CMC; 2) polyacrylamide gel (PAA-gel); 3) polyacrylamide flocculant (PAA-GS). These polymer's mass loss of the samples at 600°C with access of an air oxygen are shown in Table 3.

Table 2. *Dependence of kinematic viscosity of SK solution on pH value, temperature and dilution. pH was set as their neutralizing with H_2SO_4, mm^2/sec.*

Temperature °C	Volumetric dilution - the initial polymer: water					
	1:3	**1:4**	**1:5**	**1:6**	**1:8**	**1:10**
A stock solution, pH 12						
18	61.20	42.84	27.23	21.72	18.05	14.99
40	58.14	40.69	26.31	21.42	17.74	11.01
60	42.54	29.07	20.19	14.99	12.85	7.95
80	30.29	22.03	15.91	11.93	9.79	7.03
100	25.70	18.36	13.15	10.09	8.56	5.51

Temperature °C	Volumetric dilution - the initial polymer: water					
	1:3	1:4	1:5	1:6	1:8	1:10
The stock solution is neutralized to pH 7						
18	94.86	58.75	43.15	29.07	20.81	16.83
40	54.30	37.33	26.93	19.28	13.46	10.71
60	36.72	27.79	18.36	13.77	9.79	7.65
80	25.40	18.66	13.46	10.10	7.65	5.81
100	22.64	15.91	11.32	7.96	6.43	4.90

Table 3. *Ash of polymers Na-CMC, PAA-GS, PAA gel, Uniflok, KFG.*

Characteristics of the polymers			pH of the aqueous polymer
Product	The water content in the product, %	Ash, %	
Uniflok	1.52	25.29	12
KFG	37.06	0.12	12
PAA-GS	4.70	1.28	7
PAA-gel	70.70	0.23	7

From Table 3 it is revealed that the ash-free and technically acceptable (solubility in water, viscous current state of the solutions) polymers are the following: PAA-GS, PAA gel (as of NH_4-CMC requires the additional research).

Next task was a comparative test of polymer solutions: SK-N, PAA-GS during granulation of Mo concentrate, in the laboratory, as described in [1-2]. The compositions of the charges (indicated % concentration of binder in the charge, the rest is Mo-concentrate, the proportion of water added is not specified): Nr 1 - 9% kaolin, Nr 2 -kaolin 2%, SK-N 0.7%; Nr 3 - 2% of kaolin, PAA-GS 0.5% (Table 4.).

Table 4. *Granules' strength at different combinations of charge and temperature, °C.*

Parameter	Granule's strength, diameter 3-5 mm, under the load until destruction, MPa		
	Charge of Mo-concentrate granulation, composition's number		
	1	2	3
20°C	0.7	1.5	1.2
250°C	2.4	1.9	2.1
600°C	6.4	4.0	4.2

From Table 4 it follows that existing charge with kaolin (Nr1), a mixture of polymer SK with kaolin (Nr2), as well as a mixture of polymer PAA-GS with kaolin, with different heat treatment lead to different strengths of the granules.

Their strength matches previously identified by industry the demand for pellet strength: F = 1÷4 MPa. When under- or over this indicator sulfur content in cinder rises (S content's rate is 1.5%) [6].

It was of interest to compare the efficiency of processing granules Mo concentrate's cinder from mixtures Nr 1, 2, 3 in ammonia Mo leaching processes (mixture Nr 0 is a nitrate solution). Ammoniacal leaching tests (S: L = 1: 3) samples, washed to pH 1 with water to remove impurities, were carried out at 60 and 45 min exposition, in 25% ammonia solution, 15-25 g / l of NH_3. The resulting cake is leached, pulp is filtered and then the cake is washed with water from the residual ammonium molybdate (S: L = 1: 3) repulping, pH 7-8. Analysis were carried for Mo, Re control (Table 5).

Table 5. *Composition of pellets during firing and efficiency of their processing. Designation of states: I - part before roasting; II- composition after; III- metal recovery (%) of the raw material mixture (a mixture without a binder marked Nr 0).*

Element	Mix 0			Mix 1			Mix 2			Mix 3		
	I	II	III	I	II	III	I	II	III	I	II	III
Mo, %	41.3	-	97	37.7	39.1	97	40,0	42.2	99	39,9	42.0	99
Re, %	0.07	-	-	0.06	0.05	15	0.07	0.05	30	0.07	0.05	30

From Table 5 it follows that the charge Nr 3, Nr 2 superior in terms of Mo recovery the charge Nr 1 before and after firing; as well as residual content of Mo in the dump cake, at the norm of Mo content there not more than 3.0%, the figure was 1% of the original [6]. In addition, from the batches of compositions Nr2 and Nr3 Re_2O_7 sublimates better as well that provides an increase in the production of marketable rhenium following after sorption on Purolite ion-exchange resins [9, 10] separately from Mo [11, 12].

4. Conclusion

The composition of the product of hydrolysis of PAN (SK polymer) being a component of the charge of Mo-concentrate pelletizing is optimized. Negative factor that prompted to modify its composition - increased content of alkalis, is corrected and SK-N polymer is offered being formed at a molar ratio of PAN: NaOH = 1.0: 0.6, in contrast to SK polymer with the ratio: 1.0: 1.0, then neutralized to a pH 7 by addition of H_2SO_4 solution. Alternative ashless organic binders based on polyacrylonitrile PAA-GS are picked up. A new batch composition of Mo concentrate granulation wt %: Mo concentrate - 97.5% 2% - kaolin, polymer PAA-GS - 0.5% is offered, in compare with an existing composition (10% - kaolin, rest - Mo concentrate) facilitating the extraction of Re, Mo from the cinder.

Study of photocatalytic activity of granular materials based on molybdenite from different blend compositions, will be continued.

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