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Pelleting of Molybdenite Concentrate with Organic-Mineral Binder

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Mo Concentrate, Cinder, Kaolin, Organic Polymer, Granulation

Technology of production of the pyrite cinders of Mo middlings includes granulation, firing to oxidize sulfide minerals and to recover Re-oxide. If kaolin is used a dilution of the pyrite cinders with Mo takes place. The research is devoted to the development of alternative to kaolin organic binding agents. The approach is based on a comparison of hydrophilic, strength & technological characteristics of pellets. The new batch was developed differing from the traditional mixture with organic additive burning to the ground and minimizing Mo dilution, maximizing Re, Au, Ag hydrometallurgical recovery.

Introduction

In mining industry it is common practice to pelletize finely ground mineral ore concentrate to facilitate shipping of the ore. After screening, a binding agent is added to the wetted ore concentrate and the binder/mineral ore composite is conveyed to a balling drum for pelletizing the ore. The binding agent serves to bind the mineral ore together until after firing. For many years, bentonite was applied as the binding agent in exclusive usage mode in such operations for iron ore concentrates because the pellets possessed good wet and dry strengths. Use of bentonite, however, had disadvantage, particularly additional silica content. Organic binders have proven to be an attractive alternative to bentonite because they do not increase the silica content providing best mechanical properties to the pellets. They also burn out during ball firing operations thus causing an increase in the microporosity of the pellets. Accordingly, the pore volume and surface/mass ratio of the formed pellets produced using organic binders is larger than that of pellets produced using bentonite. Due to the larger surface area and increased permeability of the pellets the reduction of metallic oxides such as iron oxide is more efficient. Examples of some commonly mentioned organic binders include polyacrylate, polyacrylamide and copolymers thereof, methacrylamide, polymethacrylamide, cellulose derivatives such as alkali metal salts of carboxymethyl cellulose and carboxymethylhydroxyethyl cellulose, poly (ethylene oxide), guar gum, dairy wastes, starches, dextrins, alginates, pectins, and the like.

The invention is offered which relates to a binder for agglomeration of particulate material, especially iron ore, in the presence of water which comprises a binding effective amount of a water-soluble polymer and a binder enhancing effective amount of caustic [1]. Another one discloses compositions for iron ore agglomeration which comprise 10-45% by weight of a water-in-oil emulsion of a water soluble vinyl addition polymer, 55-90% by weight of a polysaccharide, 0.001-10% by weight of a water soluble surfactant and 0-15 weight % of Borax [2]. Another binder agents are used in patents [3-5] disclosing accordingly contents of water soluble sodium carboxymethylhydroxyethyl cellulose with sodium carbonate, carboxymethyl cellulose with the salt of a weak acid or with sodium tripolyphosphate. Wood related products such as sulfonated cellulose, lignine, lignosulfonates are recommended as binding agents too [6-7]. One more invention discloses a process for making pellets of iron ore. The water-soluble polymer applied may be of any typical type, e.g., natural, modified natural or synthetic. The mixture may optionally comprise a pelletizing aid which may be sodium citrate [8]. Organic binder compositions are not without their own disadvantages. They generally do not impart adequate dry strength to the pellets. Thus, there is an ongoing need for economical binders with improved properties.

It is not superfluous to emphasize and remind that available in the patent and scientific literature specific information on binders for agglomeration of mineral metallic ore relate primarily iron ores and concentrates. Their use in relation to the molybdenite concentrate there is no information at all. Therefore, the objective of the research was the selection of an alternative to kaolin mineral-organic binder in the composition of the Mo concentrate batch's providing strength to pellets during their granulation and firing; leading to no cinder's dilution on molybdenum, giving them the best hydrometallurgical properties in compare with the mineral kaolin binder. Its requirements: it should not contain any "technological poisons" (such as phosphates) adversely affecting the redistribution of cinder: leaching, sorption on ion-exchange resin of Mo (VI) ions, hydrogen reduction to metal, sintering rods. Tasks: to compare the hydrophilic, strength and technological properties of binders: kaolin and alternatives to it of organic and organic-mineral nature, being in the batch composition for pyrite cinders of molybdenum middlings production at JSC "Almalyk GMK" (Uzbekistan) [9].

Experimental

The batches for Mo concentrate granulation were of following composition (Table 1).

Table 1. *Batches for Mo-concentrate pelletization. Contraction: b - bentonite, k - kaolin, LG - liquid glass, CS - cellulose sulfonated, CMC – carboxymethylcellulose, PVA - polyvinyl acetate, SC - waste of polyacrylonitrile fiber production.*

Nr	Binder composition, %							Mo concentrate, %	Nr	Binder composition, %							Mo concentrate, %
	Mineral component			Organic binder agent						Mineral component			Organic binder agent				
	b	k	lg	SC	CMC	PVA	CS			b	k	lg	SC	CMC	PVA	CS	
1	-	-	-	-	-	-	-	100	10	-	-	1.5	1.5	-	-	-	97
2	-	10	-	-	-	-	-	90	11	2	-	-	1.5	1,5	-	-	95
3	-	-	-	3	-	-	-	97	12	-	2	-	1.5	1,5	-	-	95
4	-	2	-	3	-	-	-	95	13	-	-	3		-	-	-	97
5	2	-	-	3	-	-	-	95	14	2	-	-		1,5	-	-	96.5
6	2	-	-	-	2	-	-	96	15	2	-	-	0.5	-	-	-	97.5
7	2	-	-	-	-	2	-	96	16	-	2	-	0.5	-	-	-	97.5
8	2	-	-	-	-	-	2	96	17	1	-	-		0,5	-	-	98.5
9	-	-	-	1	-	-	-	99	18	1	-	-	0.5	-	-	-	98.5

Limiting wetting angle of batch material compacted under a pressure of 20 MPa (∅ 12, height: 4 mm) was determined from the profile of water droplets thereon [10]. The granules were obtained in the disc pelletizer and then dried at 20 °C, for 24 hrs. Their crushing strength was evaluated with the following methods: 1) of integrity of the granules dropped from a height of 2 m onto concrete; 2) of compression fracture. Their comparison revealed allowable strength criterion: $F \geq 1.2$ MPa. The content of elements in the raw materials and technological solutions was determined by ultimate analysis carried by AAS "Perkin-Elmer" 3030V with a flaming atomizer, and Aligent 7500 ICP-MS. Thus, Au and Ag in the samples were determined at wavelengths of 242.8 and 328.1 nm with preconcentration extraction in a toluene solution of sulfide oil at a ratio of organic / aqueous phases = 1/10, respectively.

IR absorption spectra were recorded in the range of 400-4000 cm^{-1} with AVATAR-360 spectrometer Nicolet. Thermograms were recorded by derivatograph Paulik Erdey at gradient 10 degrees per min, sample weight 0.200-0.250 g, in corundum crucible ∅ 10 mm, with T-900, TG-200, the DTA-1/10, DTG1/20 sensitive galvanometers and Al_2O_3 as a standard. Rontgenograms were recorded by DRON-2.0 X-ray crystal analyzer with Cu-anticathode. To calculate the interplanar distances table of ASTM standard card index was used. The relative intensity of the lines I / I (J,%) was determined as a percentage of reflex expressed at the maximum.

Results and Discussion

The Mo concentrate's composition supplied to the granulating was the following, %: Mo 38; Re 0.7; Cu 2.5; P 0.009; Sb 0.025; WO_3 0.05; S 25.2; SiO_2 10.8; humidity 0.42; peculiar to Mo concentrate quantities of Au and Ag presented there too.

Limiting wetting angles of the batches prepared on Mo-concentrate base in compare with few reference data [10] are offered in Table. 2.

Table 2. *Wetting of quartz, talc, batch mixtures (Nr listed above).*

Batch, Nr	**quartz***	**talc***	**1**	**2**	**3**	**4**	**5**	**17**	**18**
Limiting wetting angle	0	69	95	36	33	32	30	34	33

From Table 2 it is revealed that the sample Nr 1 is identified as being hydrophobic. Decrease of its hydrophobicity was facilitated with binders allowing it to be granulated. Selection of the best of them for the role of alternative to kaolin was intended to experiment aimed at a comparison between the strength of pellets with a diameter of 3-5 mm, made of MoS2-containing batch materials with binders, after their drying-firing at 20, 250, 600°C (Table 3).

Table 3. *Pellets' strength depending on the batch's composition and drying temperature.*

t, °C	**Durability of pellets ∅ 3-5 mm, under loading before destruction, MPa**																
	Batch pelletizing based on Mo-concentrate, batch mixture's Nr																
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
20	0.7	1.1	2.0	1.9	0.2	1.6	0.9	0.5	1.5	1.6	1.8	2.8	0.3	1.5	1.5	0.3	1.2
250	2.4	1.6	1.8	3.2	0.5	0.2	0.8	0.6	1.9	2.2	2.7	2.5	0.4	3.1	1.9	0.9	1.8
600	6.4	1.2	4.1	8.4	0.6	0.6	1.2	0.7	0.1	0.2	0.2	0.3	0.7	7.3	4.0	1.1	4.5

In manufacture of candle end of Mo middlings the requirement to the durability of pellets is empirically revealed, adjustable by a mode of balling in a balling drum for pelletizing the concentrate of own design, with drum's diameter made of a stainless steel equal to 2 m, as well as by batch composition, %: Mo-concentrate 92-90, kaolin 8-10. The corner of an inclination of a drum, speed of its rotation and submission of a batch with water, time of balling were selected too empirically, aspiring to the optimum size and durability of the pellets. At understating of the kaolin maintenance in granule's batch mixes their resistance to abrasive wear on a way to a furnace fell, at their overestimate - permeability of oxygen in pellets (O_2 is necessary for oxidation of molybdenite up to trioxide of Mo) was blocked: in both cases the content of sulfur in the candle end exceeded norm of State standard GOST 2677-78.

So one of the research's problems was the quantitative description of the above-stated requirement empirically revealed by the industry to durability of the pellets. The approximate allowable range of pellets' durability is established to be approximately: P=1÷4 MPa, specification of criterion demands additional researches. At understating or overestimate of this parameter in a candle end the content of sulfur could overcome its norm: 1,5 % [9].

Table 3 revealed: the current charge mixture based on kaolin Nr 2, as well as a mixture based on kaolin or bentonite: Nr 4, 5, 15-16, 18 provided a required pellets' strength: P =1÷4 MPa.

Granules and a powder received from them by means of abrasion up to 0.074 mm, placed in laboratory boat after 45 min heating at 600 °C, in a current of oxygen, are analyzed according to content of sulfur. The pellets did not contain it at all, the powder's S content was essential, because of superficial crust, interfering access of an oxygen.

It is established, that attractive, in view of 100 % of elimination of dilution of a candle end with molybdenum, refusal of a mineral component of a binding mix – kaolin or bentonite as seen in samples Nr 3 and Nr 9, led to falling of durability of burnt granules, their destruction in the furnace, to sticking to walls, incomplete oxidation of sulfides or dusting. Therefore, refusal of it, for the benefit of only one polymer, is inexpedient for molybdenite. The similar conclusion is earlier made in address of magnetite [11]. Iron ore [12] is offered for agglomerating and granulating at presence, at least, one colloid agent providing cohesion of mineral particles and one synthetic polymer – dispersing agent.

When replacing the SC polymer with CMC (Nr 6,14,17) strength values are being worse, but in the range of high concentration of bentonite and CMC (Nr 6, 14) they do satisfy the requirements for strength. At low concentration of both binder agents in Nr 17 mixture, the durability was dissatisfied. For SC exchange on sulfonated cellulose (Nr 8) or water glass (Nr 11, 13), for turning mineral binder of the mixture (kaolin or bentonite), but in the presence of SC (Nr3, 9), unsatisfactorily decrease of pellet's strength took place.

Increasing of the temperature treating from 20 upto 600 °C lead to the pellets' strength rise. An advantage of the compositions based on organic binder, for example, Nr 15-18, to mixtures without its supplement consists in a fact that the organic additives SC, CMC, PVA at thermo treating burn up to the ground causing no dilution of a calcine. Mineral binders:

bentonite, kaolin on the contrary resulted its dilution although imparting strength of the pellets. The addition of WG degrade the strength of granules, baked at 600 °C.

It was of interest to compare the technological properties of mixes Nr 1,2,16, for which of them pellets had been made, burned and subjected to ammonia leaching. From the obtained cakes Au, Ag were recovered after cyanide leaching. At all stages the samples were analyzed for the content of Mo, Re, Au, Ag. It was found out that pellets of a batch №16 had been relatively enriched with Mo before and after their firing, with minimum content of unoxidized MoS_2 and maximum of MoO_3 in their composition. Ag and Au contents in the cinder were maximal, facilitating their removal from the cakes. At 600 °C Rhenium in the form of Re_2O_7 sublimated to the maximum extent (Table 4).

Table 4. *Effect of firing of pellets made of mixtures Nr 1, 2, 16 on metals recovery (Re - from a gas phase, Mo – from the pyrite cinder of molybdenum middling by means of ammonia leaching, Au, Ag – from cinder's cake after Mo recovery by means of cyanide leaching). A designation of conditions: I – metal's content in a batch before firing; II - after it; III – metal's recovery (%); Batches were preliminary opened (sulfides oxidized), accordingly, by nitric acid - Nr 1 (without firing-roasting) and by oxygen at firing – Nr 2, 16.*

Element	Batch Nr 1 (no binder)			Batch Nr 2			Batch Nr 16		
	I	II	III	I	II	III	I	II	III
Mo, %	41,3	-	97%	37,7	39,1	97%	39,9	42,2	99%
Re, %	0,07	-	-	0,06	0,05	15%	0,07	0,05	30%
Au	38,1 g/t	-	94%	34,7 g/t	36,1 g/t	92%	36,7 g/t	38,2 g/t	95%
Ag	62,2 g/t	-	95%	56,9 g/t	59,2 g/t	93%	60,0 g/t	62,0 g/t	95%

Conclusion

As a result of comparative colloid-, physical and chemical, mechanical, technological tests effective binder compositions for granulation the Mo-concentrate are developed providing the required strength to granules being alternative to existing kaolin batch mixture (Mo concentrate 90-92%, kaolin 10-8%) and basing on two combinations: 1) kaolin (2%), SC polymer (0.7-1,0 %), Mo concentrate the rest; 2) bentonite (0,7-1,0%), SC polymer (0.7-1,0 %), Mo concentrate the rest. The organic SC polymer may be replaced by any in a group of CMC or PVA in the range of 0.7-2% concentration. The polymer SC is preferable among them, in terms of strength. The comparative molybdenum leaching from the pyrite cinder of molybdenum middling produced of traditional and new mineral-organic batches by means of ammonia leaching, precious metals from cinder's cake after Mo recovery by means of cyanide leaching) made possible to offer new Mo concentrate's batch composition differing from the traditional one with best hydrometallurgical processing features.

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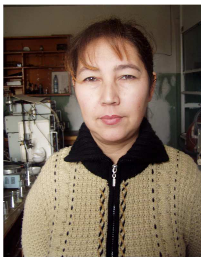

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