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STUDY ON GY NEW MINERAL PROCESSING TECHNOLOGY FOR SHIZHUYUAN POLYMETALLIC ORE

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Shizhuyuan W-Mo-Bi-CaF_2 polymetallic ore is classified to the refractory one due to its complex property, fine dissemination and close association of minerals. Through several years of researches, in line with GY new mineral processing technology developed by Guangzhou Research Institute of Nonferrous Metals, in sulfide flotation circuit, an iso-flotability flowsheet is used to replace original overall bulk flotation flowsheet, and in tungsten flotation circuit, a new chelating type-GY reagent and a special pulp-conditioning system and a new technology of wolframite slime flotation are used to replace the traditional "Caustic Soda Method"[1], the metallurgical performance is greatly improved. Besides, GY New Method has created a favorable condition for comprehensive recovery of fluoride from tungsten flotation tailings. Notable economic benefit has been achieved.
Keywords: polymetallic ore, scheelite, wolframite slime flotation, GY new method

Introduction

The ore of Shizhuyuan W-Mo-Bi-CaF_2 polymetallic mine is very difficult to treat, basically because of the following four reasons: 1) partial portions of molybdenite, bismuthinite and pyrite are of similar flotability; 2) tungsten minerals occur in the form of scheelite and wolframite, ect., their flotabilities are quite different; 3) the finelly disseminated valuable minerals are closely associated, when ore is ground to 90%-0.074mm, sulfide minerals are basically liberated, nevertheless, tungsten minerals, especially wolframite are overground, large amount of wolframite slime are produced; 4) the flotability of scheelite is very similar to that of calcium-bearing gangue minerals, such as fluoride, calcite and etc., their effective separation is hard to tackle.

The mineral processing of Shizhuyuan complex polymetallic ore which contains both sulfide and oxide minerals has long been considered a technically difficult problem. For a long time, researches on Shizhuyuan ore have been conducted, several flowsheets, such as gravitational separation-flotation, gravitational separation-flotation-gravitational separation, overall flotation trunk have been put forward. But recently, overall flotation trunk flowsheet has been widely accepted. Previously, the flowsheet of overall Mo-Bi-S bulk flotation and their subsequent separation step by step was adopted in concentrator, but the flowsheet has several shortcomings: 1) The addition of polar collector in sulfide bulk flotation creats difficulty in the separation of molybdenite and bismuthinite from pyrite. As sodium sulfide activates pyrite in the separation of molybdenite from bismuthinite, leading to easy entrance of pyrite into Mo-concentrate, meanwhile, the separation of bismuthinite from gangue minerals is difficult to control; 2) In high alkaline pulp, the collector-733 oxidized paraffin wax soap presents poor selectivity and weak collecting power for wolframite, hence the grade of W rougher concentrate is not high and recovery of W rougher is lower, meanwhile as tailing pulp presents high alkaline, resulting in high expense in treatment; 3) In tungsten flotation circuit, no effective system is available for slime recovery, large amount of fine particles of tungsten minerals, especially wolframite slime could not be recovered, total recovery is only about 55%.

In recent years, Guangzhou Research Institute of Nonferrous Metals and Shizhuyuan Polymetallic Mine has developed the GY new mineral processing technology[2]. In sulfide flotation,the flowsheet of Mo-Bi isoflotation and Bi-S isoflotation followed by the separation of molybdenite from bismuthinite and bismuthinite from pyrite as well as pyrrhotite, respectively is adopted. In tungsten rougher circuit, lead nitrate is used as an activator for tungsten minerals, modified sodium silicate as a gangue's depressor, the selective combined chelating agent GY with high efficiency as a collector; the scheelite and wolframite bulk flotation is conducted in natural pH medium instead of the recovery process of scheelite and wolframite being conducted in separate circuits and in high alkaline medium. A high grade tungsten rougher concentrate with high recovery and low CaF_2 content could be obtained. Thus, two well-known technically difficult problems: the recovery of scheelite and wolframite at a step and the separation of scheelite from calcium-bearing gangue minerals, such as fluoride, etc. have been solved. In scheelite cleaning circuit, traditional "Petrov Method" is basically used, but some improvement has been made. In the operation of pulp heating, the mixture of sodium silicate is used to replace single sodium silicate, hence intensifying the removal of reagents from minerals' surface and scheelite being activated. In addition, a new processing technology of wolframite slime has been developed, hence obviously improving the recovery of wolframite. As the pH value of tailings pulp is neutral, the recovery of fluoride will be in very favorable condition. Currently, the GY new technology has been successfully used in Shizhuyuan Mine, notable benefit has been achieved.

Properties of Ore

The main valuable minerals in the ore are scheelite, wolframite, bismuthinite, native bismuth, molybdenite, pyrite, pyrrhotite, cassiterite, magnetite, fluoride, etc.; the main gangue minerals are garnet, quartz, feldspar, chloride, calcite, mica, etc.. The dissemination of valuable minerals are relatively fine. The particle size of tungsten minerals, molybdenite and bismuthinite are ranging between 0.02-0.12mm, 0.02-0.1mm, 0.01-0.07mm, respectively. The typical elementary analysis and mineralogical analysis of ore are shown in table 1, 2, 3, 4, respectively.

Table 1 Elementary Analysis

Item	WO_3	Mo	Bi	Sn	S	Fe	SiO_2	CaF_2	Al_2O_3	MgO	P	Mn
Content %	0.5	0.08	0.17	0.1	0.65	4.0	40.5	20.6	7.4	2.6	0.015	0.4

Table 2 Tungsten's Mineralogical Analysis

Item	Scheelite	Wolframite	Tungstite	Total
Content WO_3 %	0.344	0.148	0.008	0.5
Distribution %	68.8	29.6	1.6	100.00

Table 3 Molybdenium's Mineralogical Analysis

Item	Molybdenite	Scheelite	Molybdite	Total
Content,Mo %	0.075	0.0024	0.0026	0.08
Distribution %	93.75	3.00	3.25	100.00

Table 4 Bismuth's Mineralogical Analysis

Item	Bismuthinite	Native Bismuth	Bismuth Oxide	Total
Content, Bi %	0.126	0.004	0.05	0.18
Distribution %	70.00	2.22	27.78	100.00

Flowsheets and Results of Commercial Test

Previous flowsheet and result

The previous technological flowsheet is shown in Fig.1, the result is shown in Table 5.

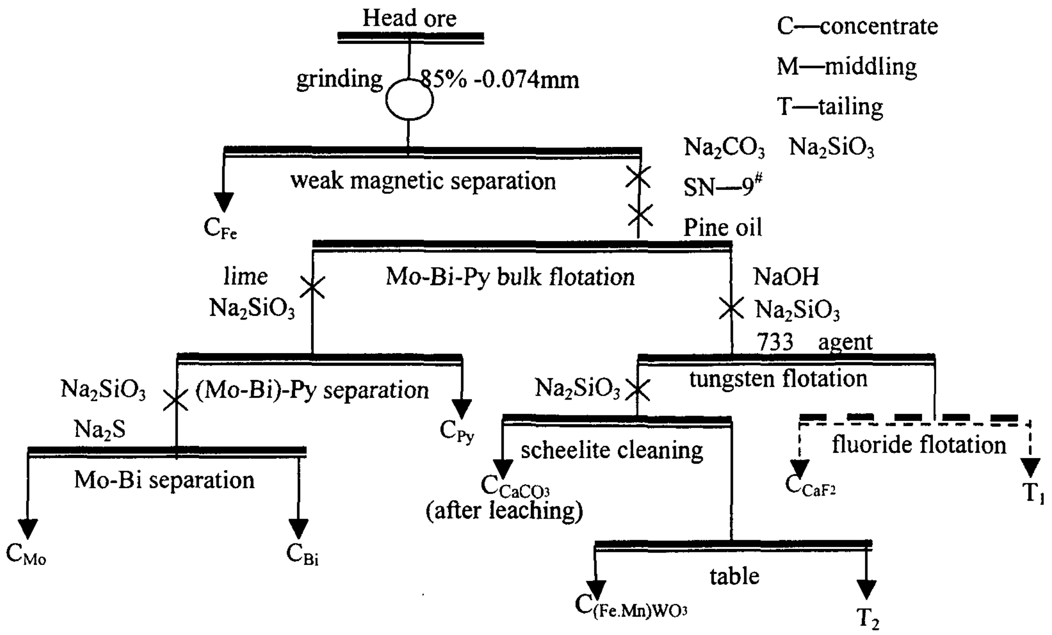

Fig.1 Previous technological flowsheet

Current GY new flowsheet

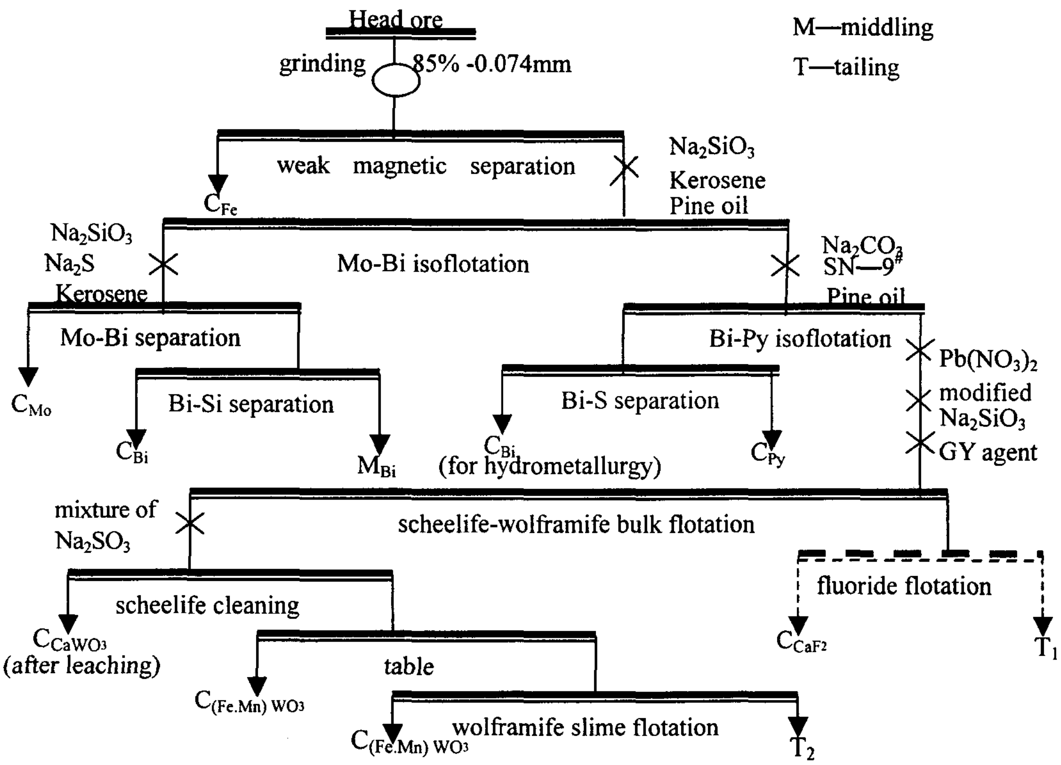

Fig.2 GY new technological flowsheet

The current technological flowsheet is shown in Fig.2, the commercial test result is also shown in Table 5.

Table 5 Results for Different Flowsheets

Item	Name of Product	GY New Flowsheet	Previous Flowsheet	Difference
Head Ore, %	WO_3	0.49	0.53	-0.04
	Mo	0.08	0.09	-0.01
	Bi	0.17	0.18	-0.01
Grade, %	Scheelite Concentrate	67.52	67.35	+0.17
	Mo Concentrate	48.41	47.30	+1.11
	Bi Concentrate	38.58	19.5	+19.08
Recovery, %	Total Tungsten concentrate	78.93	55.30	+23.63
	Mo Concentrate	85.88	84.12	+1.76
	Bi Concentrate	71.86	61.15	+10.71

Discussion on GY New Technology

It is proved by commercial test that as for GY new technology, the flowsheet is reasonable, whole process is stable and metallurgical performance is quite good. In the process of commercial test, the main technological factors affecting tungsten flotation were investigated on the basis of process mineralogy, size distribution of products, lab test and multivariable regression analysis on test data.

Ore's Property

The Shizhuyuan polymetallic ore is basically classified as greisen-skarns type ore. Several main kinds of ores can be identified by their mineralogical properties. The ore with more quartz or garnet presents relatively easy beneficiability, but the ore with large amount of fluoride, chloride or calcite presents poor beneficiability. Usually, the head grades are ranging between WO_3 0.2-0.9%, Mo 0.04-0.15%, Bi 0.14-0.25%, respectively. Besides, normally, the ratio of scheelite: wolframite is 7:3, in practice, above ratio varies obviously, ranging from 9-4:1-6. Sometimes, so called "grey tungsten mineral"which presents neither black nor white colour can be identified. As the flotability of scheelite and wolframite is quite different, correspondingly, the required processing technology is not the same. Since mixing of the ores from different mining areas is not available, the property of run of mine is not stable, resulting in more difficulty in processing.

Grinding Fineness

For Shizhuyuan polymetallic ore, the disseminations of Mo-bearing minerals and Bi-bearing minerals are quite fine, and dissemination of tungsten minerals is relatively fine and is not homogeneous. The minerals in ore with fineness of 85-90%-200 mesh are basically liberated. Sulfide flotation needs fine grinding, but tungsten flotation needs stage grinding. The suitable grinding condition for sulfide flotation often results in overgrinding of tungsten minerals especially wolframite in grinding circuit, but if grinding fineness is not enough, part of locked particle of tungsten minerals and small amount of coarse particle of tungsten minerals are easy to be losed in tailings.

Flotation Pulp Density

Both sulfide flotation and tungsten flotation need suitable pulp density. When pulp density of tungsten rougher is too low (for example R<20%), tungsten minerals are not able to float well, wolframite, sometimes even scheelite can be obviously seen in tailings. When pulp density is too high (for example R>50%), the selectivity of tungsten rougher becomes poor.

Influence of Technology of Sulfide Flotation on Subsequent Tungsten Flotation

The content of pyrite and pyrrhotite of ore is not high with S 0.4-0.6% usually. Nevertheless, recently the S content of quite a few of ores is obviously becoming higher. Currently, a small amount of xanthate, SN-9# and pine oil are added into Bi-S isoflotation, but in weak alkaline medium, small amount of collectors and frother are hard to fully float sulfides such as pyrrhotite with relatively poor floatability, pyrrhotite often enters into tungsten rougher operation and is collected by chelating agent in neutral medium, hence affecting the quality of tungsten concentrate.

Several Major Factors Affecting Tungsten Rougher Technology

GY New Reagent

Normally, chelating collector is effective for wolframite, but is poor for scheelite in contrast. The fatty acid type of collector which shows relatively strong collecting power for scheelite shows relatively weak collecting power for wolframite. Considering the coexistence of scheelite and wolframite in the ore, a new type of chelating agent---GY has been developed, its polar group is able to react with surfaces of wolframite and scheelite by means of chelation or by chemical adsorption.

Lead Nitrate

When chelating agent used, lead nitrate shows effective activation for tungsten minerals, especially for wolframite[3]. If lead nitrate is absent, tungsten minerals can not float; when the dosage of $Pb(NO_3)_2$ is increased to certain amount, tungsten minerals will start to float. Generally speaking, for ore assaying WO_3 0.4-0.5%, $Pb(NO_3)_2$ 500g/t is enough, overdose of $Pb(NO_3)_2$ only results in the increase of cost. When ore is assaying over WO_3 0.6% or the ratio of wolframite and scheelite is higher, an appropriate increase of $Pb(NO_3)_2$ dosage will benefit tungsten recovery to certain extent.

Modified Sodium Silicate

It is proved by test that the sole use of sodium silicate can not bring about effective separation of tungsten minerals from gangues, but in line with GY new technology, when sodium silicate is suitably modified, it shows effective and selective depression on calcium-bearing gangue minerals such as fluoride and calcite, etc.. The dosage of modified sodium silicate should be adequate, if it is excessive, even tungsten minerals will be depressed, if it is too low, gangue minerals will not be effectively depressed. Normally, the suitable dosage of modified sodium silicate ranges between 1500-2800 g/t, the enrichment ratio of tungsten rougher is 40-50, sometimes is 80-100, the operation recovery is as high as 75-90%.When the amount of fluoride, chloride and calcite in the ore is higher, and the grade of tungsten rougher concentrate is lower, only WO_3 12-22%, the dosage of modified sodium silicate should be increased adequately.

Scheelite Cleaning

The tungsten rougher concentrate is normally assaying WO_3 18-40%. Analyzing its mineralogical composition, besides of scheelite and wolframite, some amount of fluoride, garnet calcite, magnetite and pyrrhotite can be identified. Having reacted with chelating agent, these minerals still remain higher activity and are difficult to depress in cleaning flotation. In order to guarantee the quality of final scheelite concentrate, the traditional "Petrof Method" is basically adopted, i.e. , tungsten rougher concentrate (R50-65%) is heated to 95℃, large amount of sodium silicate are added, after being kept warm for more than 1 hour, sodium silicate is removed by dilution and rougher concentrate is repulped, tungsten cleaning flotation is conducted. It is proved to be difficult by test that final scheelite concentrate with WO_3 content over 65% can be obtained only by traditional "Petrof Method", some improvement must be made. In our test, mixture of sodium silicate is used to replace single sodium silicate, hence intensifying the selective removal of reagents from mineral surface, more strongly depressing fluoride, calcite, garnet, magnetite and pyrrhotite, possibly activating scheelite to some extent, improving the separation results. It is shown by test that when the dosage of mixture of sodium silicate is too small, the gangue minerals are not easy to depress, otherwise, tungsten minerals will also be depressed .The dosage of mixture of sodium silicate is related to the grade of rougher concentrate and the kinds of gangue minerals. If the grade of rougher concentrate is low or the content of fluoride or calcite is higher, more dosage of mixture of sodium silicate is needed, and vice versa. It is necessary to maintain a suitable pulp density in scheelite cleaning. Rare density will result in lower tungsten recovery and lower grade of scheelite concentrate.

Flotation of Wolframite Slime

The tailing from above tungsten cleaning flotaion is sent to weak magnetic separator to remove magnetite and subsequently sent to table to recover coarse wolframite. Being thickened, the table tailing is then delivered to wolframite slime flotation. The technical key problem of the operation lies in the activation of wolframite which has lost its flotability because of reagent removal from its surface at elevated temperature and the effective separation of wolframite slime from gangue minerals. In our research, the main technical principle similar to what is used in tungsten rougher flotation is still adopted. That is, lead nitrate is used to activate wolframite, GY to collect wolframite and modified sodium silicate to depress fluoride, garnet, calcite, etc., besides, SF agent is used to strengthen the depression of gangue minerals. The flowsheet includes one stage of rougher, 5 stages of cleaning and 2 stages of scavenger, the operation recovery is as high as 75-85% (6-10% for head ore), the wolframite slime concentrate is assaying WO_3 40-65%, slime concentrate can be further processed by gravitaional separation to upgrade or can be combined with coarser wolframite concentrate obtained from table according to market requirement.

Conclusions

1. Shizhuyuan W-Mo-Bi-CaF_2 polymetallic ore is quite difficult to treat because of its complex mineralogical property: fine dissemination, close association of valuable minerals, great difference in flotability of scheelite and wolframite and similarity in flotability of scheelite and calcium-bearing gangue minerals, such as fluoride, calcite etc..

2. Using iso-flotability flowsheet to replace overall bulk flotation flowsheet in sulfide flotation circuit benefits both grade and recovery of different sulfide concentrates, improves their separation efficiency.

3. In tungsten flotation, using modified sodium silicate to selectively depress gangue minerals and using GY chelating agent to selectively collect tungsten minerals activated by lead nitrate greatly improves the grade and recovery of rougher concentrate, finally benefits the reducing of subsequent processing cost, which having solved the two well known technically difficult problems: bulk flotation of scheelite and wolframite and separation of scheelite from calcium-bearing gangue minerals, such as fluoride, calcite etc..

4. The developed wolframite slime recovery system adopts unique magnetic separation-gravitational separation-flotation combined technology, effectively recovering wolframite slime, benefiting total tungsten recovery.

5. The tungsten flotation is conducted at neutral pH pulp, having creating very favorable condition for environmental protection and comprehensive recovery of fluoride from tungsten tailings.

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