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Flotation Studies on Scheelite Concentrate of Chitral, NWFP, Pakistan

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Abstract

A scheelite concentrate, containing 32% WO_3, obtained from an indigenous tungsten ore of Chitral, NWFP, Pakistan, has been beneficiated by froth flotation technique to produce high quality tungsten concentrate assaying 64.8% WO_3 with 84.47% recovery. This paper presents results on the optimization of flotation parameters like pH, pulp density and reagents. The optimum grade and recovery have been obtained at a feed size of 80 % passing 74 µm, pulp pH of 10.5, pulp solids 25%, oleic acid 0.30 kg/t, polyglycol 0.02 kg/t and sodium silicate 0.125 kg/t of the feed. The obtained tungsten concentrate meets the specifications required to produce tungsten metal and tungsten based chemicals.

Key words: Scheelite Concentrate, Beneficiation, Flotation, Grade, Recovery

Introduction

Tungsten is a whitish-gray metal with many unique properties and a wide variety of uses. Its largest use is as tungsten carbide in cemented carbides. Cemented carbides (also called hard metals) are wear-resistant materials used by the metalworking, mining and contraction industries. Tungsten metal wires, electrodes and contacts are used in lighting, electronic, electrical, heating and welding applications. It is also used to make heavy metal alloys for arnaments, heat sinks and high-density applications, such as weights and counterweights, super alloys for turbine blades, tool steels, and wear-resistant alloy parts and coatings. Tungsten composites are used as a substitute for lead in bullets and shot. Chemical uses of tungsten include catalysts, inorganic pigments and high-temperature lubricants (Shedd, 2001).

The main ores of tungsten are (a) wolframite [(Fe, Mn) WO_4] having a specific gravity of 7.1-7.9 and it is feebly magnetic and (b) scheelite ($CaWO_4$) having a specific gravity of 5.9-6.1. Scheelite is often closely associated with quartz, with which it is easily confused because of the very similar physical appearance of these two minerals. Fortunately, scheelite always fluoresces a characteristic electric blue to yellow color when irradiated with ultraviolet light, which greatly facilitates both prospecting for scheelite and the evaluation of scheelite deposits (Blackburn, 1988).

Tungsten metal has high strategic importance. High prices and ready market for acceptable tungsten concentrates present very attractive incentive for the mining and processing of tungsten ores. Since all tungsten ores are very friable and slime easily, concentration must take place as soon as the mineral has been liberated by either crushing or grinding methods. Regardless of the care taken in the selection of the route of beneficiation, a certain portion of the tungsten is going to be slimed, both during the mining and the milling process. In general the ability to recover the slime tungsten means the difference between success or failure of the milling installation and of the preceding mining operations.

The dominating processes for concentration of tungsten ores are gravity concentration and froth flotation methods. The beneficiation process used is dependent upon the type of ore. Experts like Michell and Gisler have excellent review articles on the processing of tungsten ores (Weiss, 1985). In gravity treatment, care should be taken to concentrate the value and the coarsest possible size avoiding over-grinding. Jigs, tables, rag frames, and spirals are commonly used. In original flotation practice, tungsten ores are beneficiated by using a carboxyl collector and sodium silicate as a depressant. Tannin is used as a depressant in case of associated calcite, fluorite, dolomite and apatite. However, it is quite difficult to obtain economic grade as scheelite itself is readily depressed. Many scheelite flotation mills attempted to make a 60% WO_3 concentrate by gravity means or by tabling of the flotation concentrate. Since scheelite is often finely disseminated in the ore body and tends to slime badly on grinding, such operations showed heavy tungsten losses in achieving the desired grade (Adams, 1986, Crozier, 1992, Bernhart, 2002). However, to produce economic tungsten concentrates, tungsten ores are treated by a combination of gravity concentration and flotation of fines (Zhang *et al.* 2001, Guan *et al.* 2002) or by an all flotation process. In the latter case, the ore must be ground to sufficient fineness to assure adequate liberation of the scheelite. (Adams, 1986, Crozier, 1992).

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The scheelite ore of Chitral, North Western Frontier Province (NWFP), Pakistan, containing about 0.55% WO_3, was upgraded to 32% WO_3 at Mineral Processing Research Centre (MPRC) of PCSIR Laboratories Complex Lahore, by applying a combination of mineral processing techniques such as gravity concentration and magnetic separation. The studies regarding gravity concentration and magnetic separation have been compiled to report in a separate communication. The tungsten concentrate having 32% WO_3 was further upgraded to 64.8% WO_3 by froth flotation. The present paper describes the results on the optimization of froth flotation parameters like pH, pulp density and reagents for the preparation of high quality tungsten concentrate, containing 64.8% WO_3, from the above concentrate.

Materials and Methods

For chemical analysis of flotation feed and products, ASTM methods of volumetric and gravimetric analysis were employed (Jeffery, 1989).

To avoid over grinding, the tungsten concentrate of 32% WO_3 obtained from Scheelite ore of Chitral area of Pakistan was ground carefully in a laboratory rod mill so that it may have a fair proportion of free valuable mineral particles for subsequent flotation operation. The mill was 400mm long, 160 mm in diameter and contained rods of different sizes weighing 25 kg, and it worked at a speed of 43 rpm. After performing a series of tests, grind size of the feed was found to be 80% passing 74 µm to get the optimum flotation results.

Flotation Tests

The flotation tests were carried out in a Denver D-12 flotation machine. The study was completed under different set of conditions for the optimization of flotation parameters. The set of conditions were as follows: pH 9.5-11.5, pulp density 20-40% solids, oleic acid (0.15-0.40 kg/t) as collector, sodium silicate (0.025 - 0.225 kg/t) as depressant and Polyglycol (0.015-0.035 kg/t) as frother. The conditioning time was 1-5 minutes and the froth was collected for 5-20 minutes. The cleaning flotation was carried out without addition of any flotation reagents.

Results and Discussions

Table I indicates presence of 32% WO_3, 48.96% SiO_2 and 8.26% CaO as major quantities with minor amounts of others in the tungsten concentrate originating from the Scheelite ore of Chitral area of Pakistan. The grade of the tungsten concentrate seems to be very good for beneficiation purpose as the other gangue minerals like quartz and silicates can be reduced effectively by froth flotation technique (Adams, 1986, Crozier, 1992).

Table I: Chemical analysis of tungsten concentrate

Constituents	%
WO_3	32.00
SiO_2	48.96
CaO	08.26
Fe_2O_3	00.78
Al_2O_3	05.87

The description of metallurgical balance given in Table II indicates that the tungsten concentrate of Chitral, containing 32% WO_3, can be upgraded up to 55% at rougher flotation stage with 90.5% recovery. This recovery has been obtained, as mentioned in Table III, at a feed size of 80 % passing 74 µm, pulp pH of 10.5, pulp solids 25%, oleic acid 0.30 kg/t,

Table II: Metallurgical balance for tungsten flotation

Product	Wt. %	Grade WO_3 %	Recovery WO_3%
Cleaner Concentrate	41.66	64.80	84.47
Cleaner Tailings	10.44	18.70	6.03
(Rougher Concentrate)	(52.60)	(55.00)	(90.50)
Rougher Tailings	47.40	6.43	9.50
Head Sample	100.0	32.00	100.0

polyglycol 0.02 kg/t and sodium silicate 0.125 kg/t of the feed. It is also important to note from Tables II and III that one cleaning of the rougher concentrate has been ensured a final concentrate grade of 64.8% WO_3 with 84.47% recovery, without using any additional reagents.

Table III. Optimum parameters of tungsten flotation

Parameter	Optimum Value	
	Rougher	Cleaner
Feed size	80% passing 74µm	80%passing 74µm
Pulp pH	10.5	10.5
Pulp density	25 % solids	20 % solids
Collector (Oleic acid)	0.30 Kg/T	Nil
Frother (Polyglycol)	0.02 Kg/T	Nil
Depressant (Sodium silicate)	0.125 Kg/T	Nil
Conditioning time	3 minutes	1 minutes
Flotation time	10 minutes	7 minutes

Table IV indicates the effect of pH of the pulp on the % purity and recovery of the product. The maximum purity is achieved at a pH of 10.5. Scheelite is already known for its propensity to yield better flotation results at alkaline pH 10.5 with oleic acid and our studies too have substantiated the same view (Adams, 1986, Jain, 1986).

It can be seen from Table V that the pulp density variation has a significant effect on the grade and the recovery of

Table IV: Effect of pH

pH	Grade WO_3 %	Recovery WO_3%
9.5	35	40
10	46	64
10.5	55	90.5
11	48	71
11.5	34	50

Pulp density 25% solids, Oleic acid 0.3 kg/t, Polyglycol 0.02 kg/t, Sodium silicate 0.125 kg/t, Conditioning time 3 min., Flotation time 10 min.

scheelite. It is clear from the result that as the pulp density is reduced from 40 to 20% solids, the grade of the concentrate improves while the recovery increases up to 91 and then falls as the pulp becomes more and more dilute. At pulp density of 25% solids, the grade of the rougher concentrate is better than 30% solids while there is no big difference in the recoveries.

Table V: Effect of % solids

% Solids	Grade WO_3 %	Recovery WO_3%
20	57	75
25	55	90.5
30	51	91
35	45	80
40	38	68

pH 10.5, Oleic acid 0.3 kg/t, Polyglycol 0.02 kg/t, Sodium silicate 0.125 kg/t, Conditioning time 3 min., Flotation time 10 min.

It is obvious from Table VI that an increase in the quantity of collector (oleic acid) up to 0.30 kg/t increases the grade and recovery. A dose of 0.30 kg/t of oleic acid following by the frother (Polyglycol) dose of 0.02 kg/t shows an optimum grade and recovery. Further increase in dose of oleic acid shows an adverse effect (Table VI) on grade and recovery due to the development of multi-layers of the collector on the mineral particles that reduce the selectivity. In addition, increase in the dosage of frother (Table VII) also lowers the recovery and does not have significant effect on grade due to over oiling effect (Crozier, 1992, Wills, 1992).

Table VI: Effect of collector

Oleic acid (Kg/T)	Grade WO_3 %	Recovery WO_3%
0.15	40	60
0.20	45	71
0.25	50	83
0.30	55	90.5
0.35	53	88
0.40	48	83

pH 10.5, Pulp density 25% solids, Polyglycol 0.02 kg/t, Sodium silicate 0.125 kg/t, Conditioning time 3 min., Flotation time 10 min.

Table VII: Effect of frother

Polyglycol (Kg/T)	Grade WO_3 %	Recovery WO_3%
0.015	51	86.5
0.020	55	90.5
0.025	55	87.5
0.030	54.5	86
0.035	54	85

pH 10.5, Pulp density 25% solids, Oleic acid 0.3 kg/t, Sodium silicate 0.125 kg/t, Conditioning time 3 min., Flotation time 10 min.

The separation of gangue from the desired mineral requires effective treatment to remove unwanted from the useful mineral. Sodium silicate fulfills the purpose as it is efficiently depresses the quartz and silicates by making them hydrophilic (Crozier, 1992, Kazmi *et al.* 2007). It is seen from Table VIII that sodium silicate efficiently depresses the quartz and silicates until an optimum grade and recovery of scheelite is achieved with a dose of 0.125 kg/t of the depressant. After that an increase in the dose of sodium silicate shows a negative effect on the grade and recovery probably due to the over coating of the depressant which make scheelite particles hydrophilic.

Table VIII. Effect of depressant

Sodium silicate (Kg/T)	Grade WO_3 %	Recovery WO_3%
0.025	49	85
0.075	53	89
0.125	55	90.5
0.175	50	86
0.225	46	80

pH 10.5, Pulp density 25% solids, Oleic acid 0.3 kg/t, Polyglycol 0.02 kg/t, Conditioning time 3 min, Flotation time 10 min.

Conditioning time has very significant effect on the grade of the concentrate but very little on the recovery of scheelite concentrate as it allows the surfaces of the mineral particles to react with the reagents. It appears from Table IX that a prolonged conditioning time peels off conditioner coating on the gangue resulting in lower flotation grade and recoveries. Similarly, grade and recovery decrease with short conditioning

Table IX: Effect of conditioning time

Conditioning time (Min.)	Grade WO_3 %	Recovery WO_3%
1	45	79
2	52	89
3	55	90.5
4	53	90
5	52	89.5

pH 10.5, Pulp density 25% solids, Oleic acid 0.3 kg/t, Polyglycol 0.02 kg/t, Sodium silicate 0.125 kg/t, Flotation time 10 min.

time, because collector remains unable to coat all the mineral particles present in the pulp. A conditioning time of 3 minutes was found to be sufficient for an optimum contact with the mineral particles under the conditions existing in the flotation cell, for an optimum recovery and grade.

Moreover, Table X indicates that the grade of the concentrate falls by almost 2.5% with 5 minutes increase in the froth collecting period. A flotation time of 10 minutes was found to produce better grade and recovery and this was selected as optimum value.

Table X. Effect of flotation time

Flotation time (Min.)	Grade WO_3 %	Recovery WO_3%
5	54.5	89.4
10	55	90.5
15	52.5	90
20	50	89

pH 10.5, Pulp density 25% solids, Oleic acid 0.3 kg/t, Polyglycol 0.02 kg/t, Sodium silicate 0.125 kg/t, Conditioning time 3 min.

The chemical analysis of the final tungsten concentrate presented in Table XI shows the presence of 64.80% WO_3, 15.7% Ca and 14.13% SiO_2 as major quantities with minor amounts of others.

Table XI. Chemical analysis of final tungsten concentrate

Constituents	%
WO_3	64.80
SiO_2	14.13
CaO	15.70
Fe_2O_3	00.48
Al_2O_3	20.35
P	Nil
S	Nil

It is clear that the obtained tungsten concentrate meets the specifications required to produce tungsten metal and tungsten based chemicals as the marketing specification of the high quality tungsten concentrates is 60% WO_3 content with phosphorous and sulfur levels below 0.05% each (Hawley, 1981, Johnstone, 1961).

Conclusion

Beneficiation of Scheelite by flotation is considered very sensitive and difficult job. The research and development work established that the indigenous tungsten concentrate, containing 32% WO_3, could be beneficiated to the high grade concentrate assaying 64.80% WO_3 with a recovery of 84.47%. This concentrate seems to be quite suitable for the production of tungsten metal and tungsten based products. It is a big achievement as tungsten concentrate is not available in the international market. Flotation studies on Scheelite of Chitral area of Pakistan have not been done earlier and the present work is the first investigation of its kind.

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