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Beneficiation studies of tungsten ores – A review

Xiaosheng Yang

GTK Mintec, Tutkijankatu 1, 83500 Outokumpu, Finland

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ABSTRACT

Scheelite ($CaWO_4$) and wolframite ($(Fe, Mn)WO_4$) are the only tungsten minerals mined commercially and are mainly found in five types of deposits: skarn, vein/stockwork, porphyry, disseminated and stratabound. Gravity concentration and flotation are the beneficiation techniques most commonly applied to scheelite ore, and gravity and/or magnetic separation for wolframite ore. With increasing exploitation, the primary tungsten resources become poorer in grade, finer in grain size and more complex in mineralogy, which makes the processing of the tungsten ores more difficult. Research and investigations into various approaches to improving the beneficiation efficiency of tungsten ores are reviewed in this paper, including selective flotation of scheelite from other calcium containing minerals such as calcite and fluorite using more selective reagents, very fine scheelite and wolframite flotation, optimization of concentration of complex tungsten ores by a combined gravity-magnetic-flotation process and recovery of associated Mo, Cu and Bi sulphides from tungsten ores.

1. Introduction

Tungsten, also known as wolfram, with symbol W and atomic number 74, has the highest melting point of all metals (3422 ± 15 °C). With its density of 19.25 g/cm3, tungsten is also among the heaviest metals. Tungsten features the lowest vapour pressure of all metals, very high moduli of compression and elasticity, very high thermal creep resistance and high thermal and electrical conductivity. Tungsten is the most important metal for thermo-emission applications, not only because of its high electron emissivity, which is caused by trace additions of other elements, but also because of its high thermal and chemical stability. Tungsten usually contains small concentrations of carbon and oxygen, which impart considerable hardness and brittleness (ITIA, 2017).

Cemented carbides, also called hardmetals, are the most important applications of tungsten today. Tungsten monocarbide (WC) is the main constituent and has a hardness close to diamond. Hardmetal tools are used for the shaping of metals, alloys, ceramics and other materials. About 54–72% of the tungsten produced globally is used for hardmetals. Steel and alloys, mill products such as lighting filaments, electrodes, electrical and electronic contacts, wires, sheets, rods etc., and a widespread variety of chemicals represent other important uses of tungsten.

Due to its very significant economic importance and high supply risk, tungsten has been listed as one of the 20 critical materials in Europe (EC, 2014). The world production of tungsten concentrate is distributed over a quite large number of countries but over 80% of it is produced in China. According to a report by the USGS in 2016 (Jewell and Kimball, 2016) the total global mine production of tungsten in 2015 was 87, 000 t, of which 71,000 t was from China. Currently, four EU countries including Austria, Portugal, Spain and UK are producing tungsten concentrate and a total of 2830 t of tungsten was produced in 2015. The consumption of tungsten in EU is about 10,000 t per year and demand is predicted to slightly increase over the next decade (Starck, 2013). Therefore, increasing the production of tungsten from primary resources should be one of important pathways to satisfy the demand of the metal in the EU market.

The average abundance of tungsten in the earth's crust is estimated to be 1.25–1.5 ppm, about the same as that of tin and molybdenum. It is more abundant in granite (about 2 ppm) than basaltic (1 ppm) and ultra-mafic rocks (0.5 ppm). There are numerous tungsten minerals, but only scheelite ($CaWO_4$) and wolframite ($(Fe, Mn)WO_4$) are of economic importance (Schmidt et al., 2012a, 2012b; BGS, 2011). However, wolframite is not a mineral species but a series between ferberite ($FeWO_4$) and hubnerite ($MnWO_4$). The domination of either iron or manganese would result in forming one of two minerals. The iron dominated one will result in forming ferberite while the manganese dominated one will result in forming hübnerite (Errandonea and Segura, 2010).

The world reserves of tungsten are estimately 4.000.000 t W of which China holds about 40% (Bernhart, 2015). The five major types of tungsten ore deposits from which most ore is currently produced are skarn, vein/stockwork, porphyry, disseminated or greisen, and stratabound (BGS, 2011). Typical grades (WO_3%), tungsten minerals,

E-mail address: Jason.yang@gtk.fi.

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Table 1
Major types of tungsten ore deposits.

Deposit type	Typical grade, WO_3%	Tungsten mineral	Accompanying metals	Mine
Skarn (deposit size < 10^4–5×10^7 t)	0.3–1.4	Scheelite	Cu, Mo, Zn and Bi	Cantung (Canada); Los Santos (Spain); Vostok-2 (Russia)
Vein/stockwork deposit size < 10^5–10^8 t)	variable	Wolframite	Sn, Cu, Mo, Bi and Au	Pasto Bueno (Peru); Panasqueira (Portugal); San Fix (Spain); Chollja (Bolivia) Drakelands mine (UK)
Porphyry (deposit size < 10^7–10^8 t)	0.1–0.4	Wolframite or/and scheelite	Mo, Bi and Sn	Xingluokeng (China); Yangchuling (China); Northern Dancer (Canada); Climax (USA)
Disseminated (deposit size < 10^7–10^8 t)	0.1–0.5	Wolframite and scheelite	Sn, Bi, Mo	Shizhuyuan (China)
Stratabound (deposit size < 10^6–10^7 t)	0.2–1.0	Scheelite		Mittersill (Austria); Damingshan (China); Mount Mulgine (Australia)

accompaning minerals and mines of these deposits are shown in Table 1. Other deposit types include pegmatite, placer, brine/evaporate and hot springs.

As the largest producer of tungsten, China has more than ten major tungsten mines with an annual output over 1300 tonnes of WO_3. Most of these mines are located in Jiangxi and Hunan, in the south of China. The Xianglushan deposit located in Jiangxi is the largest tungsten mine in China with an annual output of over 5700 tonnes of WO_3. The Shizhuyuan in Hunan is a large polymetallic tungsten mine with an annual output of 5500 tonnes of WO_3. It is a W-Sn-Mo-Bi polymetallic deposit and characterized by low grade and complicated composition (Han et al., 2017). The ore contains scheelite, wolframite, molybdenite, cassiterite, bismuthinite, and fluorite. The Nui Phao mine in Vietnam is the largest tungsten mine outside of China and an unique polymetallic mine with significant amounts of tungsten, fluorspar, bismuth and copper. The mining reserves are 66 million tonnes of ore with an average grade 0.21% WO_3 (Masan Resources, 2012). The Vostok-2 is Russia's largest skarn deposit containing high grade sulfide–scheelite ore with substantial base metal and gold mineralization. It has been mined since 1969, firstly from an open pit, and subsequently by means of underground mining operations (Soloviev and Krivoshchekov, 2011). The Cantung mine located in western Northwest Territories of Canada is a skarn type of deposit with the reserves of 1.8 million tonnes at the grade 0.81% WO_3. It is continuously operating underground, with seasonal mining from an open pit.

The Mittersill mine in Austria hosts the largest tungsten deposit in Europe producing scheelite concentrates. The deposit consists of two parts, the Ostfeld open pit mine and the Westfeld underground mine (Thalhammer et al., 2008; Holzer and Stumpfl, 1980). The Los Santos mine is an open pit scheelite skarn deposit located in western Spain with reserves of 3.58 million tonnes at an average grade 0.23% WO_3. It was originally opened in 2008 according to a report by Almonty Industries (Wheeler, 2015). The Barruecopardo tungsten project in Spain is planned to be an open pit operation and one of the biggest tungsten projects in Europe. Tungsten mineralisation is found in quartz veins mostly less than 10 cm in thickness, in the form of coarse grained scheelite with minor traces of wolframite (http://www.miningtechnology.com/projects/barruecopardo-tungsten-project-castilla-y-leon/). The Panasqueira mine is Portugal's largest tungsten-producing mine with reserves of 4.91 million tonnes of ore at 0.22% WO_3 and is mined using underground methods. Drakelands mine, formerly known as Hemerdon mine, is a tungsten and tin mine. It is situated in Devon England and was opened in 2015. The deposit hosts 35.7 million tonnes of ore at 0.18% WO_3 in wolframite and 0.03% Sn mined by open pit methods. The mineralization includes an oxide-silicate stage consisting of wolframite, cassiterite, arsenopyrite, topaz, muscovite and tourmaline.

In this paper, the industrial beneficiation and technical challenges for tungsten (scheelite and wolframite) ores are presented and discussed, and various investigations and studies undertaken in recent years on the beneficiation of complex tungsten ores are reviewed.

2. Beneficiation of tungsten ores and technical challenges

The beneficiation process of scheelite and wolframite ores generally consists of pre-concentration after crushing and grinding, followed by roughing, cleaning and final purification stages to produce a concentrate with 65–75% WO_3, to meet the requirements of international trading (Krishna, 1996; Lassner and Schubert, 1998). Only scheelite is readily amenable to flotation. Wolframite, in contrast to scheelite, is paramagnetic. Thus beneficiation techniques of gravity concentration and flotation are applied to scheelite ore, and gravity and/or magnetic separation applied to wolframite ore.

Due to the brittle character of both scheelite and wolframite, comminution is carefully designed to avoid overgrinding, that is, to minimise formation of fines; at every stage of comminution, appropriate sizing techniques (screening, hydro-classifications by using hydrocyclones or classifiers) are used, and rod milling is more commonly used than ball milling. Rod milling of scheelite has another benefit compared to ball milling according a study by Li and Gao (2017), which concluded that the rodmilled scheelite particles are deemed to be more hydrophobic and have a higher flotation recovery due to stronger interaction with the collector and easier attachment to air bubbles. In recent years, quantitative mineralogical analyses techniques such as mineral liberation analysis (MLA) have been used to compare the liberation performance during comminution of different tungsten ores (Hamid et al., 2017).

X-ray sorting and gravitational methods are normally used for pre-concentration. Optical sorting and/or hand-picking methods are also used for pre-concentration of wolframite ore. The high density of both scheelite and wolframite facilitates their separation from the gangue minerals by gravity techniques. Jigs, spirals, shaking tables and centrifugal concentrators (the Knelson, Kelsey and Falcon concentrators) are usually used in operations where there is a wide range of particle size.

Normally, two concentration flowsheets are used for scheelite ore flotation: (1) whole ore flotation after pre-concentration and; (2) gravity-flotation flowsheet. Gravity concentration is to remove the low-density fraction (e.g. calcite, fluorite etc.) before flotation of scheelite. Scheelite flotation is performed in an alkaline medium, with sodium carbonate or sodium hydroxide to adjust the pH to about 9–10.5. The most important collectors are fatty acids such as oleic acid, linoleic acid and palmitic acid (Bernhart, 2015), and sodium oleate, tall oil or oxidized paraffin soap (Han et al., 2017). In the case of the Petrov process, which is normally applied for further separation of scheelite from other calcium minerals, flotation with fatty acids is undertaken at elevated temperatures which increase the selectivity between scheelite and other Ca-bearing minerals. In China, higher temperatures are used in the cleaner flotation, together with using depressants (e.g. sodium silicate) for effective depression of Ca-bearing minerals other than scheelite. Besides sodium silicate, phosphates and organic compounds such as starch, quebracho and tannic acid have also been used as modifiers in scheelite flotation (Li and Li, 1983). The beneficiation flowsheet of