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ScientEvents

ProScience 4 (2017) 31-35

Conference Proceedings

2nd International Conference on Applied Mineralogy & Advanced Materials - AMAM2017

Pyrometallurgical recovery of tin from tailings of Penouta Sn-Ta-Nb deposit

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Abstract

A concentrate obtained of a mining waste containing mainly cassiterite from the Penouta mine (provided by Strategic Minerals S.L) was reduced for the production of Sn. The fluxes used in pyrometallurgical reduction reactions were $CaCO_3$, Na_2CO_3, K_2CO_3 and borax; the reducing agent was graphite. The greatest recovery of Sn (>95%) was obtained when using $CaCO_3$ as a flux, with a Sn purity of 96%. A slag is also produced during the recovery. of the Sn, equivalent to 25% of the mass of the initial concentrate. Its content in Nb2O5 and Ta2O5 reached 45%, adding further value to the mine tailings.

Keywords: Cassiterite; Columbotantalite; Carbothermic reduction; Tin

1. Introduction

The Penouta Sn-Ta-Nb deposit is located in the Central Iberian Zone (CIZ) towards the innermost part of the Iberian Variscan Belt in Galicia, northwestern Spain. Here, the Viana do Bolo Series (which consists mainly of highly metamorphic rocks) and the Ollo de Sapo Formation (best represented in this zone by an augen gneiss) crop out. The deposit is largely a sheet-like albitized and greisenized granitic cupola, elongated in the SW-NE direction, with a maximum length of about 1100 m, a maximum E-W width of 700 m, and a maximum depth of over 200 m (Llorens et al., 2017; López et al., 2017). It is mainly composed of quartz, albite, muscovite and K-feldspar, with garnet and beryl as common accessory minerals. Banded pegmo-aplite dikes commonly occur in the apical zone of the

ISSN: 2283-5954© 2017 The Authors. Published by Digilabs
Selection and peer-review under responsibility of AMAM-ICAM 2017 Scientific Committee
DOI:10.14644/amamicam.2017.006

granite. The cupola system culminates with the development of a stockwork of quartz veins up to 2 m thick which caused the strong greisenization of the hosting augen gneiss and the granitic cupola. The deposit was extensively mined during the 1970s to obtain cassiterite from the granitic cupola and the related hydrothermal quartz veins. Tantalum was obtained as by-product. The open pit methods employed targeted the kaolinized leucogranite and those portions of the country rock that had become muscovitized and soft enough to be extracted using free dig methods. These materials were not milled, and only fragments up to 2 mm in size were treated in the gravity plant. Thus, large amounts of cassiterite and columbite group minerals were never liberated from the host rock. Unused host rock was progressively dumped in tailing ponds.

Strategic Minerals Spain S.L. is now constructing a specialised gravity plant designed to process these wastes. Pyrometallurgical reduction smelting (Peng & Mackey, 2013) is a very effective way of obtaining Sn from gangue minerals, and some authors have examined the reduction of cassiterite by carbonaceous reductants (Pommier & Escalera, 1979). SnO_2 is mainly reduced by the gaseous intermediates of CO and H_2, and the overall reduction rate of SnO_2 controlled by the gasification of carbon ($C + CO_2 \rightarrow CO$, Boudouard reaction). Some admixtures, e.g., K_2CO_3, SiO_2, Al_2O_3, CaO or metallic Sn, can accelerate the reduction of cassiterite by graphite. All of these admixtures reduce the activation energy required for the reduction reaction to occur - they have catalytic effects on the Boudouard reaction (Komkov et al., 2009). The present work examines the carbothermic reduction of these mining residues for the production of Sn.

2. Experimental

A concentrate obtained by the milling, gravimetric concentration and magnetic separation of a mining waste containing mainly cassiterite from the Penouta mine (provided by Strategic Minerals S.L) was used as the experimental material. The concentrate was analyzed by X-ray fluorescence spectroscopy (XRF) using a Bruker S8 Tiger, and atomic absorption (AA) using a SpectrAA 220 FS AA spectrometer. The phase compositions were characterized by X-ray diffraction analysis (XRD) using a Siemens D5000 apparatus (Fig. 1) and quantified by the Rietveld method. The concentrate was also subjected to morphological examination by scanning electron microscopy (SEM) using a JEOL JSM 6500 microscope equipped with an Oxford EDX energy-dispersive X-ray (EDX) analyzer for semi-quantitative chemical analyses (FE-SEM-EDX).

Sn was obtained from the concentrate (held in graphite crucibles) via pyrometallurgical reduction in an AFI-02 induction furnace containing an argon atmosphere. Different combinations of coke (Desulco® 9012S) plus the above fluxes were tested (Table 1) as a means of reducing the melting point and to increase the Nb and Ta content of the slag produced. The furnace temperature was raised to 1200 ºC. The Sn samples obtained were subjected to optical emission spectrometry (OES) using a Varian ICP-OES 725-ES instrument. The samples were attacked with lithium metaborate at 1050 ºC and acidified with HNO_3 before taking readings. The slag in the processing of the concentrate was characterized by electron microprobe microscopy (EMP) using a JEOL JEM 2100 microprobe apparatus.

Table 1. Blends used in carbothermic reduction

% (weight)	**Blend A**	**Blend B**	**Blend C**
Concentrate	85.5	80.0	74.6
$CaCO_3$	8.6	-	7.5
Borax	-	5.5	-
Na_2CO_3	-	6.5	7.5
K_2CO_3	-	-	5.2
Coke	6.0	8.0	5.2

2. Results and discussion

2.1. Chemical and mineralogical characterization of the concentrate

The concentrate to be mainly composed of SnO_2 (67.20 wt.%), Ta_2O_5 (8.45 wt.%), Fe_2O_3 (6.99 wt.%) and Nb_2O_5 (5.40 wt.%). The majority phase was cassiterite (64.4%), followed by columbotantalite (21.5%) and different phases containing Nb and Ta, such as ixiolite [(Sn,Fe)(Sn,Ta,Nb)$_2$O$_6$] and finally quartz (Fig. 1).

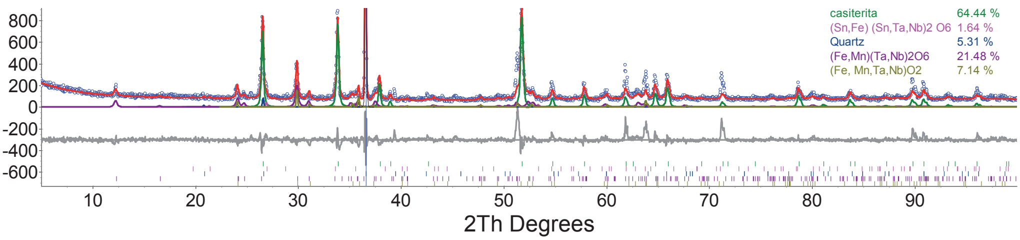

Fig. 1. Rietveld analysis of the concentrate

2.2. Obtaining Sn from the concentrate

The greatest recovery of Sn (>95%) was obtained when using $CaCO_3$ as a flux (blend A; Table 2). OES analysis returned a percentage purity of 96% (blend A, Table 3), similar to that obtained with ores and other industrial wastes. However, the recovered metallic Sn had a Fe content of >3%; any Sn recovered by this method therefore requires purification.

Table 2. Tin recoveries in the pyrometallurgical process depending on the type of mixture used in the process

Blend	**Sn Recovery (%)**
Blend A	95.2±3.8
Blend B	87.6±0.6
Blend C	54.0±0.3

Table 3. Chemical composition of Sn obtained by carbothermic reduction

Element	OES (wp,%)
Sn	96.06
Fe	3.46
Mn	0.19
Nb	998 ppm
Cr	899 ppm
Ti	385 ppm
Cu	276 ppm

2.3. Characterisation of the slag

A slag ($Ca_2(Nb,Ta)_2O_7$: 86.7%; $Ca(Nb,Ta)O_3$: 6.6%; $(Fe,Mn)(Ta,Nb)_2O_6$: 4.2% and SiO_2: 2.4%) is also produced during the pyrometallurgical recovery of the Sn, equivalent to 25% of the mass of the initial concentrate. Fig. 2 shows the SEM image of the slag.

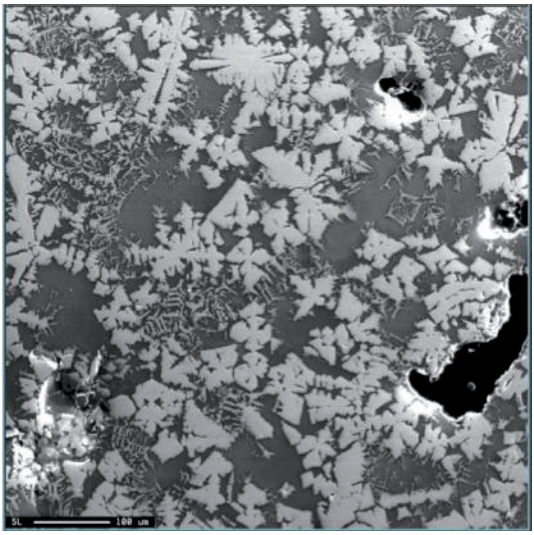

Fig. 2. Microprobe image of the slag

Table 4 shows the chemical composition of the slag. Its content in Nb_2O_5 (21.4 wt.%) and Ta_2O_5 (25.5 wt.%), adding further value to the mine tailings.

Table 4. Chemical characterization of the slag

Oxide	XRF (wt.%)
Ta_2O_5	25.48
Nb_2O_5	21.43
CaO	15.79
SiO_2	10.00
MnO	7.23
SnO_2	5.66
ZrO_2	3.68
Al_2O_3	3.23
Fe_2O_3	0.73
TiO_2	0.62
K_2O	0.51
Na_2O	0.30
MgO	0.14

3. Conclusions

The results show that the present mining waste is a good source of cassiterite from which Sn can be obtained. When this is recovered by pyrometallurgical reduction, the best flux to use is $CaCO_3$. The purity of the recovered Sn is some 96%. The slag produced contains Nb and Ta, adding further value to the mine tailings. Further work is underway examining how these latter elements may best be recovered from this slag.

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