Trace Metals in Tin Extraction Plant Wastes

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SHORT COMMUNICATION

TRACE METALS IN TIN EXTRACTION PLANT WASTES

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In mud waste and slag waste produced during the extraction of tin by different processes 25 trace metals have been determined by atomic absorption and optical emission spectroscopy. The usefulness of tin wastes for the recovery of Nb and Ta is indicated.

KEY WORDS: Tin extraction, trace metals, niobium, tantalum.

INTRODUCTION

The tonnage of tin produced in the world seldom exceeds 0.2 million tonnes a year; Malaysia produces 45,500 tonnes of tin annually. Cassiterite, the principal tin ore, was first found in India in the Bastar District of Madhya Pradesh State in 1973, and it laid the foundation of a large tin industry in the country[1].

In tin extraction, two processes are used, the chemical treatment process, and the arc furnace process. In the chemical treatment process, the powdered cassiterite and sodium hydroxide flakes are mixed together in 1:1 ratio by weight and then pyrolysed in a furnace at 825°C for 3 h. The pyroprocessed mixture is then leached with water in a container. The water-soluble fraction containing tin is separated and neutralised to pH 6.5–7.0 using hydrochloric acid. Gelatinous tin oxide settles at the bottom of the container in about 3 h. The water insoluble-fraction which is about 4.5% of the total ore processed, is discarded as mud waste. In the arc furnace process, cassiterite is powdered and then mixed with fine coke and fed to an arc furnace from which the tin is obtained. About 20% of the total ore processed is transformed into the slag which mainly contains the impurities originally present in the tin ore.

Tin ore is known to contain tantalum and niobium metals as associated elements. Bales and co-workers[2] have determined the levels of Ta, Nb and several other metallic elements in the slags by X-ray fluorescence. Faye and Inman[3] have reported the

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isolation and separation of oxides of Ta and Nb from mineral concentrates by liquid-liquid extraction. Zeng and Zhausen[4] have reported the spectrophotometric determination of Ta with 4,5-dibromo-*o*-nitrophenylfluorescein. Jiayou and Yu[5] have applied fluorescence spectrophotometry for the determination of micro amounts of Nb with morin in the presence of cetylpyridinium chloride. Kreingol and Yutal[6] have determined Ta in Nb_2O_5 by extraction with methylisobutyl ketone and subsequently a reaction with malachite green.

In the work reported here, Ta and Nb, as well as W, La, Ga, V, Y and Yb have been determined in tin slags by optical emission spectroscopy. A number of other trace metals (Cu, Ni, Co, Pb, Zn, Mn, Sb, Bi, Cr, Ba, Li, Ag, Mo, As and Rb) have been determined by atomic absorption spectrophotometry. A comparison of the concentrations of the metallic elements in the mud waste and slag waste discharged by a tin extraction plant located at Raipur (India) has been made.

MATERIALS AND METHODS

Sample collection. Three samples (500 g each) of the mud and slag waste were collected from different storage points of the waste materials. The samples of each category were then composited. The composite samples were dried in an oven at 110°C and then powdered to 100 mesh size.

Procedure. Weighed aliquots (1 g each) of samples were treated in a PTFE digestion bomb using 10 ml of an acid mixture of hydrochloric acid, hydrofluoric acid and nitric acid. The bomb was put in an oven at 180°C for 30 min[7]. Thereafter, the solutions were made up to 100 ml in 0.1 M EDTA to suppress interference by phosphate, carbonate, iodide, fluoride or acetate. The determination of Cu, Co, Ni, Pb, Zn, Cr, Mn, Li, Sb, Ba, Ag, Be, As, Mo, and Rb was done using an atomic absorption spectrophotometer (Varian Tachtron Model AA575) following the recommended conditions of operation of the instrument[8]. During calibration, the standard solutions of the metals were diluted to match the concentrations of the sample solutions within the measurement sensitivity[9].

The determination of Sn, Nb, Ta, W, La, Ga, V, Y and Yb was performed on an optical emission spectograph (Hilger Watts). The common matrix (pegmatite base) consisting of sixty parts of quartz, forty parts of microcline and one part of ferric oxide was synthetically prepared. This was then reduced to 50 mesh size using an agate mortar and washed with conc.HCl (1:1). The cleaned material was checked for elements other than K, Na, Al and Si which were found to be absent. Known quantities of the elements that were to be determined were added to the matrix, and mixed thoroughly in the agate mortar. These were diluted using the synthetic matrix to match the concentrations of the samples within the measurement sensitivity during the calibration of the instrument. The diluted samples were thoroughly mixed with spec-pure graphite powder in a 1:1 ratio, and 30 mg of the sample were placed in the hole of the cupped graphite electrode and then arced for 3 min. A Kodak-1N was used for photographing; the spectral lines were measured using a projection

Table 1 Metallic constituents in tin extraction plant wastes

Element	Concentrations[a] (µg/g) in	
	Mud waste	Slag waste
Cu	46	8
Co	12	6
Ni	65	16
Pb	660	24
Zn	230	34
Cr	10	55
Li	20	5
Bi	50	ND[b]
Sb	ND	ND
Ba	550	210
Ag	ND	ND
Be	ND	ND
As	ND	ND
Mo	250	25
Rb	ND	ND
Ga	ND	10
V	ND	ND
La	210	102
Yb	ND	ND
Y	40	10
Mn	8.14%	1.64%
Sn	2.64%	4.08%
W	1.06%	0.52%
Nb	3.26%	1.24%
Ta	1.12%	0.70%

[a] Average of 3 replicate determinations.
[b] ND, not detectable.

microphotometer following the recommended conditions of operation of the instrument[10,11].

RESULTS AND DISCUSSION

The mean values obtained from three replicate determinations of each element in the mud and slag waste are shown in Table 1. The high alkalinity of the mud waste (pH 11.5 in 10% slurry in water) indicated a caustic and corrosive nature of the waste matter. The mud waste also showed a fair solubility in water (2.33 g/100 ml at 32°C). The results show that all elements determined here have higher concentrations in the mud waste than in the slag waste, suggesting that the chemical treatment process has a higher extractability of the trace metals than the arc furnace process. In the mud waste the concentrations of the elements decrease in the order:

Mn > Nb > Sn > Ta > W > Pb > Ba > Mo > Zn

> La > Bi > Cu > Y > Li > Co > Cr.

In slag waste, the order is as follows:

Sn > Mn > Nb > Ta > W > Ba > La > Cr > Zn

> Mo > Pb > Ni > Y = Ga > Cu > Co > Li.

On the basis of the results in Table 1, recovering Nb and Ta from mud waste appears more interesting than doing so from slag waste.

The findings point out the usefulness of tin wastes for the recovery of Nb and Ta, apart from the information with regard to the association of other metallic elements with the waste materials. The occurrence of Nb and Ta in tin ores of Indian origin has also been reported by other workers, who, by electron probe method, found Ta and Nb in the ranges of 1.80–7.57% and 0.17–2.45%, respectively, in tin concentrates originating from a neighbouring area (Koraput, Orissa, India)[12].

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