

# Recovery of niobium and tantalum from low grade tin slag – A hydrometallurgical approach

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## ABSTRACT

*Niobium and tantalum are known to co-occur with cassiterite deposits. During the process of extraction of tin by cassiterite smelting, these metals join the slag phase and the slag is processed for the recovery of niobium and tantalum. The processed slag rich in niobium and tantalum is digested with hydrofluoric acid, and subjected to solvent extraction for the removal of additional impurities as well as for the separation of niobium and tantalum. This paper reports on the upgradation of tin slag typically containing 3.4%  $Nb_2O_5$  and 3.0%  $Ta_2O_5$  by a combination of chemical treatments. In the process, unwanted associations in the slag viz. alumina, silica, calcia, iron oxide etc., are selectively solubilized by a sequential treatment with alkali and acid leaching leaving a residue containing 10.6%  $Nb_2O_5$  and 10.4%  $Ta_2O_5$  with a recovery of 86.5 and 95.5% respectively. The product represents an enrichment of about 3.24 times and was found to be suitable for the extraction of niobium and tantalum by  $HF-H_2SO_4$  dissolution.*

**Keywords** : Niobium/Tantalum recovery, Leaching, Solvent extraction, Cassiterite

## INTRODUCTION

Tin smelting slags are generally upgraded<sup>(1)</sup> by a pyrometallurgical process, involving the production of ferro-alloy called block metal which acts as a collector for niobium and tantalum. The block metal is further upgraded by a simple acid leaching or by a combination of oxidative smelting followed by acid leaching of the slag derived from the second smelting. The upgraded slag is used for the extraction of niobium and tantalum by hydrofluoric acid. A number of hydrometallurgical processing schemes<sup>[2-6]</sup> have been developed for treatment of tin slags. From the limited information available in the literature, it appears that hydrometallurgical processing of low grade (<10% Niobium + tantalum oxide)

tin slags is not practised in the industry. The selective extraction of niobium and tantalum from the slag is somewhat complicated and depends to a large extent on the structure and composition of the slag. Gaballah <sup>[7]</sup> and co-workers have recently reported on characterization of tin slags by electron probe microanalysis and have tried to explain the leaching behaviour of various slags. These studies have shown that an Indonesian slag containing silicon, iron and aluminium as neighbours in a calcium pseudo-structure, on acid leaching, leads to the dissolution of calcium, aluminium and iron there by resulting in the collapse of the configuration and liberates fine silicon dioxide particles as a colloidal solution. Where as a slag from Zaire with niobium and tantalum as neighbours surrounding calcium will lead to loss of niobium and tantalum with the dissolution of calcium. This paper presents the results of experimental studies carried out on laboratory scale to develop a hydrometallurgical route for processing a low grade tin slag.

## EXPERIMENTAL

### Raw Material

The tin slag used in the present studies was of Malaysian origin. Chemical analysis of a typical sample is shown in Table 1 and the sieve analysis of the ground slag is shown in Table 2. Sodium hydroxide, hydrochloric acid and other chemicals used in these studies were of analytical reagent grade.

*Table 1 : Chemical analysis of tin slag (as oxides in wt. %)*

|                                |   |       |
|--------------------------------|---|-------|
| SnO <sub>2</sub>               | : | 1.33  |
| Nb <sub>2</sub> O <sub>5</sub> | : | 3.43  |
| Ta <sub>2</sub> O <sub>5</sub> | : | 3.05  |
| SiO <sub>2</sub>               | : | 23.07 |
| Al <sub>2</sub> O <sub>3</sub> | : | 10.42 |
| Fe <sub>2</sub> O <sub>3</sub> | : | 22.77 |
| CaO                            | : | 13.12 |
| TiO <sub>2</sub>               | : | 7.97  |

### Procedure

Contents of the tin slag can be grouped into three categories viz. refractory metals (Nb, Ta, Ti), acid solubles (Fe, Ca, Mn, Al) and acid insoluble oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>). The flowsheet developed essentially consists of a combination of alkali and acid processing steps to separate the impurities and obtain a product

Table 2 : Size analysis of tin slag

| Mesh No.    |   | % by weight |
|-------------|---|-------------|
| + 100       | : | Nil         |
| - 100 + 150 | : | 4.6         |
| - 150 + 230 | : | 30.7        |
| - 230 + 270 | : | 22.7        |
| - 270 + 325 | : | 38.3        |
| - 325       | : | 3.7         |

enriched with Nb-Ta values which could serve as a suitable starting material for the extraction of niobium and tantalum by hydrofluoric acid. Three different alkali processing techniques namely (1) Caustic soda solution leaching (2) Caustic pugging and (3) Caustic soda fusion were investigated for separation of silicon and aluminium species.

#### *Caustic Solution Leaching*

Weighed quantity of slag sample was leached in NaOH solution of known strength using a beaker, stirrer assembly installed in a hot water bath. The leaching experiments were carried out for 4 hrs at the given temperature with a initial solid : liquid ration of 1:10.

#### *Alkali Pugging*

The slag sample was mixed with a known quantity of NaOH pellets and a limited amount of water just sufficient to form a thick paste. This paste was taken in a mild steel vessel and heat soaked in the temperature range of 150° to 300°C for required duration. The baked mass was leached in hot water (60°C) for 60 minutes.

#### *Alkali Fusion*

The sample was reacted with sodium hydroxide by fusion at 650°C for 4 hrs. The fused mass after cooling was water leached to solubilise sodium slats. In all the three methods the leach liquor was filtered and the filtrate analysed for Al and Si contents. Nb and Ta contents of the leach liquor also were tested in a few selected experiments.

#### *Acid Leaching*

Weighed quantity of the slag sample was leached in hydrochloric acid of known strength (4.33, 6.5 and 13.0 N) at temperatures of 30°, 50°, 70° and 80°C

for duration varying between 15 to 120 minutes. The clarified leach liquor was analysed for Ca, Fe, Al, Ti, Nb and Ta values. These experiments were conducted to optimise the parameters for alkali processing as well as acid leaching on a batch size of ~10 gms of slag. Further runs were carried out starting with 100 gms of slag so as to collect sufficient materials for the second step and for generating some quantity material of upgraded product.

The residue (enriched product) obtained after removal of impurities by the combination of acid – alkali processing (AC – AL) (AL – AC) was washed free of chemicals, dried and weighed. This enriched slag was digested in 20 N HF at 60°C for 60–90 minutes with a small addition of sulphuric acid to attain a near complete dissolution. The fluoride solution was analysed for its Nb and Ta contents and the recovery of niobium and tantalum from the slag was then computed. Analysis of all the liquid samples were carried out using atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

### Caustic leaching

It was observed that caustic leaching was not very effective in solubilizing silicon and aluminium values of the slag. A maximum dissolution of 8.2% aluminium and 18.4% silicon was obtained by leaching in 5N sodium hydroxide solution at 80°C for 4 hrs (Table 3). Considering the low solubility and the operation problems in handling hot strong caustic solution, further experiments at higher temperatures or longer durations were not considered.

### Alkali Pugging

Results of alkali pugging experiment indicated that the solubility of aluminium increases with the increase of alkali in the charge as well as the temperature of soaking. In the case of silicon a maximum dissolution of 36% was attained and any further increase in alkali or temperature did not further increase the solubility of silicon. About 19.3% of Al and 35.2% of Si were solubilized by pugging treatment of the slag with twice the quantity of sodium hydroxide at 250°C for 4 hrs. (Table 3).

### Caustic Fusion

Caustic fusion experiments also showed a trend similar to the pugging experiments. Solubility of silicon remained close to 36% whereas that of aluminium increased with the alkali content of the charge. Experimental conditions and analysis of leach liquor of two fusion experiments are presented in Table 3. The

Table 3 : Alkali processing of tin slag

|                   |  |    |         |        |      |
|-------------------|--|----|---------|--------|------|
| Solution Leaching | Strength, N                              | -  | 5       |        |      |
|                   | Temperature, °C                          | -  | 80      |        |      |
|                   | Duration, Hrs.                           | -  | 4       |        |      |
|                   | Leach liquor analysis<br>(% Solubilized) | -  |         |        |      |
|                   |  | Al | -       | 8.2    |      |
|                   | Si                                       | -  | 18.4    |        |      |
| Pugging Leaching  | Slag : NaOH                              | -  | 1:2     |        |      |
|                   | Temperature, °C                          | -  | 250     |        |      |
|                   | Duration, Hrs.                           | -  | 4       |        |      |
|                   | Leach liquor analysis<br>(% Solubilized) | -  |         |        |      |
|                   |  | Al | -       | 19.3   |      |
|                   | Si                                       | -  | 35.2    |        |      |
| Fusion            | Slag : NaOH                              | -  | I 1:0.5 | II 1:1 |      |
|                   | Temperature, °C                          | -  | 650     | 650    |      |
|                   | Duration, Hrs.                           | -  | 4       | 4      |      |
|                   | Leach liquor analysis<br>(% dissolved)   | -  |         |        |      |
|                   |  | Al |         | 21.7   | 43.3 |
|                   |  | Si |         | 35.0   | 37.0 |

results of alkali processing experiments showed that a maximum of 36% Si can be solubilized from the slag and this is achieved either by pugging at 250°C followed by water leaching or by caustic fusion.

### Acid Leaching

Experiments on hydrochloric acid leaching of the slag has shown the solubility of the concerned elements in the decreasing order can be written as Al, Fe, Ca, Ti, Nb and Ta in the present studies. It was observed that when 40% or more calcium was dissolved, the solution appeared turbid indicating the presence of colloidal silica. Niobium values in the solution were generally low at <0.4%. When nearly complete dissolution of Al, Fe, Ca and Ti was accomplished, niobium losses in the leach liquor increased to a value of 20% or more. Even under such severe leaching conditions tantalum in solution reported a value of less than 4%. Analysis of the liquor obtained after leaching the sludge in 4.33 N HCl at 50°C for 30 min is presented in Table 4.

Table 4 : Acid leaching of tin slag

|  |    |        |
|--|----|--------|
| Strength of HCl, N                       | –  | 4.33   |
| Temperature, °C                          | –  | 50     |
| Duration, min                            | –  | 30     |
| Leach liquor analysis<br>(% Solubilized) |    |        |
|  | Ca | – 28   |
|  | Fe | – 28   |
|  | Al | – 40   |
|  | Ti | – 13   |
|  | Nb | – 1.44 |
|  | Ta | – <1.1 |

**Sequential Acid – Alkali Processing (AC-AL)**

The residue obtained after acid leaching of the slag (Table 4) was used for further alkali processing experiments. Alkali pugging yielded an enriched product containing 6.6% Nb<sub>2</sub>O<sub>5</sub> and 7.7% Ta<sub>2</sub>O<sub>5</sub>. The leach liquor in this experiment was reported to contain 68% Si, 7.2% Al and 15% Nb based on original slag analysis. Caustic solution leaching of the acid processed slag in 5N NaOH at 70°C for 6 hrs dissolved 57.5% Si and 1.5% Al and yielded an enriched product analysis 7.7% Nb<sub>2</sub>O<sub>5</sub> and 7.9% Ta<sub>2</sub>O<sub>5</sub> with a recovery value of 82.2% for Nb and 95% Ta. Losses of Nb and Ta in the leach liquor were very low at 1.38 and 1.84% respectively (Table 5).

Table 5 : Alkali processing of acid leached sludge (AC – AL process)

|                  |   |            |            |
|------------------|---|------------|------------|
| Caustic Leaching | Solution strength, N                        | –          | 5          |
|                  | Temperature, °C                             | –          | 70         |
|                  | Duration, Hrs.                              | –          | 6          |
|                  | Leach liquor analysis in<br>(% Solubilized) |            |            |
|                  |   | Si         | – 57.5     |
|                  |   | Al         | – 1.5      |
|                  | Nb  | – 1.38     |            |
|                  | Ta  | – 1.84     |            |
| Residue          |   |            |            |
|                  |   | Analysis % | Recovery % |
|                  | Nb <sub>2</sub> O <sub>5</sub>              | 7.7        | 82.2       |
|                  | Ta <sub>2</sub> O <sub>5</sub>              | 7.9        | 95.0       |

### Sequential Alkali – Acid Processing (AL–AC)

The dissolution of acid soluble species and also of titanium and niobium of the slag was found to be enhanced after alkali processing, compared with the fresh slag. In other words, less severe acid leaching conditions were sufficient to leach out the impurities after alkali processing. Optimum experimental parameters for combined alkali–acid processing of tin slag sample, analysis of leach liquor and the product are presented in Table 6. The acid leaching conditions were set at 3.25 N HCl, 50°C and 15 minutes of duration. The leach liquor was analysed to contain 48, 45, 43, 76, 4 and 2.23% of Al, Ca, Fe, Ti, Nb and Ta. The residue obtained after combined processing was analysed to contain 10.6% Nb<sub>2</sub>O<sub>5</sub> and 10.4% of Ta<sub>2</sub>O<sub>5</sub> with a recovery of 86.5% and 95.5% of niobium and tantalum. When the acid leaching was continued for 30 minutes the loss of niobium in the leach liquor was high and the product contained only 5.6% Nb<sub>2</sub>O<sub>5</sub>.

In the present slag, solubility of aluminium is found to be more in acid than in alkali. For the purpose of computation of impurities Al can therefore be taken to be soluble in acid impurity in the present case. The number and the measure

Table 6 : Optimum conditions for processing of tin slag

|                      |                                |              |         |              |    |   |      |
|----------------------|--------------------------------|--------------|---------|--------------|----|---|------|
| A) Alkali Processing |                                |              |         |              |    |   |      |
|                      | Type                           | –            | Pugging |              |    |   |      |
|                      | Slag : NaOH                    | –            | 1:2     |              |    |   |      |
|                      | Temperature, °C                | –            | 250     |              |    |   |      |
|                      | Duration, Hrs.                 | –            | 4       |              |    |   |      |
| B) Acid Leaching     |                                |              |         |              |    |   |      |
|                      | Strength of HCl, N             | –            | 3.25    |              |    |   |      |
|                      | Temperature, °C                | –            | 50      |              |    |   |      |
|                      | Duration, min                  | –            | 15      |              |    |   |      |
|                      | Leach liquor analysis          | –            |         |              |    |   |      |
|                      | (% Solubilized)                | Al           | –       | 48           | Ti | – | 76   |
|                      |                                | Ca           | –       | 45           | Nb | – | 4    |
|                      |                                | Fe           | –       | 43           | Ta | – | 2.23 |
| C) Residue           |                                |              |         |              |    |   |      |
|                      |                                | Analysis (%) |         | Recovery (%) |    |   |      |
|                      | Nb <sub>2</sub> O <sub>5</sub> | 10.6         |         | 86.5         |    |   |      |
|                      | Ta <sub>2</sub> O <sub>5</sub> | 10.4         |         | 95.9         |    |   |      |
|                      | TiO <sub>2</sub>               | 7.0          |         | –            |    |   |      |

of acid soluble impurities in the slag are more than that attacked by the alkali and a processing scheme which enhances the dissolution of acid solubles would be preferable.

In the present study it is seen that alkali processing releases 35% Si and 20% Al into solution. Though Nb and Ta are also expected to form their respective salts of sodium during alkali processing, their solubilities are negligible in alkaline solutions. Thus alkali processing breaks down the structure of the slag and also increases the porosity of the slag which could be the reasons for the enhanced dissolution during the subsequent leaching with acid.

## CONCLUSION

A hydrometallurgical processing scheme has been developed to extract niobium and tantalum values from low grade tin slag. A slag containing 6.5% of Nb + Ta oxides was first given an alkali treatment by solid state reaction with sodium hydroxide at 250°C to open up the structure and remove some of the impurities such as silica and aluminium. The treated slag is leached with hydrochloric acid to obtain a product containing 21% of Nb + Ta oxides which was found to dissolve in hydrofluoric acid and suitable for further extraction of Nb and Ta.

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