

## Salting Out Effect of Electrolyte Solutions in The Extraction of Tantalum and Niobium Using Aqueous Biphasic System

\*N.S. Maina and E. Solomon

Department of Chemical Engineering, Ahmadu Bello University, Zaria.  
 [\*Corresponding author: [nsmaina@abu.edu.ng](mailto:nsmaina@abu.edu.ng) or [nsmaina@yahoo.com](mailto:nsmaina@yahoo.com)]

**ABSTRACT:** The salting-out effect of various solutions of electrolyte in the extraction of tantalum and niobium using aqueous biphasic system (ABS) was investigated. This was achieved by leaching ball-milled Tantalite ore with mineral acids ( $H_2SO_4$  and HF) in the ratio of 3:1. The leached liquor was then divided into five parts and each part mixed with ABS formed (e.g. PEG-3350/20wt/wt  $Na_2CO_3$ ) for the extraction of tantalum and niobium and then with  $Na_2SO_4$ ,  $K_2CO_3$ ,  $K_2SO_4$ , KBr, and KI salts in turn. The amount of tantalum pent oxide extracted was determined using X-ray fluorescence method. The results show that the percentage tantalum extracted was in the range of 28.17% to 54.93% i.e. increased in the order  $KI < KBr < K_2CO_3 < Na_2SO_4 < K_2SO_4$  with 28.17%, 30.28%, 34.51%, 43.31% and 54.93% respectively; while that of niobium pent oxide increased in the order  $KI < KBr < K_2CO_3 < Na_2SO_4 < K_2SO_4$  with 27.3%, 29.35%, 33.78%, 34.64% and 41.98% respectively. In conclusion electrolyte with high ionic charge and hydration radius salts-out  $Ta_2O_5$  better in the ABS/electrolyte system than those with low values.

**Keywords:** Tantalum, niobium, salting-out, extraction, aqueous biphasic

### INTRODUCTION

A good number of works have been reported on the hydrometallurgical extraction of elements from their ores using various extractants, such as in liquid-liquid extraction-to mention but one (Jide *et al.*, 2005, Maina and Chinda, 2006 and Baba *et al.*, 2007). Limited reports have, however, been published on the salting out effect of electrolytes in the extraction of Tantalum using aqueous biphasic system (ABS). Tantalite-columbite or tantalite-niobium ores are oxides of tantalum, niobium, iron and manganese, (Fe, Mn)  $(Ta, Nb)_2O_6$ . Tantalum is a rare hard blue-grey, lustrous transition metal, highly corrosion resistant which occurs naturally in the mineral tantalite, always together with the chemically similar niobium (Baba *et al.*, 2005). It is part of the refractory metals group, which are widely used as minor component in alloys. The chemical inertness of tantalum makes it a valuable substance for laboratory equipment and a substitute for platinum, but its main use today is in tantalum capacitor (Ayanda and Adekola, 2011).

Tantalite- columbite ore is mined primarily from pegmatite and associated alluvial sediments (Jide *et al.*, 2005). Within the last decade, ore processors have made considerable progress in the processing of tantalum and niobium minerals using different methods such as pyrometallurgy, chlorination or hydrometallurgy (Jide *et al.*, 2005).

Aqueous biphasic systems (ABS) or aqueous two phase systems are clean alternatives for traditional organic-water solvent extraction systems. Beijerink in 1896 first noted an incompatibility in solutions of agar, a water-soluble polymer, with soluble starch in gelatin. Upon mixing, they were separated into two immiscible phases. Subsequent investigation led to the determination of many other aqueous biphasic systems, of which the polyethylene glycol (PEG)- dextran system is the most extensively studied. Other systems that form aqueous biphasic are: PEG-Sodium carbonate or PEG and phosphates, citrates or sulphates. Aqueous biphasic systems are used during downstream processing mainly in biotechnological and chemical industries (Rogers *et al.*, 1996).

ABS are formed when 2 materials, one polymer and one kosmotropic salt, or two salts (one chaotropic salt and the other Kosmotropic salt) are mixed together at appropriate concentration or at a particular temperature (Rogers *et al.*, 1996 and Sada, 2008). The two phases are mostly composed of water and non-volatile components thus eliminating volatile organic compounds. ABS retains all of the practical advantages of liquid-liquid extraction and also has a number of unique advantages due, in large part, to their aqueous nature. Polyethylene glycol-based aqueous biphasic systems (PEG-ABS) are virtually nontoxic and non-flammable (Rogers *et al.*, 1996).

Liquid/ solid extraction (also known as leaching) may be considered as the dissolving of one or more components in a solid matrix by simple solution, or by the formation of a soluble form by chemical reaction. Liquid/ liquid extraction separates the components of a homogeneous liquid mixture on the basis of differing solubility in another liquid phase, because it depends on the difference in chemical potentials. Liquid/ liquid extraction is more sensitive to chemical type than to molecular size (McGraw Hill, 1982). This makes it complementary to distillation as a separation technique. In the present study the salting out effect of various electrolytes in the extraction of Tantalum using aqueous biphasic system was investigated.

## MATERIALS AND METHODS

### Size Reduction of the Tantalite Ore

The tantalite ore procured from a market in Jos, Plateau State (but sourced from Nasarawa State) was crushed using a crusher (Retsch Type BB1 Masch Nr. 70992) and then ball milled for six (6) hours using medium ball mills (Suesterberg machine No. 6083). The ball milled ore was then sieved to particle size of  $74\mu\text{m}$  using 200 mesh sieve (BS 410, Endecott filter, PAT, No. 667924). The undersize particles were analysed for elemental composition using X-ray fluorescence (Mini Pal 4 PW4025, Philips Analytical) at the Nigerian Metallurgical Development Center (NMDC) Jos, Nigeria.

### The Leaching Process

Fifty grams (50g) of the ball milled Tantalite ore was mixed with 150g (81.7ml) of 98%  $\text{H}_2\text{SO}_4$  (10.8M) (El Hussain, 2004) and then 15M solution of HF (81.7ml) was added immediately (El Hussain, 2004) in a conical flask to improve on the leaching. The mixed solution in the conical flask was heated for three hours at  $80^\circ\text{C}$  (Jide *et al.*, 2005) on a hot plate while being stirred continuously using a magnetic stirrer. The mixture was then allowed to cool for a period of 5 minutes. The leached liquor was then decanted and the residue washed using de-ionized water. The washed residue was dried in an oven at  $80^\circ\text{C}$  (Maina and Chinda, 2006) and then analysed with an X-ray fluorescence spectrometer.

### Preparation of Aqueous Biphasic System

Polyethylene glycol (PEG-3350),  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , KBr, and KI were of reagent quality and used without further purification. The aqueous biphasic system was prepared by dissolving 40% (wt/wt) polyethylene glycol (MW 3350) in distilled water to make the required concentration. Thereafter, 20% (wt/wt) sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) at PEG/salt ratio of 1:1 (El Hussein, 2004) was also prepared. Equal aliquots were added and the mixture shaken for 30 seconds to facilitate mixing.

### Salting-Out Effect of the Extraction Process using the various electrolytes

The decanted leached liquor was divided into 5 samples and each of the respective samples was mixed with the ABS solution at leached liquor/ABS solution ratio of 1:1 (Rogers *et al.*, 1995). Each of the electrolyte solution of  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , KBr, KI and  $\text{K}_2\text{CO}_3$  was respectively added to the mixture (liquor/ABS solution) to enhance the salting-out process. Each was vigorously shaken for 30 seconds to facilitate mixing and formation of two-phases. The PEG-rich phase (upper phase) was then separated from the salt-rich phase (lower phase) in a separatory funnel after attaining equilibrium. The two phases were separately recovered and analysed for elemental composition using X-ray Fluorescence.

## RESULTS

Table 1 presents the elemental analysis for the milled tantalite ore and its residues after leaching. From the table,  $\text{Ta}_2\text{O}_5$  is the most predominant oxide in the ore (38.3%). The residues showed reduction in Ta and Nb. Table 2 presents the effect of electrolytes on the extraction of Ta and Nb. The amount of  $\text{Ta}_2\text{O}_5$  extracted was in the range of 28.17% to 54.93%. Different electrolytes appear to have differing extraction efficiency for the two elements. Table 3 presents the distribution coefficients and separation factor for Ta and Nb.  $\text{K}_2\text{SO}_4$  has the highest value (1.219) and KI the lowest value (0.392) of  $D_1$ . Similarly  $\text{K}_2\text{SO}_4$  has the highest value of  $D_2$  being 0.72 and KI the lowest (0.38). The separation factor of the two metal ions values give the extent to which the two solutes were separated by the electrolytic system, with the highest separation ratio of 1.059 for KI and lowest (0.59) for  $\text{K}_2\text{SO}_4$ .

**Table 1:** Elemental Composition (%)for the Milled Tantalite Ore and Residues After Leaching

Compound	Tantalite ore	Residues
SiO <sub>2</sub>	0.04	0.10
CaO	0.82	0.24
TiO <sub>2</sub>	6.09	7.00
V <sub>2</sub> O <sub>5</sub>	0.14	0.14
Cr <sub>2</sub> O <sub>3</sub>	0.10	5.69
MnO	15.10	18.10
Fe <sub>2</sub> O <sub>3</sub>	13.00	14.00
SrO	0.04	0.04
Y <sub>2</sub> O <sub>3</sub>	0.13	0.03
ZrO <sub>2</sub>	0.52	0.22
Nb <sub>2</sub> O <sub>5</sub>	21.40	20.00
SnO <sub>2</sub>	0.58	0.58
Ta <sub>2</sub> O <sub>5</sub>	38.30	33.30
PbO	0.16	0.16
ThO <sub>2</sub>	0.17	0.17
U <sub>3</sub> O <sub>8</sub>	0.23	0.23

**Table 2:** Effect of Electrolytes on Extraction of Tantalum and Niobium

Electrolyte type	Ta <sub>2</sub> O <sub>5</sub> extracted (%)	Nb <sub>2</sub> O <sub>5</sub> extracted (%)
K <sub>2</sub> CO <sub>3</sub>	34.51	33.79
Na <sub>2</sub> SO <sub>4</sub>	43.31	34.64
K <sub>2</sub> SO <sub>4</sub>	54.93	41.98
KI	28.17	29.35
KBr	30.28	27.30

**Table 3:** Distribution Coefficients and Separation Factor  $\beta$  of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>4</sub>

Electrolyte	D <sub>2</sub>	D <sub>1</sub>	B
K <sub>2</sub> CO <sub>3</sub>	0.51	0.52	0.98
Na <sub>2</sub> SO <sub>4</sub>	0.53	0.76	0.70
K <sub>2</sub> SO <sub>4</sub>	0.72	1.22	0.59
KI	0.42	0.40	1.05
KBr	0.38	0.43	0.88

Note: D<sub>1</sub>, D<sub>2</sub> –are distribution coefficients for tantalum and niobium, respectively.  $\beta$  - is the separation factor.

## DISCUSSION

### Size Reduction of the Tantalite Ore Elemental/ Compositional Analysis

A number of mineral systems have shown that the leaching rate can be enhanced by milling (Welham, 2001), the enhancement being greater than that expected from the increase in surface area. This enhancement has been assigned to the increase in strain in the mineral and formation of steps and kinks on the surface.

It has been noted that the smaller crystallites formed during milling dissolve more rapidly than larger crystallites and this is considered to be due to the increased surface energy of smaller crystallites compared with larger crystallites (Welham, 2001).

From Table 1, Ta<sub>2</sub>O<sub>5</sub> is the most predominant oxide in the ore (38.3%) as expected. However it contains other compounds e.g. Niobium pent oxide (21.4%), Manganese oxide (15.1%) etc. The results are comparable with those of Habashi (1970), Sada (2008) and Maina and Chinda (2006).

### The Leaching Process

Leaching is concerned with the extraction of a soluble constituent from a solid by means of a solvent (Perry, 1997; Backhurst and Richardson, 2002). The soluble constituent may be solid or liquid; and it may be incorporated within, chemically combined with, adsorbed upon, or held mechanically in the pore structure of the insoluble material. Table 1 shows the XRF result for the residue left after leaching. From the result, the relative amounts of both tantalum pentoxide and niobium pentoxide in the residues are less than in the unleached material which implies that fractions of the elements have been dissolved. This result is in close agreement with results obtained by Jide *et al.* (2005).

### Salting-Out Effect of the various electrolytes on the extraction of Tantalum

Table 2 presents the effect of electrolyte on the extraction process of tantalum and niobium from the leached liquor. The amount of Ta<sub>2</sub>O<sub>5</sub> extracted was in the range of 28.17% to 54.93%. Different electrolytes appear to have differing extraction efficiency for the two elements with increase in the order KI < KBr < K<sub>2</sub>CO<sub>3</sub> < Na<sub>2</sub>SO<sub>4</sub>, < K<sub>2</sub>SO<sub>4</sub> for both metals. The increase can be attributed to the negative Gibbs free energy of hydration for the electrolytes i.e. K<sub>2</sub>SO<sub>4</sub> with the largest negative

Gibbs free energy salted-out better as such gives more of Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>, while KI with the least negative Gibbs free energy extracted less Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>, as reported earlier by Rogers, *et al.*, (1996) and EL Hussaini(2004).

The relative salting-out ability was reported to depend on ionic charge, hydration radius, and specific interactions between the salt and PEG. The ability of an anion to salt-out PEG was also correlated to the anion's lyotropic number. Lyotropic number, hydration radius, charge-to-size ratio, and charge can all be related to an ion's Gibbs free energy of hydration (Rogers *et al.*, 1996).

The distribution coefficient D<sub>1</sub> for Ta<sub>2</sub>O<sub>5</sub> and D<sub>2</sub> for Nb<sub>2</sub>O<sub>5</sub> are shown in Tables 3 K<sub>2</sub>SO<sub>4</sub> has the highest value (1.219) and KI the lowest value (0.392) of D<sub>1</sub>. Similarly K<sub>2</sub>SO<sub>4</sub> has the highest value of D<sub>2</sub> being 0.72 and KI the lowest (0.38). This also supports the fact that K<sub>2</sub>SO<sub>4</sub> salts-out better than the remaining salts. Similar result was reported EL Hussaini(2004).

The separation factor of the two metal ions values give the extent to which the two solutes were separated by the electrolytic system, with the highest separation ratio of 1.059 for KI and lowest (0.59) for K<sub>2</sub>SO<sub>4</sub>. These values also indicate that separation of solutes was achieved since the values are not equal to one (Habashi, 1970).

## CONCLUSIONS

The salting-out effect of various solutions of electrolyte in the extraction of tantalum using aqueous biphasic system (ABS) was investigated. The results obtained, show that electrolyte with high ionic charge, hydration radius salts-out Ta<sub>2</sub>O<sub>5</sub> better in the ABS/electrolyte system than those with low values. The percentage of tantalum extracted was in the range of 28.17% to 54.93% with the highest of 54.935% for K<sub>2</sub>SO<sub>4</sub> and the lowest of 28.17% for KI; while that of niobium was in the range of 29.35% to 41.98%. Among the electrolytes investigated, K<sub>2</sub>SO<sub>4</sub> gave the best salting-out effect in the extraction of tantalum.

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