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Possible methodology for niobium, tantalum and scandium separation in ferrocolumbite

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ABSTRACT

Ferrocolumbite is a well-known source of Ta, Nb and Sc. However, separation of these elements from such ores/process tailings, as well from each other is problematic, and typically involves numerous separation steps and very corrosive and hazardous chemicals. An investigation was therefore launched to evaluate alternative separation options. As part of this endeavour it was necessary to investigate accurate quantification methods to be able to trace the elements during any proposed process.

Ferrocolumbite was successfully dissolved with $NH_4F{\cdot}HF$ (1:10 sample to flux ratio at 200 °C for 60 min), which yielded solutions containing 91% Ta, 96% Nb and 99% Sc recoveries while satisfactory LODs (0.07768, 0.01045 and 0.001085 mg/L respectively) were also obtained. Inclusion of a magnetic separation step (only 31% Fe in magnetic portion) to simplify the down-stream beneficiation processes did not contribute to the successful removal of Fe/Ti. Methyl isobutyl ketone (MIBK) successfully extracted the Ta in the ore (94%) into the organic layer and left Nb (88%) and Sc (99%) in the aqueous layer at $[H_2SO_4] < 8$ M. At higher acid levels ($[H_2SO_4] > 10$ M) the Sc present in the non-magnetic portion of the ore migrated in significant amounts and quantities (95%) to the organic layer. Thus a possible process for the separation of the three elements from one another was created. Octan-1-ol yielded similar results to MIBK while methyl isoamyl ketone (MIAK) successfully removed Ta from the aqueous layer (87%), but left the two other elements in the aqueous layer, even at 16 M $[H_2SO_4]$. A much simplified process flow sheet compared to current operational practices for the possible separation of Nb, Ta and Sc from ferrocolumbite and mine tailings is proposed.

1. Introduction

Columbite-tantalite (coltan) refers to a solid solution series, which is formed between two different minerals, namely columbite and tantalite with columbite the niobium-rich group member and tantalite the tantalum-rich member (Beurlen et al., 2008). The international Mineralogical Association (IMA) refined the general reference to columbite as mineral and replaced it with the more specific designations of ferrocolumbite (Columbite-(Fe)), which is rich in Fe and manganocolumbite (Columbite-(Mn), which is rich in Mn (Burke, 2008). Ferrocolumbite is the most common columbite specimen, the manganocolumbite less common while the Mg rich columbite, magnesiocolumbite (columbite-(Mg)) is the least common. In general, despite being refined, the name columbite is still often used without further designations.

The columbite found in Brazil is normally mined for its rich niobium content (31–79% Nb_2O_5) (Pohl, 2011) and not necessarily for its smaller amounts of tantalum. The chemical characterization of the these minerals also indicate the presence of moderate quantities of iron and titanium, as well as small quantities of scandium (0.135%) and another “adopted” rare earth element, yttrium (0.17%). The chemical characterization of the discarded mine tailings after the initial processing of the columbite ore at these mines or processing plants indicate the presence of large amounts of iron, moderate amounts of tantalum and niobium and smaller amounts of scandium (0.996%) and yttrium (0.38%).

The tantalite found in most African countries are normally tantalum rich and niobium poor and are often referred to as “blood or conflict minerals” due to the fact that finances obtained from the selling of these minerals are used to buy weapons and ammunition (Hayes and Burge, 2003). These armed and criminal elements then commit serious human rights violations, which include the mistreatment of the miners and other civilians, the use of child labor, committing widespread sexual violence as well as indiscriminate executions. International efforts such as the “Dodd-Frank Act” (Section 1502 of the US law) require that

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companies using gold, tin, tungsten and tantalum in the manufacturing of their products need to make efforts to determine if those materials came from the DRC or an adjacent country and to carry out a "due diligence" review of their supply chain (bag-and-tag) to control and legalize the tantalum market and to prevent the funding of armed or criminal groups in eastern DRC (Wolfe, 2015; Lee, 2011).

The main elements in the columbite-tantalite series, namely tantalum and niobium, are extremely important in modern day technology. Ta is used in cell phones, laptops and iPads, while Nb is used as superconductors and in the manufacturing of super alloys in the construction industry (Eckert and Hermann, 1996; Ruiz et al., 2002) and as implants in medical applications (Matsuno et al., 2001). The presence of Sc as impurity in the Brazilian columbite is very interesting. Sc is not a scarce element in the earth's crust (42 most abundant element in earth's crust), but it has a low affinity for other minerals and is therefore seldom found in high grade, high volume deposits, which is commercially viable for production (Kemp and Wolf, 2006). Even at elevated concentrations in minerals it's processing is difficult. It is commonly found in association with tungsten and tin in minerals such as wolframite, thortveitite, monazites and some granitic pegmatites (Krebs, 2006). Current estimates indicate the global market volume for Sc is between 10 and 15 tons per annum (U.S. Geological Survey, 2015). At these low levels of production, it is not surprising that the development of new products containing the metal is almost non-existent, although the metal has enormous potential to be used in high-tech applications due its unique properties. Added to aluminum, it produces an alloy which is heat-resistant, corrosion-resistant, strong, and has excellent weldability properties, which is in high demand in the aircraft and automobile industry (Krebs, 2006). It is also used in the production of high-intensity lamps due to its unique optical properties and in the manufacturing of solid oxide fuel cells due to its exceptional heat resistance and electrical properties (U.S. Geological Survey, 2015).

A number of studies (Agulyanski, 2004; Deblonde et al., 2016a; Deblonde et al., 2016b; Zhou, et al., 2005a, Zhou, et al., 2005b, Nete et al., 2017) have investigated the dissolution of Ta/Nb minerals using different chemical reagents. It is important to note that only a few studies (Nete et al., 2017) have documented the successful separation of Ta and Nb in a non-halogen environment and no study has reported the isolation of Sc from Ta/Nb minerals or waste materials. Recently we completed a comprehensive and fundamental investigation on the dissolution and subsequent hydrometallurgical separation of Ta and Nb in different tantalite samples from different locations in Africa (Nete et al., 2012, 2013, 2014). Results from these studies indicated that methyl isoamyl ketone (MIAK) was very successful as solvent extractant to remove Ta from the rest of the elements in an 8 M H_2SO_4 solution with almost no Nb contamination. The Nb was successfully separated from the rest of the elemental impurities present in the mineral ores using a Dowex Marathon wba anion exchange resin.

A number of objectives were targeted in this study. The first was to accurately quantify the three elements of interest (Ta, Nb and Sc) in natural columbite as well as in mine tailings, secondly to determine whether the dissolution and separation process mentioned above is also viable for columbite beneficiation and thirdly to determine the efficiency of the extraction process at higher acidity levels. The study also included the tracing of the three elements during each of the hydrometallurgical process steps to determine a possible extraction and isolation process for Sc from these kinds of minerals and waste material.

2. Experimental

2.1. Equipment and materials

Adjustable-volume Gilson Pipetman (100–1000 µL) and Brand Transferpettes (1– 10 mL) micro-pipettes were used for the accurate measuring and transfers of solutions. The glassware (beakers and volumetric flasks) used for all the elemental analysis was of Schott Duran, grade (A) type. The magnetic susceptibility of the samples was determined with a Sherwood Scientific magnetic susceptibility balance (MSB) at 25 °C. A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer was used for the qualitative and quantitative analyses of the ferrocolumbite and mine tailing samples. The operating conditions reported in Table 1 were maintained for all the analyses.

Table 1
Operating conditions ICP-OES.

Parameter	Condition
RF power	1.2 kW
Coolant gas flow	14.0 L/min
Plasma gas flow	1.2 L/min
Carrier gas flow	0.7 L/min
Sample uptake method	Peristaltic pump
Spray chamber	Glass cyclonic
Type of nebuliser	Concentric

Ultra-pure water (0.02–0.00 µS/cm) obtained *via* reverse osmosis was used for all the analytical solution preparations. All chemicals, reagents and samples (with their known purity) were used without further purification. HCl (32%), HNO_3 (65%), H_2SO_4 (95–99%), MIAK (≥98%), H_2SO_4 (95–97%), ammonium bifluoride ($NH_4F{\cdot}HF$) and the ICP standards containing 1000 mg/L Nb, Ti, Sn, W, Si, Ta, Y and Sc as well as a multi-element standard (32 elements) containing 1000 mg/L each of Mn, Al, Fe and other more common elements were bought from Merck. Th and U standards (1000 mg/L) were bought from De Bruyn Spectroscopic and the ICP standard solution containing 100 mg/L Sc was bought from Spectrascan. The ICP standard solution containing 100 mg/L Zr was purchased from Sigma-Aldrich. 1-octanol (99.5%) was purchased from Associated Chemical Enterprises, while the methyl isobutyl ketone (MIBK) (99%) was sourced from Saarchem. The two different mineral samples, namely the columbite sample and Ta/Nb residue/tailing sample, labelled as Sample A and Sample B respectively (see Fig. 1), originating from Brazil, were supplied by the London and Scandinavian Metallurgical Co. (LSM) with known concentrations of the different elements therein. The analytical results reported in this paper represent the average of three replicate analyses and were compared with the given values while the standard deviations are reported in such a way that it reflects the uncertainty in the calculated results (last digit of a result).

2.2. Preparation of standard solutions

All glassware used in this study was soaked in 55% HNO_3 for about 24 h and then rinsed 2–3 times with ultra-pure water and dried prior to use. A set of calibration standards for ICP-OES analysis was prepared by dilution of the appropriate volumes of the primary ICP standards with water in 100.0 mL volumetric flasks to make 0.5, 1.0, 3.0, 5.0 and 10.0 mg/L concentrations. The acidity of the solutions was adjusted by addition of 10 mL 95–97% H_2SO_4 before they were filled to the mark with ultra-pure water. Blank solution preparations were similar to the calibration solutions and were used for background corrections. All prepared standard solutions were homogenized and left to stand for 5 h before use. Quantitative analyses were performed using the ICP-OES at the selected wavelengths. Wavelength selection was based on sensitivity of the analytical line and the lack of interference by other elements in solution. Ta, Nb and Sc were analysed at 228.916, 309.418 and 361.384 nm respectively. The limit of detection (LOD) was determined using an average of the triplicate measurements of the standard solutions' intensities and ten replicate measurements of the blank solution.