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Comparative study of tantalite dissolution using different fluoride salts as fluxes

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ABSTRACT

Six different fluoride salts, $NH_4F{\cdot}HF$, KF, $KF{\cdot}HF$, CaF_2, NaF and $HF{\cdot}NaF$, were evaluated as fluxes in the fusion dissolution of Ta/Nb containing minerals, and compared with the commercially employed HF dissolution. The cold fusion products were dissolved in dilute H_2SO_4 for both the dissolution and matrix matching purposes. Analytical results indicated that the KF, $KF{\cdot}HF$ and $NH_4F{\cdot}HF$ dissolution procedures were the most effective for dissolving and recovering the main elements from the tantalite mineral. CaF_2, NaF and $NaF{\cdot}HF$ yielded the lowest recoveries of Ta and Nb from the tantalite mineral sample under study. This comparative study indicated that the dissolution and separation of Ta and Nb from one another and from other elements in minerals depended heavily on fluoride concentration, acidity as well as temperature for the formation of the metal–halogen complexes.

Dissolution of the minerals using $KF{\cdot}HF$ and $NH_4F{\cdot}HF$ as fluxes are recommended as alternatives to HF dissolution due lower energy demands, elemental recoveries, cost, separation efficiency and ease of the dissolution step.

1. Introduction

One of the most outstanding properties of Ta metal is its resistance to chemical attack. For example, it is used in the manufacturing of Cl_2 containers used in large-scale CCl_4 production [1]. The formation of a thin oxide layer (Ta_2O_5) on the surface of the Ta metal makes it resistant to oxidation or acid attack [2]. Therefore, the chemical inertness of Ta_2O_5 contributes to this highly valued property of Ta metal. The chemically inert metal oxides, Ta_2O_5 and Nb_2O_5, are predominantly present in many of the Ta/Nb containing mineral ores. Tantalum and niobium naturally occur together in more than 150 minerals. The successful separation of Nb and Ta from each other and from other elements in a complex mineral matrix depends primarily on the selection of appropriate sample dissolution techniques. It is therefore not surprising that the choice or development of effective dissolution processes for the chemical characterization and subsequent separation of these chemically resistant minerals remains an interesting challenge.

Sample dissolution remains one of the most critical steps in the overall success of any analytical process involving the chemical characterization of mineral samples such as tantalite or its metals. The three main techniques available to dissolve these samples are flux fusion (molten salts) [3–5], acid dissolution (wet ashing) [6,7] and microwave digestion [5,8]. The ultimate goal using either of these methods is the conversion of the highly inert mixture of elements (always in their most stable oxidation states) in the mineral to individual, water soluble chemical species (hydrated metal ions or metal complexes) [9]. The accurate quantification is the final process in the chemical characterization of the mineral in question.

The solubilization of the elements in the minerals such as tantalite involve the chemical attack on the strong metal–ligand bonds (normally oxides) present in the inert mineral sample and the reaction can involve any one, or a combination of the three main types of inorganic reactions, namely oxidation, neutralization and complexation. In the case of wet ashing, simple protonation of the metal–oxide bonds can lead to dissolution while acids with strong oxidizing properties (e.g. HNO_3) can induce solubility by the oxidation of the metal center to a new, more water soluble oxidation state. Flux fusion on the other hand, produces a "new" solvent (salt heated to temperatures above its melting point) with either acidic, basic, oxidizing and/or complexation properties, which will attack the metal–oxide bonds to render the elements

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water soluble. Microwave digestion relies mainly on temperature and heat (changing kinetic properties) in the presence of an acid to destroy the chemical structure of the mineral.

Recent studies [5,10] have shown that lithium tetraborate, a combination of mono and disodium hydrogen phosphate as well as ammonium bifluoride as fluxing agents are successful in dissolving Ta and Nb minerals. In the case of the phosphates, the formation of linear polyphosphates is responsible for the successful dissolution of the mineral. These polyphosphates are strong complexing agents and react with the metal oxides to form soluble Nb and Ta complexes [10]. Lithium tetraborate (non-oxidizing acidic flux) is successful in digesting different tantalite ore samples [5]. The dissolution, however, requires that H_2SO_4 and methanol are added simultaneously after the fusion process to prevent the formation of an insoluble boric acid in the reaction mixture. This step also facilitates the removal of the excess boron as the volatile boron ester at ~40 °C prior to sample analysis.

The most efficient and frequently applied dissolution method for Ta and Nb containing mineral samples involves the use of HF as wet ashing reagent. HF is successfully used on both naturally occurring (mineral ores) and artificial (metal alloys) sample dissolution, either alone or in combination with other acids at elevated temperatures. Experimental results indicate the formation of different soluble metal fluoride complexes. These include the possible formation of heptafluorides, hexafluorides or oxyfluorides, which is extremely important in the subsequent separation and purification of the two metals. Often the HF method does not completely dissolve the sample, but completely leaches Nb and Ta from the mineral sample. Literature studies [8,11] have also shown that tantalum and niobium dissolution can be improved by combining microwave digestion in the presence of solvents such as H_2SO_4 and HF. Microwave digestion has the added benefits of fast and uniform heating as a result of microwave energy absorption by the sample. The improved recoveries using the combination of experimental conditions are attributed to the improved reaction rate between the reagents while the types of complexes remain similar to those obtained from HF dissolution.

Despite its efficiency, the use of HF is discouraged in routine laboratories due to its high corrosiveness and safety aspects [12,13]. Literature studies [13–15] have shown that fluoride salts can be used for dissolution and fluorination of Ta and Nb in place of HF. Fluoride salts in general have an advantage of being less toxic, easy to handle and to store. However, it is important that such fluoride salts are evaluated for the optimal dissolution of a good representative of the Ta and Nb containing minerals.

The use of ammonium bifluoride both as a flux in a fusion technique [14] and as an additive (fluorinating agent) in H_2SO_4/$NH_4F{\cdot}HF$ [13] tantalite dissolution were recently reported. Very good Ta and Nb recoveries were reported, but some results pointed to incomplete sample dissolution. A recent study by Nete et al. [15] demonstrated a successful application of $NH_4F{\cdot}HF$ flux fusion procedure on various Ta/Nb containing minerals originating from three different African countries. The possible use of other fluoride containing salts such as KF, NaF and CaF_2 was also suggested [13] for the tantalite dissolution, but no experimental results have been reported. It is anticipated that the high fluoride concentration depolymerizes the polymeric hydrolytic oxides in the mineral to form monomeric fluoride complexes suitable for further analytical and beneficiation procedures [16].

The aim of this study was to evaluate the use of different fluoride salts, namely $NH_4F{\cdot}HF$, KF, KF·HF, CaF_2, NaF and NaF·HF as fluxes for the dissolution of a Ta/Nb mineral sample originating from Mozambique. Results obtained at optimum experimental conditions for each fluoride flux were then compared with those obtained using traditional dissolution techniques with special interest in energy consumption and eco-friendliness.

Table 1
Chemical compositions of Ta and Nb mineral using HF/H_2SO_4 dissolution.

Analyte	Concentration (%)
Ta_2O_5	27.8(6)
Nb_2O_5	27.2(5)
TiO_2	2.7(1)
Mn_3O_4	7.79(6)
Fe_2O_3	7.54(4)
Al_2O_3	1.9(2)
SnO_2	1.4(3)
U_3O_8	2.92(2)
WO_3	1.19(2)
ThO_2	0.48(6)

2. Results and discussion

2.1. Characteristic composition of the mineral samples

The ICP-OES results of the tantalite sample dissolved using the well-known HF/H_2SO_4 digestion method are given in Table 1. The results obtained in this part of the study were used as the reference for the assessment of all the subsequent dissolution procedures. These results were found to be in good agreement with those obtained by Nete et al. [5] on the same sample using the lithium tetraborate flux. However, SiO_2 could not be analyzed in this study due to the Si contamination caused by Si containing components of the ICP-OES, such as the glass nebulizer.

2.2. Comparison between different fluoride salts as fluxing agents

2.2.1. Influence of sample:flux ratio

Visual inspection indicated incomplete dissolution of the sample by all the flux fusions at the initial 1:10 ratio. KF·HF had the smallest amount of undissolved solids (~0.1%) followed by $NH_4F{\cdot}HF$ (~1%). The analytical results for the digestion of the samples using a sample:flux ratio of 1:10 are given in Table 2. Generally, lower concentrations of metal oxides were obtained for most elements by the different fluxes at a sample:flux ratio, 1:10 compared those obtained for the HF/H_2SO_4 dissolution. Good recoveries were obtained for most of the elements using $NH_4F{\cdot}HF$ and KF·HF compared to HF/H_2SO_4, with exceptions for Ta_2O_5 [24.3(5)% and 26.3(6)% compared to 27.8(6)%, respectively], ThO_2 [0.3(1)% and 0.27(4)% compared to 0.48(6)%, respectively] and U_3O_8 [0.9(2)% for $NH_4F{\cdot}HF$ compared to 2.92(2)%].

The sample:flux ratio was changed to 1:20 and this alteration improved recoveries for most elements (Table 3). For example, Nb_2O_5 and Ta_2O_5 dissolutions by NaF increased respectively from 18.02% to 23.68%, and 6.72% to 22.87%. Nearly complete recoveries for most elements were obtained for KF, KF·HF and $NH_4F{\cdot}HF$ as indicated by the recoveries for Ta and Nb in Fig. 1. Visual inspection of the samples indicated complete sample dissolution using KF·HF, but only partial to nearly complete dissolution for $NH_4F{\cdot}HF$ and KF. The NaF·HF fusion still produced poor recoveries with no obvious improvement for most elements under these new set of experimental conditions. However, there was a clear increase in Nb_2O_5 recovery from 8.08 to 21.41% (from 1:10 to 1:20 ratio) and Ta_2O_5 recovery from 1.63 to 9.60% under the same experimental conditions for the NaF·HF fusion.

The sample:flux ratio was increased again to 1:30 for those fluoride fusions (NaF and HF·NaF) that produced poor elemental recoveries for most of the elements in the sample (Table 4). These results indicated no significant change in the dissolution of many of the elements by these salts. The Al_2O_3 and SiO_2 results for all the fluxes at all three different flux concentrations were highly inaccurate and inconsistent and as such were not reported. The