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APPLICATION OF ENERGY-DISPERSIVE XRF TECHNIQUE IN THE HYDROMETALLURGY STUDY OF LOCAL ZIRCON

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Abstract

In this study, energy-dispersive X-ray Fluorescence (EDXRF) was used to analyse the elemental composition of the starting zircon mineral as well as that of associated elements in the leaching solution. Besides analysing the major elements i.e.of zirconium, silicon and hafnium, trace elemental analysis for iron, titanium and the naturally occurring radioactive element thorium and uranium are important in establishing the grades of Malaysian zircon. The technique was also used in determine the optimum conditions for zirconium and hafnium recovery during the leaching process.

Introduction

Energy-dispersive X-ray Fluorescence (EDXRF) is a qualitative and quantitative instrumental technique for elemental analysis. The technique is based on the fact that when a sample is being excited by a x-ray source, electron shell transitions tend to occur. This will eventually result to the release of photons, whose energy is characteristic to that of its elemental contents. Detection limit is from ppm to 100% and this normally is more sensitive as the atomic number is greater . It is normal for this technique to determine elements from sodium (atomic no. = 11) to uranium (atomic no. = 92) but of late this could even be enhanced to detect fluorine using windowless x-ray tube and operated under vacuum. One of the advantages of this technique is its capability of analysing all the elements simultaneously and the spectrum acquisition can be done in less than 100 seconds. In most instances, samples are analysed with minimal sample preparation and the sample could be either solid, powder, liquid or thin films. The nondestructiveness of the method is also important when analysing precious and small samples, also this will help to do repeatitive analysis on a given sample.

Besides cassiterite (tin ore), Malaysian alluvial tin mines also produce a by-product of mixed heavy minerals that is locally termed as *amang*. One of the major heavy mineral that is found in this by-product is zircon ($ZrSiO_4$). Even though zircon is widely used in both the traditional and high technology applications, most of its export from Malaysia is in the form of raw mineral. Production of zircon reached its peak in 1989 where 25,671 tons were produced[1] . Thereafter the volume dropped and this may be attributed to the low market price, low demand of this mineral and also the closing of tin mines in Malaysia [1,2].

A study was done to process local zircon into value-added zirconia products by means of hydrometallurgy. Malaysian zircons from different localities have to be analysed for its grade and also impurities present. The elements of interest are zirconium, silicon and hafnium as the major elements and also iron, titanium , uranium and thorium as its impurities.

One of the important stages in hydrometallurgy study is the leaching process. The amount of associated element that is being leached out will directly relate to its elemental recovery. Various parameters such as acid concentration, temperature and time are incorporated in this process for maximum recovery . The leaching process for the dissolution of sodium- zirconyl silicate, a product formed after the alkaline fusion of zircon, can be represented by the reaction below[3] ;

$$Na_2ZrSiO_5 + 4HCl \rightarrow ZrOCl_2 + 2NaCl + SiO_2 + 2H_2O$$

The accuracy of the investigation is much depends on the elemental analysis technique. As hafnium is also present in substantial quantity and has properties similar to zirconium , the analyses of these two elements are carried out by the EDXRF technique.

Experimental Method

a) Zircon sample

The zircon samples used in this study are collected from tin mines and *amang* plants throughout the country. Only drying and grinding was carried out for the samples to produce a sample of 150 micron particle size. This is to ensure a better homogenous sample during the analysis [4] . Parameters used for the acquisition of the spectrum are shown in Table 1.

Quantitative analysis of the zircon samples was based on reference materials of the same minerals produced by British Chemical Standards (BCS 388 zircon) and Standards Association of Australia (ASCRM-008 zircon). Quantitative method of analysis was by using a software called NBS-GSC Fundamental Parameters Technique. The technique that was developed by the U.S. National Bureau of Standards and the Geological Survey of Canada is suitable for analysis involving minimum number of reference standards [5].

Table 1 : Parameters used in determining zircon

Element (atomic no.)	K,L,M lines	Absorption Energy (KeV)	Low energy range (eV)	High energy range (eV)	Counting technique
Zirconium (40)	Kα	15.774	15050	16400	Net
Hafnium (72)	Lα	11.264	7680	8160	Gross
Silica (14)	Kα	1.740	1610	1920	Gross
Iron (26)	Kα	6.403	6210	6670	Net
Titanium (22)	Kα	4.510	4330	4800	Net
Thorium (90)	Lα	20.460	12720	13170	Gross
Uranium (92)	Lα	21.753	13520	13820	Gross

b) Zirconium and Hafnium in leaching solution

A 10ml leaching sample is drawn from the leaching reactor for every 30 minute. The sample is then filtered through ashless filter paper before being placed on prolene covered sample cups.

Quantitative analysis was done by the regression method and 10,000 ppm standard reference material solutions of zirconium and hafnium produced by National Institute of Standard and Technology, U.S.A were used as the stock solutions. Different concentrations of zirconium and hafnium are then used as calibration standards. The concentration ranges of the standard solutions and the regression data from the calibration graphs are shown in the table 2.

Table 2 : Concentration ranges and regression coefficients of standard Zr and Hf solutions

Elements	Concentration range (ppm)	Regression coefficient (R)
Zr	500 - 10,000	0.9980
Hf	100 - 1,000	0.9983

c) EDXRF analysis

A Baird Ex-3000 EDXRF instrument located at Malaysian Institute for Nuclear Technology Research (MINT), Bangi was used for the analysis. Different acquired conditions were applied for the mineral and leach solution samples. For the zircon sample, the x-ray tube was operated at 30 kV and 0.12 mA. The time of irradiation for the standards and samples was 100 seconds. While for the leach sample, the x-ray tube was operated at 20 kV and 0.5 mA. Here, the sample was placed under normal condition for an irradiation time of 50 seconds. Background peaks are corrected by using Rh filter.

Results and Discussion

Figure 1 shows a zircon spectrum with peaks of the elementsof interest obtained by using the EDXRF instrument. Accuracy of the quantitative method was established by comparing the result of this analysis with that of the certified values for a zircon standard reference material produced by South East Asia Tin Research and Development Centre (SEATRADC). The result is as that shown in Table 3.

Table 3 : Comparisons of certified [6] and measured values of SEATRADC zircon standard reference material

Oxide	EDXRF result (%)	Certified value (%)	% error
ZrO_2	62.44	61.21	1.2
HfO_2	1.47	1.43	2.8
SiO_2	31.00	31.87	2.7
TiO2	0.61	0.72	15.3
Fe_2O_3	0.13	0.15	1.6
ThO_2	0.17	not available	-
U_3O_8	0.16	not available	-

Only small differences occur between the EDXRF result with that of the certified value for most elements except titanium. The higher error in Ti may be due to its low content in the zircon sample compared to lighter element like Si. Another factor that may contribute to this is that the energy peak of titanium seems to overlap possibly by that of rare earths that is also present in similar energy range .

Analysis of zircon samples from different mining districts was also carried out and the result is as that shown in the table 4.

Table 4 : EDXRF results for different Malaysian zircon samples

Content for different zircon samples (%)				
Oxide	Zircon Kemaman	Zircon Puchong	Zircon Dengkil	Zircon Lahat
ZrO_2	51.92	58.15	63.07	63.12
HfO_2	1.60	1.54	1.56	1.51
SiO_2	25.65	28.85	34.16	31.99
Fe_2O_3	1.37	0.11	0.09	0.08
TiO_2	6.75	0.03	0.12	0.27
ThO_2	0.07	0.06	0.02	0.06
U_3O_8	0.06	0.16	0.15	0.18

The above result shows that different zircon samples have different elemental composition. Contents of Zr in samples from Kemaman and Puchong are much less due to low grade material. These two samples also have higher impurities of Fe, U and Th. Naturally occurring radioactive elements, U and Th seems to be present in all the local samples and this may be attributed to the presence of radioactive minerals like monazite and xenotime in *amang* [7].

Analysis of the leaching solution was done to determine the amount of Zr and Hf present. To obtain maximum recovery for these two elements, different conditions had been tried. Temperature is one of the conditions that can effect the recovery of the elements, increase in temperature will help in improving the dissolution of these elements. Thus as shown in Table 5, Zr and Hf contents increase as a higher temperature is used in the leaching system.

Table 5 : Recovery of Zr and Hf as a function of temperature and time

Leaching Time (minutes)	Elemental recovery at different temperature (ppm)			
	Temperature = 70 °C		Temperature = 90 °C	
	Zr	Hf	Zr	Hf
30	17,339	677	17,902	716
60	18,521	692	20,053	848
90	20,247	705	20,809	860
120	20,542	779	22,264	885
150	21,672	817	22,465	921
180	21,740	826	22,836	989

Conclusion

EDXRF has proved to be a very important tool in the hydrometallurgy of zircon. The technique can be used to analyse solid mineral as well as leaching solution in a relatively short time, with little sample preparation and good accuracy.

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Figure 1 : EDXRF spectrum of a local zircon