

Concentration of rare earth elements from monazite by selective precipitation

S M Xaba^{1*}, M Nete² and W Purcell^{1,3}

¹Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa

²The South African Nuclear Energy Corporation SOC Ltd. (Necsa), P.O. Box 582, Pretoria 0001, South Africa

³School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

*sbu012@gmail.com

Abstracts: Pure rare earth elements and their compounds play a unique role in a wide range of green technology and different industrial applications such as medicine, aerospace and clean energy production. The aim of this study was to concentrate and separate rare earth elements from the monazite matrix. Monazite was digested using a mixture of $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ fluxes at 900 °C. Precipitation of rare earth elements was investigated with biphenyldicarboxylic acid and acetyl acetone chelating agents. The precipitates were re-dissolved in sulphuric acid and analysed together with the filtrate solutions using inductively coupled plasma optical emission spectrometry. Analytical results indicated selective precipitation of rare earth elements with both biphenyldicarboxylic acid and acetyl acetone. The results also revealed a negative Na^+ influence (from the flux) on the rare earth elements recovery in solution which is attributed to easily ionisable behaviour of Na which affects the flame properties of the inductively coupled plasma optical emission spectrometry. Na was removed as NaCl by addition of concentrated HCl prior rare earth elements precipitation. This step improved the rare earth elements recovery in the precipitate from 90.2(1) and 101.68(3) %, while the impurities concentrations remained below 30 %. These results indicated the successful concentration and separation of most rare earth elements from monazite by selective precipitation.

1. Introduction

The rare earth elements (REE) are defined as 15 lanthanide (lanthanum to lutetium) group elements with many similar chemical properties together with yttrium and scandium. These elements are usually divided into two groups namely the light (LREEs) and heavy (HREEs). The LREEs consist of the elements from lanthanum (La) to gadolinium (Gd) on the periodic table, while the HREE are from terbium (Tb) to lutetium (Lu) [1]. REEs and their compounds are widely used in modern technologies. For example, neodymium alloys are used in manufacturing of permanent magnets used in catalytic production of ammonia and petroleum field [2]. REEs are also in industrial applications such as in electronics, laptops, mobile phones, electrical transportation, medical, clean energy and defence [3]. Their properties improve energy efficiency and performance at higher temperatures in digital technologies [4],[5].

Monazite and bastnäsite are considered to be the most important source of LREE worldwide, while xenotime is the main source of many HREEs and yttrium [6]. Monazite is also an important source of Th and can be highly radioactive depending on the thorium (Th) quantities in the mineral. Monazite concentrate commonly contains up to 45 % REE_2O_3 , 18 % P_2O_5 , 8.8 % ThO_2 and 600 ppm uranium deposits [7]. South Africa is known to have reasonably large deposits of the REE with highest mineral grades which are mined at the Steenkampskraal in the Western Cape Province. The mine has a



Mineral Resource Estimate (MRE) of 605000 tons of ore with an average grade of 14.36 % containing 86900 tons Total Rare Earth Oxides (TREO) [8]. The REE minerals (mainly the cerium type monazite (Ce) - (Ce, La, Nd, Th, Y)) are mined in SA and due to their Th (and some traces of uranium (U) in significant concentration) [9] content which makes the mineral radioactive they are primarily processed near the mining site.

The radioactive elements, U and Th, can add a huge financial and operational burden in beneficiation of the REEs in monazite. The similar chemical properties between the REEs make the separation of these elements from one another highly challenging and often costly. In previous studies [10],[11],[12], REE, Th and/or U were selective precipitated from the other elements in a REE mineral samples using the different precipitating agent. Sulphuric acid (H_2SO_4) leaching or sodium hydroxide (NaOH) fusion flux methods were used to extract these elements from the mineral into an aqueous solution. From the weakly acidic solution ($\text{pH} < 4$), REE, Th and/or U were then precipitated as hydroxides, oxalate, double sulphate, carbonate and fluoride [13]. The aim of this work was to develop separation and purification methods using selective precipitation of LREE from monazite using different complexing (precipitating) agents (Figure 1). The selective precipitation of LREE, Th and/or U in the dissolved monazite sample was investigated with biphenyldicarboxylic acid and acetyl acetone as precipitating agents. Experimental factors which were investigated include the influences of acid matrix, sodium phosphate flux as well as sample:reagent mole ratios.

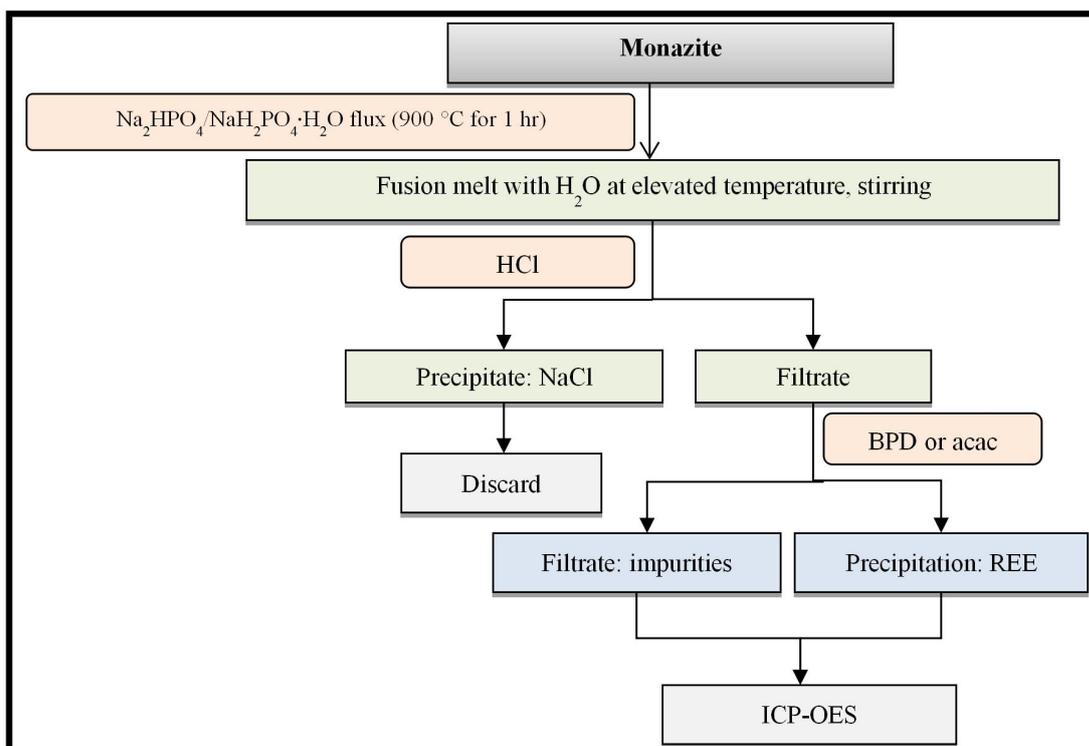


Figure 1: Scheme for the separation selective precipitation and concentration of rare earth elements from monazite.

2. Experimental

2.1 Reagents and glassware

Crushed monazite ore was supplied by the Steenkampskraal mine. Analytical grade HCl (32 %) and H_2SO_4 (98 %) and ethanol (99.5 %) were bought from Merck. Sodium phosphate dibasic (Na_2HPO_4) $\geq 99\%$ and Sodium dihydrogen phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) $\geq 98\%$ were purchased from Sigma-Aldrich. Acetyl acetone (acac) 99.5 % and 2, 2'-biphenyldicarboxylic acid (BPD) $\geq 98\%$ were bought from Riedel-de Haen AG and Merck respectively. The REE ICP multi-element standard containing 1000 mg/L (Ce, La, Pr, Y and Sm) in HNO_3 7 % v/v, was purchased from Inorganic

Ventures Inc. while a multi element standard 1000.000 mg/L (Ca, Fe and Mg) in dilute HNO₃ was purchased from Merck. Individual ICP standard solutions of 1000 mg/L Nd (in 2 % HNO₃ v/v), Si (traces in HNO₃ and HF), U (5 % HNO₃ v/v) and Th (5 % HNO₃ v/v) ICP standards were sourced from Inorganic Ventures Inc. and Ti in H₂O was purchased Merck. Grade B glass volumetric flasks and Schott Duran type beakers were bought from Merck and Sigma-Aldrich respectively. Centrifugation was performed in a rotor bought from MSE. A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer was used for the qualitative and quantitative analysis of all elements in aqueous solutions. Ultra-pure water (conductivity, 0.00 mS/cm) was prepared in the laboratory with an ultra-reverse osmosis system bought from AJD Traders and was used for preparation of all solutions.

2.2 Sample preparations and measurements

2.2.1 Preparation of calibration curves. 2.0 g of 1:1 Na₂HPO₄/NaH₂PO₄·H₂O fluxes was accurately weighed in a platinum crucible and mixed thoroughly before been placed in a pre-heated furnace oven at 900 °C. The resultant melt was dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask. Calibration solutions of 0.0, 1.0, 2.0, 3.0, 5.0, and 10.0 ppm analyte concentrations were prepared by dilution of appropriate volumes of the primary ICP-OES standard solutions. Quantitative analyses were performed at selected analytical lines of 383.826 nm for Mg, 252.852 nm for Si, 412.323 nm for La, 234 nm for Fe, 437.494 nm for Y, 410.946 nm for Nd, 318.020 nm for Th, 385.466 nm for U, 334.904 nm for Ti, 428.079 nm for Sm, 446.021 nm for Ce and 428.293 nm for Pr. The wavelength selections were based mostly on selectivity (less or no interference) and sensitivity for high detections. ICP-OES experimental conditions of 1.2 kW of RF power, 14.0 L/min coolant Ar flow, 1.2 L/min plasma Ar flow and 0.5 L/min carrier Ar gas flow were used and maintained throughout the study.

2.2.2 Dissolution of monazite using a mixture of Na₂HPO₄/NaH₂PO₄·H₂O as a flux. Approximately 0.1 g of monazite sample was accurately weighed and homogenously mixed with Na₂HPO₄/NaH₂PO₄·H₂O in a mass ratio of 1:15 sample:flux. The mixture was quantitatively transferred into a platinum crucible and heated at 900 °C in a closed oven with a periodical swirling at 15 min intervals. Visual inspection of the sample indicated a complete digestion after 60 min. The resultant melt was cooled to room temperature and dissolved in 30 mL of water. The dissolved melt was quantitatively transferred to 100.0 mL volumetric flask and filled to the mark with water. Analytical determinations were performed in triplicate to determine the elemental concentrations of the constituents in the mineral (Table 1, Expected).

2.3 Selective precipitation of REE from the solution containing the flux

0.5002 g of 2, 2'-biphenyldicarboxylic acid and 0.51 mL of acetyl acetone were separately dissolved in 100 mL in volumetric flask with ethanol and/or water, depending on which dissolves the precipitating agent completely. 10.0 mL aliquot of monazite solution (see **Section 2.2.2**) was subsequently transferred to a 100 mL beaker, in H₂SO₄ medium. 10 mL of precipitating agent was added to these mixture with a mole ratio of 1:5 sample:precipitating agent. Immediately after adding the chelating agents to a colorless solution, both reaction mixtures changed colour to yellow. The reaction mixture was stirred for 10 min and then left overnight to allow for precipitation to occur. Visual inspection of the samples on the following day indicated a white precipitate had formed in the acac solution and a yellow precipitate in BPD mixture. The solutions were separated from precipitate by centrifugation and decantation and the filtrate was quantitatively transferred into 100.0 mL volumetric flasks. The precipitates were also dissolved with H₂SO₄ and quantitatively transferred into 100.0 mL volumetric flasks. Both precipitate and filtrate solutions were filled to the mark with water. Then the solutions were analysed using ICP-OES (see Table 1).

Table 1. Metal content in the precipitation from the monazite matrix before removing NaCl.

M _x O _y (%)	Exp(s)*	Acac				BPD			
		Ppt(s)*	RSD (%)	Fil(s)*	RSD (%)	Ppt(s)*	RSD (%)	Fil(s)*	RSD (%)

MgO	0.2(3)	0.11(1)	0.83	0.25(2)	9.84	0.16(2)	7.07	0.22(1)	4.12
SiO ₂	3.0(1)	1.2(1)	3.72	3.8(2)	8.28	1.3(1)	4.21	3.5(2)	8.13
CaO	8.1(1)	8.4(1)	1.84	11.1(6)	7.17	8.7(3)	3.66	11.0(6)	7.17
TiO ₂	0.34(2)	0.02(8)	23.74	0.55(3)	9.56	0.03(2)	7.25	0.54(4)	11.45
Fe ₂ O ₃	3.90(6)	2(2)	41.63	5.5(3)	6.44	0.1(3)	7.84	6.0(3)	8.96
Y ₂ O ₃	1.59(1)	1.24(6)	3.89	0.49(6)	3.99	1.26(1)	0.34	0.44(1)	7.16
La ₂ O ₃	8.9(1)	8.74(4)	0.50	nd	--	8.7(1)	1.15	nd	--
Ce ₂ O ₃	17.9(1)	17.4(1)	0.60	nd	--	17.4(2)	0.85	nd	--
Pr ₂ O ₃	0.7(1)	0.48(2)	9.17	nd	--	0.4(2)	26.92	nd	--
Nd ₂ O ₃	6.59(3)	6.25(7)	1.00	nd	--	6.24(3)	0.51	nd	--
Sm ₂ O ₃	0.64(7)	0.56(2)	3.43	nd	--	0.53(9)	13.82	nd	--
ThO ₂	5.28(6)	4.99(2)	0.45	0.2(1)	2.57	4.96(7)	1.28	nd	--
U ₃ O ₈	3.2(3)	2.8(3)	8.34	nd	--	2.6(3)	10.10	nd	--

M_xO_y(%) – Metal oxide percentage Exp(s) – Expected(standard deviation) Ppt(s) – Precipitate(standard deviation),
 Fil(s) – Filtrate(standard deviation) Tot – Total nd - not detected *Average of 3 replicates

2.4 Selective precipitation of REE from the solution without the flux.

An additional procedure was applied to reduce the salt (Na⁺) concentration. 20 mL of 32 % HCl was added to the clear monazite solution (see Section 2.2.2) and then left overnight to allow for maximum precipitation of Na as NaCl. The same procedure (see the second paragraph on Section 2.3) was repeated for both precipitating agents with the 10.0 mL aliquot of monazite solution. Then precipitate and filtrate solutions were analysed using ICP-OES (see Table 2).

Table 2: Metal content in the precipitation from the monazite matrix after removing NaCl.

M _x O _y (%)	Exp(s)*	Acac				BPD			
		Ppt(s)*	RSD (%)	Fil(s)*	RSD (%)	Ppt(s)*	RSD (%)	Fil(s)*	RSD (%)
MgO	0.2(3)	0.01(1)	3.05	0.14(1)	3.57	0.01(1)	8.36	0.12(1)	6.14
SiO ₂	3.0(1)	0.1(1)	4.77	2.8(2)	5.42	nd	--	0.5(4)	12.44
CaO	8.1(1)	7.2(6)	6.88	11.1(4)	4.51	10.8(5)	6.66	9.8(7)	8.20
TiO ₂	0.34(2)	nd	--	0.25(2)	0.69	nd	--	0.09(1)	1.87
Fe ₂ O ₃	3.90(6)	0.02(9)	2.18	4.25(6)	1.58	0.1(2)	4.93	4.2(2)	4.93
Y ₂ O ₃	1.59(1)	0.72(4)	2.43	0.90(8)	4.79	0.73(3)	1.95	0.81(7)	4.26
La ₂ O ₃	8.9(1)	8.0(2)	2.80	1.0(8)	8.49	8.64(6)	0.63	0.6(3)	2.97
Ce ₂ O ₃	17.9(1)	17.0(1)	0.55	nd	--	17.5(2)	1.25	nd	--
Pr ₂ O ₃	0.7(1)	0.38(5)	8.19	nd	--	0.50(2)	0.30	nd	--
Nd ₂ O ₃	6.59(3)	6.08(1)	1.50	nd	--	6.68(5)	0.83	nd	--
Sm ₂ O ₃	0.64(7)	0.47(2)	3.51	nd	--	0.32(3)	39.71	nd	--
ThO ₂	5.28(6)	4.85(1)	0.19	0.37(6)	11.64	4.2(1)	2.82	0.3(5)	8.65

U_3O_8	3.2(3)	3.1(1)	4.53	0.11(7)	2.03	2.33(7)	2.07	0.6(1)	3.59
M_xO_y (%) – Metal oxide percentage	Exp(s) – Expected(standard deviation)			Ppt(s) – Precipitate(standard deviation),					
Fil(s) – Filtrate(standard deviation)	Tot – Total			nd - not detected			*Average of 3 replicates		

3 Results and discussion

3.1 Selective precipitation of REE from the solution with and without the flux

Two different precipitating agents were investigated for a possible selective precipitation and purification of LREE, U, Th (or removal of impurities) from monazite. Complete sample dissolution was accomplished using a flux fusion digestion with a mixture of $Na_2HPO_4/NaH_2PO_4 \cdot H_2O$ flux. The sample/salt melt dissolves in water. Therefore, precipitation studies were investigated in water. The results indicated that both chelating agents (biphenyldicarboxylic acid and acetyl acetone) preferentially precipitated LREE, U and Th from the monazite matrix. Most of the LREEs together with U and Th were obtained in the precipitate and their recoveries (based on values in Table 2) ranged between 80.5(2) to 98.74(9) % while most of the other elements had remained in solution. However, analysis of the filtrate solution (see Figure 2) indicated higher than acceptable recoveries for the remaining elements. This observation prompted the investigation of the flux influence on the analysis of the solutions. Literature study has indicated that Na^+ ion negatively influence the flame properties of the ICP-OES and commonly enhances analyte intensities [14]. The high Na^+ concentration was reduced by addition of HCl [15] for precipitation of Na as NaCl (*cf* Tables 1 and Tables 2). The selective precipitation was repeated on the solutions with low Na^+ content and the results are presented in Figure 4.

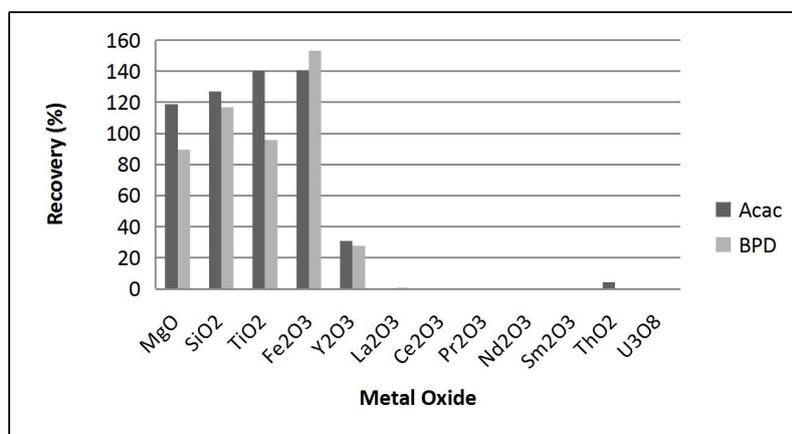


Figure 2: Elemental recoveries in high Na^+ concentration filtrate solution.

Recoveries of all the elements in the filtrate improve and ranged between 72.2(4) to 101.38(3) % (Figure 4) and thus giving the confidence in the obtained analytical results. Moreover, the RSD values in the low Na content separations were generally lower and in acceptable range (Table 2) when compared with those in high Na concentration which were mostly > 10 % (Table 1). The majority of the LREEs were not observed in the filtrate which is in agreement with the results in Table 2. However, the results indicated that La, Th, U and Y precipitation was not complete in this one step precipitation procedure. A significant concentration of Y had remained in the filtrate solution with some minor concentrations of La, Th and U.

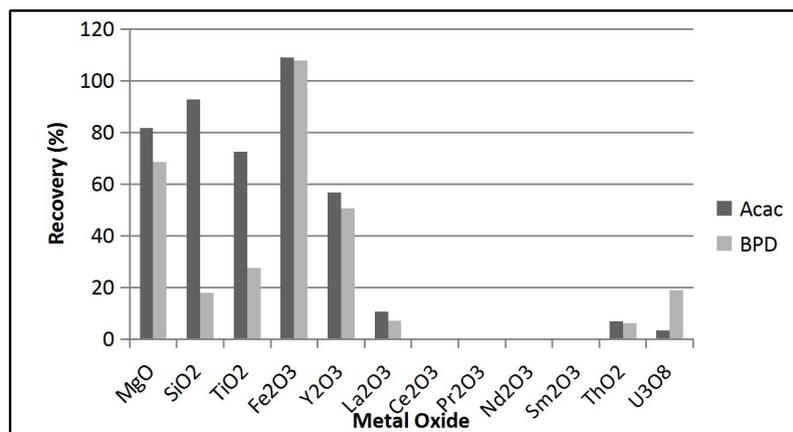


Figure 3. Elemental recoveries in low Na⁺ concentration filtrate solution.

4. Conclusion

The separation of LREE from the monazite matrix using organic ligands as chelating agents was investigated in a sulphate medium. The mineral sample was digested by fusion with Na₂HPO₄/NaH₂PO₄·H₂O flux and the melt was dissolved in water. Analytical results of the sodium phosphate fluxes indicated higher elemental concentrations for some elements and this led to a doubt about the accuracy of the rest of the analytes. The influence of Na on these analyses was reduced by prior precipitation of Na as NaCl using HCl and the results indicate improvement in the accuracy of LREEs, U and Th (their recoveries ranged between 72.2(4) to 101.38(3) % as well as the rest of the analytes. Results of the selective precipitation of the LREEs indicated that LREEs, U and Th were preferentially precipitated from the monazite matrix with both BPD and acac. Most of the other elements which constituted this mineral remained in the filtrate solution. This study has successfully separated the REEs from the monazite matrix. The precipitation method developed in this study can be used as a purification step for monazite beneficiation and for the concentration of low grade LREE containing minerals. The concentrated “mineral” can be used for as a starting material for the separation of REEs into their individual purer compounds.

Acknowledgements

The authors gratefully acknowledge the financial support given by the South Africa Nuclear Energy Corporation SOC Limited (Necsa) and the Nuclear Materials Development Network (NMDN) of the Advanced Metals Initiative (AMI) of the Department of Science and Technology of South Africa (DST) as well as University of the Free State for the research facility.

References

- [1] Xaba S M 2015 *Method development for the quantification of selected early rare earth elements* (Bloemfontein: University of the Free State, M.Sc. thesis) p 1
- [2] Jha M K, Kumari A, Panda R, Kumar J R, Yoo K and Lee J Y 2016 *Hydrometallurgy* **165** pp 2-26
- [3] Joseph A 2016 *Investigating Seafloors and Oceans: From Mud Volcanoes to Giant Squid* 1st Ed (Amsterdam: Elsevier) pp 115-116
- [4] Rivera V A G, Silva O B, Ledemi Y, Messaddeq Y and Marega Jr. E 2014 *Collective plasmon-modes in gain media: Quantum emitters and plasmonic nanostructures* (Cham Hiedelberg New York: Springer) p 118
- [5] Bünzli J C and Pecharsky V K 2015 *Handbook on the physics and chemistry of rare earths* Vol 48 1st Ed (North Holland: Elsevier) p 288
- [6] Amaral J C B S and Morais C A 2010 *Miner. Eng.* **23**(6) pp 498-503.
- [7] Pike D R 1959 *The monazite deposits of the Van Rynsdorp division* (Pretoria: University of Pretoria, M.Sc. thesis) p 127

-
- [8] Steenkampskraal rare earths, the mine [Accessed 04-05-2018]. Available from:<http://www.steenkampskraalrareearths.co.za/the-mine/>
- [9] Sinding-Larsen R and Wellmer F W 2012 *Non-renewable resource issues: Geoscientific and societal challenges* (Netherlands: Springer) p 139
- [10] Habashi F 2013 *Can. Metall. Q.* **52**(3) pp 224-233
- [11] Abreu R D and Morais C A 2010 *Miner. Eng.* **23** pp 536-540
- [12] Bahri C N A C Z, Al-Areqi W M, Ab-Majid A and Ruf M I F M 2016 *Mal. J. Anal. Sci.* **20**(1) pp 44-50
- [13] Gupta C K, and Krishnamurthy N 2005 *Extraction Metallurgy of Rare Earths* (New York, Washington: Taylor & Francis e-Library) pp 176-177
- [14] Chiweshe T T 2015 *Quantification of iridium and other platinum group metals in the presence of naturally occurring contaminants in geological ore* (Bloemfontein: University of the Free State, PhD. Dissertation) p 216-255
- [15] Moila A, Chetty D and Ndlovu S 2017 *J. South. Afr. Inst. Min. and Metall* **117**(7) pp 615-621