Plasma dissociation of monazite

H Bissett¹, M M Makhofane¹, R van der Merwe¹, S J Lotter¹

¹ The South African Nuclear Energy Corporation SOC Ltd (Necsa), Church Street West Ext, Pelindaba, Pretoria 0001, South Africa

E-mail: hertzog.bissett@necsa.co.za

Abstract. Monazite is a phosphate mineral which contains a significant amount of rare earth elements (REE) with thorium (Th) and a low concentration of uranium (U). The radioactive components of monazite, Th and U, make it an unattractive source of REE due to the added cost associated with radioactive waste handling. The mineral is also chemically inert requiring the use of corrosive reagents at elevated temperatures to effectively extract REEs. According to thermodynamic calculations, monazite dissociation into oxides of REE and phosphorus (P) is favourable at temperatures greater than 1000ºC, while the reverse reaction occurs well below a 1000ºC. Rapid cooling is required to prevent the reverse reaction. Achieving these high temperatures, with rapid heating and cooling, is possible by means of thermal plasma treatment such as a radio frequency plasma. This type of plasma system offers superior control of plasma/particle interaction, quenching rates and plasma gas composition. The objective of this study was to determine the parameters for dissociation of the monazite under various conditions to reduce its chemical inertness. Dark and grey powders were obtained under reducing conditions, while lighter powder formed in the presence of an oxygen plasma with increase particle circularity observed after plasma treatment. While SEM-EDS analysis indicated no notable change in powder composition after plasma treatment, dissolution tests proved that monazite was not only more reactive, but also more susceptible chemical reaction after treatment.

1. Introduction

Monazite is a phosphate mineral which contains a significant amount of rare earth elements (REE) such as cerium (Ce), lanthanum (La), praseodymium (Pr), neodymium (Nd) and yttrium (Y) while also containing the radioactive elements Th and U [1]. REE are increasingly being used in the development of advanced materials in clean energy technology applications such as wind turbines, electric cars and permanent magnets [2].

The processing of monazite is difficult and expensive due to the fact that highly corrosive chemicals such as sodium hydroxide and sulfuric acid at elevated temperatures are required to dissolve this phosphate based mineral [3]. New and innovative technologies have been suggested to improve extraction efficiencies by changing the monazite structure in such a way that it makes it more susceptible to chemical attack. One such method is thermal cracking of the monazite crystal lattice [4].

The use of thermal plasma technology has been successfully applied at the South African Nuclear Energy Corporation SOC Ltd. (Necsa) to dissociate zircon (ZrSiO₄), which made use of a direct current non-transferred arc plasma. In past investigations, harsh alkaline treatment was required to extract zirconium (Zr) from the chemically inert crystal structure of zircon. With the assistance of thermal plasma technology, the zircon was converted into plasma-dissociated zircon (PDZ – ZrO₂·SiO₂) which was more chemically reactive and could be processed making use of less aggressive chemicals at lower temperatures [5, 6]. Necsa has purchased a 15 kW RF thermal plasma system from TEKNA Plasma
Systems Inc., by making use of the National Equipment Programme managed by the National Research Foundation of South Africa. This system operates with a versatile, inductively coupled radio-frequency (RF) plasma torch, which allows for the use of various plasma gas compositions (H₂/Ar, He/Ar, O₂/Ar) in a range of 9 -15 kW plasma plate powers.

The purpose of this paper is to provide details on how the monazite was treated under reducing, inert and oxidizing plasma conditions. The untreated monazite was compared with the plasma treated monazite making use of optical microscopy and Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDS) to observe morphological and compositional particle changes. Subsequently, all untreated and plasma treated monazite samples were evaluated by hydrochloric acid dissolution tests.

2. Thermal decomposition of monazite

In the 1990s a direct current (DC) non-transferred arc plasma process was developed by Necsa to dissociate zircon [5]. Analogous to monazite, zircon sand is chemically inert and requires aggressive chemical attack to dissolve the mineral structure for beneficiation of valuable zirconium metal. Although an arc plasma pilot plant was used to dissociate the zircon, followed by rapid quenching to prevent the re-association of the ZrO₂ and SiO₂, the same principle can be applied for thermal “cracking” of the monazite in a RF thermal plasma.

In a paper by Kemp and Cilliers [4] the theoretical decomposition of monazite was discussed. In this study it was implied from a physical strength perspective that the monazite crystal is weaker and could therefore be dissociated more easily than zircon [7]. As the zircon crystal lattice was dissociated by means of the thermal plasma, it was expected that the monazite crystal could also be dissociated in a similar manner. Although monazite contains various rare earth phosphates, the most important rare earths (RE) in the monazite structure are Ce, La, Nd, Pr and Y. Calculating the Gibbs free energy to estimate the temperature at which the individual rare earth phosphates dissociate into the given oxides and phosphorus-oxygen complexes, it can be predicted whether plasma dissociation of the monazite can be accomplished using Equation 1:

$$2 \text{REPO}_4 \rightarrow \text{RE}_2\text{O}_3 + 2 \text{PO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$$  

(1)

According to literature zircon dissociates into PDZ at 1673 ± 10°C, while from the Gibbs free energy calculations, the dissociation of CePO₄ occurs at 1700 °C and the remaining rare earth phosphates dissociate between 2500 and 3000 °C. Therefore, it is expected that a higher plasma temperature will be required to dissociate the monazite into the various rare earth oxides compared to zircon dissociation into ZrO₂ and SiO₂. The conversion of monazite into rare earth oxides would improve the leachability when using diluted mineral acid when compared to leaching of rare earth phosphates [8]. Various studies have investigated the dephosphorisation behavior of rare earth phosphates. Converting the REPO₄ to the oxides should make the mineral more susceptible to chemical attack required for enhanced dissolution rates. The high temperature conversion of the rare earth phosphate to obtain rare earth oxides was examined. The studies indicated that the reaction temperature was the main factor influencing the dephosphorisation efficiency. According to thermodynamic calculations and real initial reaction temperature conditions, all rare earth phosphates were converted to the oxides at temperatures higher than 1400 °C. [9, 10].

3. RF thermal plasma for dissociation or “cracking” of the monazite

Thermal plasmas, characterised by their extremely high temperatures (3000 - 10 000 °C) and rapid heating and cooling rates (~ 10⁶ °C/s) under oxidizing, reducing or inert conditions. This makes them particularly suitable for thermal treating of powders at high temperatures, followed by rapid quenching once they pass through the plasma. Residence times of particles in the plasma region ranges from 5 to 20 ms and is dependent on the gas flow rates used during the treatment. Although various plasma methods can be used, radio-frequency (RF) induction plasmas are the preferred method, based on the longer residence times possible. For an induction torch, the energy coupling between the electric
generator and the plasma itself is done by a cylindrical coil [11]. A typical induction set-up is illustrated in Figure 1.

![Figure 1. RF induction plasma within the confinement tubes with an induction coil](image)

The plasma “flame” properties are dependent on various parameters such as input power, frequency from the RF power supply, pressure inside the reactor and the plasma gas composition. Less power is required at higher frequencies and lower gas pressures to maintain a stable plasma. For instance; when comparing argon and hydrogen, less power is required to maintain an argon plasma since argon ionizes more easily than hydrogen. A higher plasma temperature can however be obtained when making use of gases that ionize less readily, while higher plasma gas temperatures can also be obtained at higher operating pressures. In most instances Ar was used as plasma gas (central gas) and carrier gas, while the sheath gas was a mixture of Ar and an optional gas such as H₂, He and O₂ depending on the application [11].

4. Experimental

Mineral sand from Richard’s Bay was upgraded / floated to a monazite concentrate (> 90 %) by Mintek and used for all experimental work. The monazite was plasma treated at various conditions and characterised by optical microscopy and SEM-EDS. Dissolution tests on all samples were conducted in hydrochloric acid.

4.1. Thermal decomposition of monazite

TEKNA’s 15 kW induction plasma system makes use of a PL-35M induction torch which can operate between 2 to 5 MHz. For the purpose of this study, the PL-35 torch was mounted on a reactor chamber equipped with a “catch pot” for the collection of the plasma treated monazite powder. Experiments were conducted in either a reducing, inert and/or oxidizing environment. In Table 1 the plasma treatment conditions are indicated.

| Plasma gas mixture | Optional gas concentration (% v/v) | Plasma plate power (kW) |
|--------------------|-----------------------------------|------------------------|
| H₂/Ar              | 7.5                               | 15                     |
| He/Ar              | 50                                | 15                     |
| O₂/Ar              | 60                                | 12                     |
A mass balance of the powder before and after plasma treatment was conducted in order to determine if there were any loss in material during operation. Optical images of the plasma treated powders collected in the “catch pot” below the reactor were acquired using a Nikon SMZ-T2 optical microscope equipped with a Nikon D70s camera.

4.2. SEM-EDS and image processing
Four samples of monazite, one raw (untreated) and three plasma treated, were mounted and materialographically prepared (ground and polished down to 1 μm) beforehand, with the surface carbon coated prior to produce a conductive surface for required for SEM imaging of the powders. SEM and EDS analyses were performed using a Quanta FEI 200 D SEM with an EDAX Octane Elect SD detector running the TEAM™ EDS Analysis System. Elemental and phase mapping of each sample surface (cross-sections) was conducted at 155 x magnification.

Image processing was applied on the Back-scattered Electron (BSE) images when applying elemental maps. The Carl Zeiss Zen 2 Core software package was used to determine if there was a quantifiable change in the particle morphology under different conditions. The average circularity was determined by evaluating a number of particles and making use of Equation 2.

The shape factor \( f_{\text{circ}} \) is the circularity, a function of the perimeter \( P \) and the area \( A \):

\[
f_{\text{circ}} = \frac{4\pi A}{P^2}
\]

In this instance the circularity varies between 1 and approaching 0, with the circularity of a circle equal to 1.

4.3. Dissolution study
The raw (untreated) monazite and the three plasma treated samples were subjected to acid dissolution tests in order to compare the chemical amenability of the feed monazite and the variously treated plasma products by comparing the degree of digestion observed during each test. For each sample a mass of between 0.1 and 0.3 g was weighed off accurately to 0.0001 g into a round bottomed flask. A total of 5 ml of 32% analytical grade hydrochloric acid was added to the flask was connected to a reflux condenser and placed in a heating mantle. The sample was heated and allowed to boil for a period of 4 h in order to ensure that as much sample material dissolved into the acid as possible. The acid selected was chosen based on commonly used reagent with the reflux conditions selected to ensure a constant concentration throughout a dissolution test. Hydrochloric acid forms a constant boiling azeotrope at 108.6 °C with a concentration of 20.2% [12]. Upon completion, the sample was allowed to cool, then diluted slightly with deionised water during filtration and transferred quantitatively to a 50 ml volumetric flask, after which it was filled to the mark with more deionised water. These samples were submitted to Pelindaba Analytical Laboratories (PAL) for inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis of the elemental content of the dissolved component. Though the dissolution rate was not determined for the purpose of this portion of the study, the ease with which plasma treated monazite did dissolve in comparison to untreated powders was investigated.

5. Results and discussion
5.1. Thermal decomposition of monazite
For the powder treated making use of H₂/Ar and O₂/Ar a loss in mass of 15 % in both these instances was observed, while a mass loss of 14 % was observed in the He/Ar plasma. Although a negligible quantity of powder deposited on the reactor wall, this loss in mass might indicate the evaporation of light elements from the monazite. It was apparent that a deposit formed on the top-section inside the plasma reactor. In the presence of H₂ a yellow deposit was observed while a “brownish” and a white deposit was formed when He and O₂ was used, respectively. Due to the small quantity (<1 g) of deposit that formed, accurate analysis of this powder was not possible. It is however realistic to assume that all these deposits were some kind of phosphorus containing compounds caused by dephosphorisation of the monazite at high temperatures, based on the colouration of the deposits observed [9,10].
In Figure 2 the optical images of all samples are shown. It is clear that a colour change of the monazite had occur in all instances, with mostly dark particles forming after treatment in the H$_2$/Ar plasma and lighter particles formed using a O$_2$/Ar plasma. The use of the He/Ar plasma resulted in a mixture of dark, grey and white particles with predominantly grey particles present. From this visual comparison it was apparent that the respective reducing and oxidizing environments tested had a physical effect on the plasma treated monazite.

![Figure 2. Optical images of the (a) raw untreated monazite, (b) plasma treated monazite in H$_2$/Ar, (c) plasma treated monazite in He/Ar and (d) plasma treated monazite in O$_2$/Ar.](image)

5.2. **SEM-EDS and Optical image processing**
In Figure 3 the SEM-EDS images of the raw monazite cross-sections are shown. From the BSE image it is clear that the monazite particles were irregularly shaped. According to the element / phase mapping conducted, most of the particles consisted of REEs with some contamination of Zr$_x$Si$_y$O$_z$ (typically zircon) and some oxide-containing beach sand.
In Figure 4 to 6 the samples plasma treated in H\textsubscript{2}/Ar, He/Ar and O\textsubscript{2}/Ar are shown. Elements, in phases as identified on the backscatter images (BSE), were successfully quantified. Still, no noteworthy compositional changes were recorded for raw monazite samples after plasma treatment. Some elements were more abundant in samples after treatment, which could be attributed to the inhomogeneity of the sample. EDS should not be used to assume the elemental composition of the entire bulk sample as it takes into account elements in a very small spot (300 µm maximum) on the sample surface, also carrying an error of ± 1 % (wt. %). For the above mentioned reasons it was also difficult to quantify the difference in phosphorus composition before and after plasma treatment which might have been attributed to the dephosphorisation of the monazite.

Some morphological changes were observed after plasma treatment of the monazite powder. The most apparent were the increase in particle circularity and voids present after plasma treatment of the raw monazite powder. Though some voids were distinct on the BSE images, they were more evident on the secondary SEM images (taken with the Everhart-Thornley detector) not presented in the current work.

**Figure 3.** SEM-EDS images of the floated monazite. The BSE image is shown on the left and the image overlaid with elemental/phase mapping on the right. The colour coding indicates the following elements/phases: O/Ce/Nd/P/La/C/Zr; C/O; O/Si/Fe; Si/Zr/O/P; Ti/O/La/Ce; Ca/Si/O/C/Fe.

**Figure 4.** SEM-EDS images of the monazite treated in H\textsubscript{2}/Ar plasma. The BSE image is shown on the left and the image overlaid with elemental/phase mapping on the right. The colour coding indicates the following elements/phases: O/Ce/Nd/P/La/C/Zr; C/O; O/Si/Fe/Al/Ca; Ti/O/La/Ce; Ca/Si/O.
Figure 5. SEM-EDS images of the monazite treated in He/Ar plasma. The BSE image is shown on the left and the image overlaid with elemental/phase mapping on the right. The colour coding indicates the following elements/phases: - O/Ce/Nd/P/La/Zr; - C/O; - O/Si/Fe/Ca; - Si/O/Zr/O/P; - Ca/Si/O.

Figure 6. SEM-EDS images of the monazite treated in O₂/Ar plasma. The BSE image is shown on the left and the image overlaid with elemental/phase mapping on the right. The colour coding indicates the following elements/phases: - O/Ce/Nd/P/La/Zr; - C/O; - O/Si/Ca; - Si/O/Zr/O/P.

The SEM images obtained were subjected to optical image processing making use of the Carl Zeiss Zen 2 Core software package, used to quantify changes in the particle morphology under different plasma conditions. The results can be seen in Table 2. All plasma treated samples showed an increase in circularity, a metric which was used as a 2-dimensional equivalent to sphericity.

| Plasma gas composition       | Number of particles measured | Average circularity (-) |
|-----------------------------|-----------------------------|-------------------------|
| Raw Monazite                | 130                         | 0.79                    |
| Plasma treated in H₂/Ar     | 133                         | 0.83                    |
| Plasma treated in He/Ar     | 140                         | 0.86                    |
| Plasma treated in O₂/Ar     | 188                         | 0.85                    |
5.3. **Dissolution study**

Initial results can be seen in Figure 7. The sample labeled “raw monazite” is the recovery of the untreated monazite from the HCl dissolution medium. The other samples were plasma treated with varying power settings and chemical environments. The best extraction from a monazite powder appears to be associated with the 15 kW plasma setting with hydrogen as a gas additive with an extraction of 44% obtained when compared to the 20% extraction of raw monazite sample. Further tests are required to properly define the degree of improvement from the baseline sample, but an initial increase in extraction of more than double is highly encouraging. An extraction of 35% was also observed for the sample treated in the He/Ar plasma. The sample treated at 12 kW in the presence of oxygen did not result in an improvement in the extraction during dissolution. The reason for this is not clear at this stage. Only total extraction percentage was measured here. The extraction rate (extraction percentage vs time) and optimum conditions will be determined in future work. This basic dissolution study was intended solely to guide the plasma treatment process.

![Figure 7. Dissolution results of the raw monazite and the three plasma treated samples in HCl. The colour coding indicates the following main elements determined in solution by ICP-OES:](image)

6. **Conclusions**

Raw monazite concentrate samples were treated in the TEKNA 15 kW induction plasma system in reducing, inert and oxidizing environments from 12 to 15 kW plasma plate powers. In all instances a loss in material mass around 15% were observed indicating possible dephosphorisation of the rare earth phosphate. According to visual observations, the treatment of the monazite powder in H₂/Ar and He/Ar plasma resulted in the formation of mostly dark and grey particles, while lighter particles were produced making use of a O₂/Ar plasma. SEM-EDS analysis of the samples indicated no notable compositional changes when comparing the untreated monazite to all the plasma treated samples. Clear morphological changes of the powder were observed with an increase in particle circularity for all plasma treated samples. The average circularity increased from 0.79 for the untreated monazite to around 0.85 for all plasma treated powders. Dissolution of the raw monazite and the three plasma treated samples indicated an extraction of 44% and 35% for the samples treated in H₂/Ar and He/Ar plasma respectively, compared to the 20% extraction obtained for the raw monazite. The results showed that plasma treatment could make the monazite mineral more reactive and susceptible to reaction with chemicals.
7. Acknowledgements
The authors would like to acknowledge the Department of Science and Technology (DST), through the Advanced Material Initiative (AMI), for the financial support in conducting this study. The South African Nuclear Energy Corporation (Necsa) is acknowledged for their financial support. Mintek is also acknowledged for supplying monazite concentrated.

8. References

[1] Kim W, Bae I, Chae S and Shin H 2009 J. Alloy. Comp. 486 610
[2] Abreu R D and Morias C A 2010 Miner. Eng. 23 536
[3] Kumari A, Panda R, Jha M K, Kumar J R and Lee J Y 2015 Miner. Eng. 79 102
[4] Kemp D and Cilliers A C 2016 J. S. Afr. Inst. Min. Metall. 116 901
[5] Havenga J L and Nel J T 2012 J. S. Afr. Inst. Min. Metall. 112 12
[6] Rentorff N M, Suarez G, Conconi M S, Singh S K and Aglietti E F 2012 Proc. Mater.Sci. 1 337
[7] Cotrelli T L 1958 2nd edn. Butterworth, London
[8] Peelman S, Sun Z H I, Sietsma J and Yang Y 2014 Proc. ERE2014L 1st Eur.RER Conf. 446
[9] Xing P, Li F, Guo J and Tu G 2010 J. Rare Earths 28 194
[10] Xing P, Zhuang Y, Tu G and Guo J 2010 Trans. Nonferrous Met. Soc. China 20 2392
[11] Boulos M I 1985 Pure Applied Chem. 57 (9) 1321
[12] http://www.jsia.gr.jp/data/handling_02e.pdf