

# Effect of the value of $x$ in $\text{NH}_4\text{F} \cdot x\text{HF}$ on the digestion of plasma-dissociated zircon

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## ABSTRACT

Ammonium acid fluoride ( $\text{NH}_4\text{F} \cdot x\text{HF}$ ) has been identified as an alternative fluorinating agent for zircon, and may provide a method by which a wide variety of anhydrous metal fluorides can be synthesized. Data on the kinetics of the reaction of  $\text{NH}_4\text{F} \cdot x\text{HF}$  with plasma-dissociated zircon, combined with the thermodynamic parameters, are essential for the development of an industrial process for the production of a precursor for the manufacture of zirconium metal, viz. anhydrous  $\text{ZrF}_4$ . The reaction yields  $(\text{NH}_4)_3\text{ZrF}_7(\text{s})$  and  $(\text{NH}_4)_2\text{SiF}_6(\text{s})$ , the latter forming volatile products at relatively low temperatures, affording easy separation of silicon from the zirconium compound. Another useful aspect of the process is the possibility of recycling, since the ammonia and hydrogen fluoride in the waste stream can be recombined, making them available for re-use as the acid fluoride. It was found that the reaction constant  $k''$  varies exponentially with temperature at a set value of  $x$ , but linearly with changes in  $x$  at a set temperature. The activation energy for the digestion is between 20 and 47  $\text{kJ} \cdot \text{mol}^{-1}$  for the values of  $x$  investigated.

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## 1. Introduction

South Africa is currently the world's second largest producer of zircon ( $\text{ZrSiO}_4$ ), after Australia, and has the largest zircon reserve base in the world (30%), of which a large portion is exported. Globally only 5 to 10% of all zircon is destined for metal manufacturing, primarily the production of zircalloy (the generic name for metal alloys containing predominantly zirconium, along with minor alloying agents such as tin and niobium). Zircalloy is used in water-cooled nuclear reactors as cladding for fuel rods because of its low thermal neutron cross-section, its excellent thermal stability, and corrosion resistance.

Zirconium and hafnium always occur together in nature in a ratio of roughly 50:1. These two elements have near identical chemical and physical properties, but are opposites in terms of their thermal neutron capture cross section. For this reason hafnium, a strong neutron absorber, finds application in nuclear reactors as control rods, while zircalloy is used as cladding for fuel rods. It is therefore imperative that hafnium is only present as trace amounts in zirconium alloys and vice versa.

Another important specification for nuclear-grade zirconium metal is that the levels of oxygen, hydrogen and nitrogen are extremely low to prevent brittleness of the zircalloy tubes. A product that conforms to this specification can be more efficiently manufactured by

implementation of a dry, anhydrous processing route. Ammonium acid fluoride ( $\text{NH}_4\text{F} \cdot x\text{HF}$ , with  $x$  known as the acid number) is generated as waste in certain industrial processes, e.g. for the non-electrolytic production of  $\text{NF}_3$ , with significant cost implications for these manufacturers. A process that uses the ammonium acid fluoride waste as a fluorinating agent for zirconium may provide a solution to the issue of zirconium processing, and a use for ammonium acid fluoride waste.

Zircon is notoriously difficult to process because it is chemically inert and insoluble in most conventional acids under normal conditions (Kaiser et al., 2008). Current processing involves digestion of the mineral in large quantities of sodium hydroxide at temperatures varying from 150 °C (Abdel-Rehim, 2005) to above 900 °C (Biswas et al., 2010a, 2010b), or by conversion to zirconium tetrachloride via a carbonylation process, followed by liquid–liquid extraction using methyl isobutyl ketone. Both of these methods are energy-intensive and/or generate large liquid waste streams. A more cost-effective and environmentally-friendly process would therefore be a huge advantage.

Plasma-dissociated zircon has been studied by several researchers over the last four decades (Khor, 1997; Syamaprasad et al., 1992; Wilks et al., 1972). E.g. a plasma process was developed whereby zircon can undergo phase dissociation at temperatures above 1700 °C by the South African Nuclear Energy Corporation (Nel and C.I.P. Office, 1995). Conversion of 95% is achieved within 15 ms contact time. This procedure was employed when preparing the PDZ samples for this study. The product consists of particles with a 120  $\mu\text{m}$  outside diameter (determined by sedimentation analysis) which is a conglomerate of zirconia

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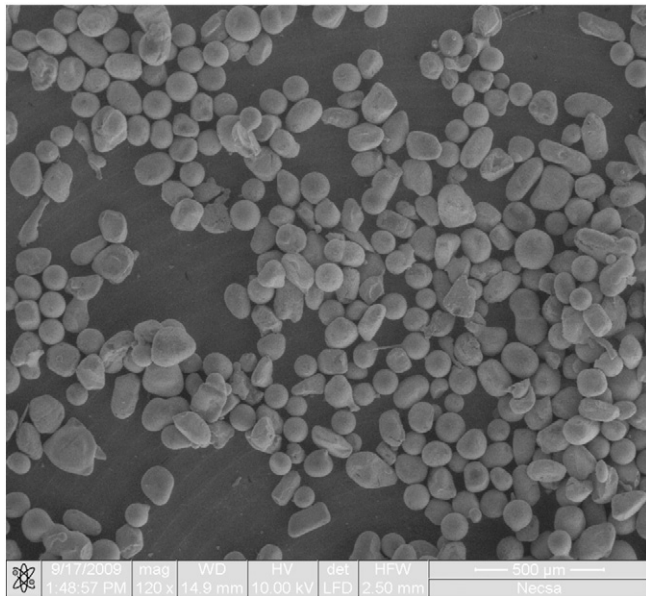


Fig. 1. SEM Image of plasma dissociated zircon particles.

(ZrO<sub>2</sub>) crystals (<1 µm) embedded in an amorphous silica (SiO<sub>2</sub>) matrix. This phase dissociated zircon (known as plasma-dissociated zircon, PDZ, ZrO<sub>2</sub>·SiO<sub>2</sub>) is chemically much more reactive than zircon and can be processed more efficiently. SEM analysis (Fig. 1) of the PDZ particles used in this study indicates that the particles are roughly spherical.

For reasons of efficiency, cost-effectiveness, and environmental friendliness, a dry processing route for PDZ is preferred. Candidates are treatment with elemental fluorine, anhydrous hydrogen fluoride, or NH<sub>4</sub>F·xHF. This article reports results achieved with the latter compound.

The reaction of NH<sub>4</sub>F·xHF with metal oxides yields intermediates known as ammonium fluorometallates (Mel'nichenko et al., 1994; Mikhailov et al., 1973; Onishi et al., 1993). In the case of PDZ, the intermediates (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> are formed. At temperatures higher than the initial temperature at which the fluorination takes place, these intermediate compounds decompose to the corresponding metal fluoride and gaseous HF and NH<sub>3</sub> (Kinsman and Hanney, 1995). The ammonium fluorosilicate compound decomposes at a lower

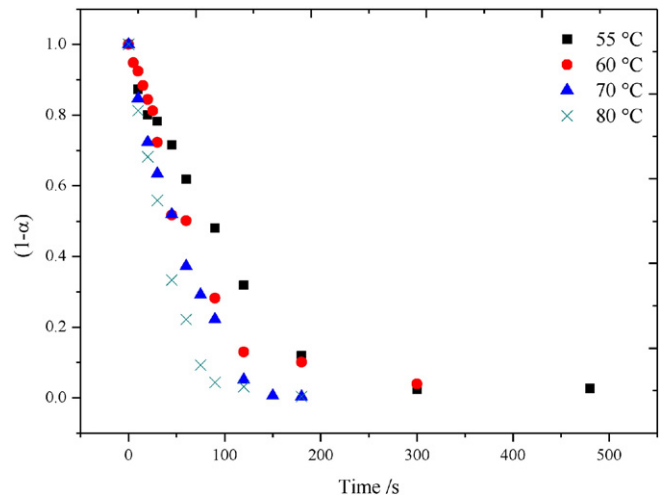
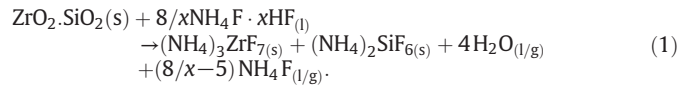


Fig. 3. Conversion of plasma-dissociated zircon with NH<sub>4</sub>F·1.5HF at different temperatures.

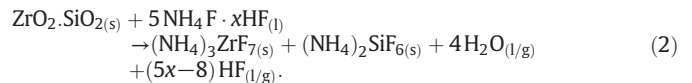
temperature (Mel'nichenko et al., 2004) than the zirconate, enabling desilication (Mel'nichenko et al., 1996).

The stoichiometric reaction of plasma-dissociated zircon with ammonium acid fluoride to produce ZrF<sub>4</sub> can be described by the chemical reactions below:

For  $0 \leq x \leq 8/5$ :



For  $x > 8/5$ :



The product NH<sub>4</sub>F, which may be gas or liquid, decomposes thermally to form gaseous ammonia and hydrogen fluoride while silicon tetrafluoride decomposes to gaseous products as well:

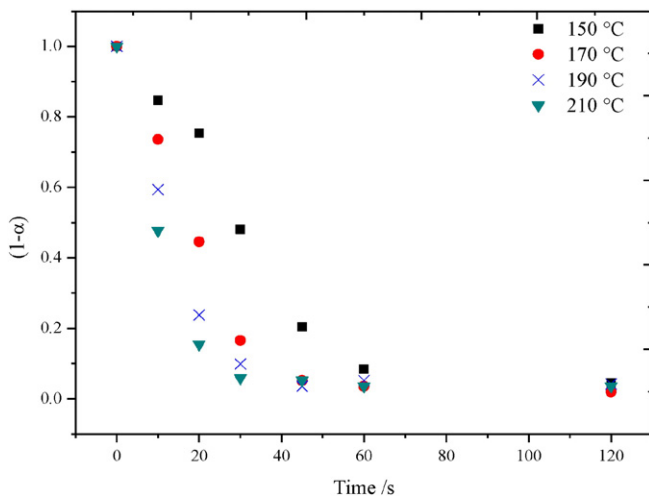
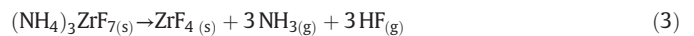


Fig. 2. Conversion of plasma-dissociated zircon with NH<sub>4</sub>F·HF at different temperatures.

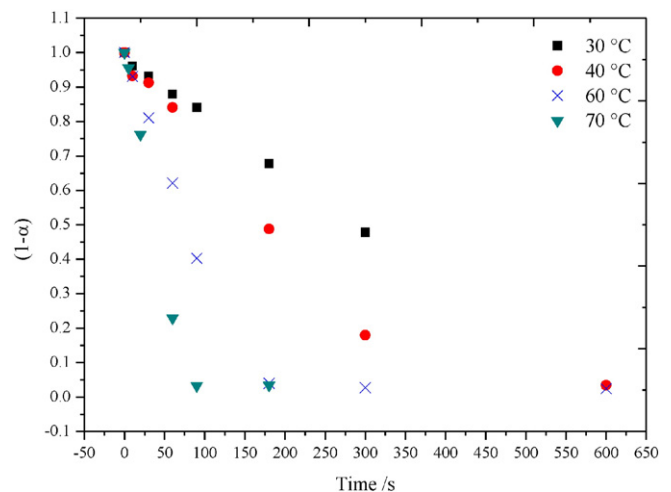


Fig. 4. Conversion of plasma-dissociated zircon with NH<sub>4</sub>F·2HF at different temperatures.

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