Effect of the value of *x* in NH$_4$F·*x*HF on the digestion of plasma-dissociated zircon

W. du Plessis[a1], A. D. Pienaar[a*], C.J. Postma[a], P.L. Crouse[b]

[a]The South African Nuclear Energy Corporation SOC Ltd. (Necsa), P.O Box 582, Pretoria, 0001, South Africa, [b]Department of Chemical Engineering, University of Pretoria, Pretoria, 0002, South Africa.

*Corresponding Author e-mail: andrew.pienaar@necsa.co.za
Tel: (+27)12 305 3269
Fax (+27)12 305 3197

Abstract Ammonium acid fluoride (NH$_4$F·*x*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 NH$_4$F·*x*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 ZrF$_4$. The reaction yields (NH$_4$)$_3$ZrF$_{7(s)}$ and (NH$_4$)$_2$SiF$_{6(s)}$, 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 kJ.mol^{-1} for the values of *x* investigated.

1. Introduction

South Africa is currently the world's second largest producer of zircon (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

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[1] Relocated to Department of Science and Technology, Private Bag X894, Pretoria, 0001

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 ($NH_4F \cdot xHF$, with x known as the acid number) is generated as waste in certain industrial processes, *e.g.* for the non-electrolytic production of 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; Biswas *et al.*, 2010b), or by conversion to zirconium tetrachloride *via* a carbo-chlorination 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, 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 μm outside diameter (determined by sedimentation analysis) which is a conglomerate of zirconia (ZrO_2) crystals (< 1 μm) embedded in an amorphous silica (SiO_2) matrix. This phase dissociated zircon (known as plasma-dissociated zircon, PDZ, $ZrO_2 \cdot SiO_2$) is chemically much more reactive than zircon and can be processed more efficiently. SEM analysis (Figure 1) of the PDZ particles used in this study indicates that the particles are roughly spherical.
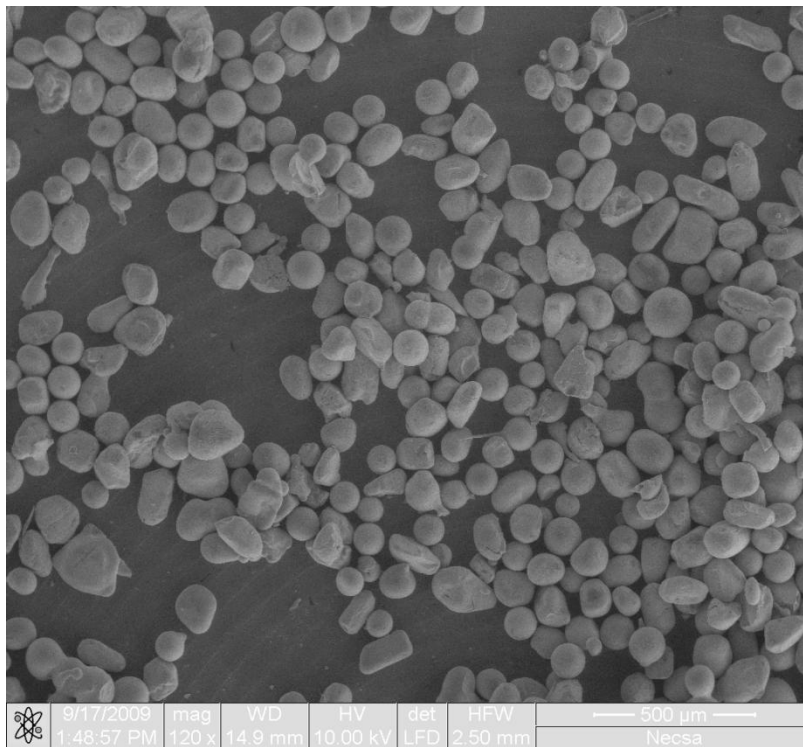

Figure 1 SEM Image of plasma dissociated zircon particles.
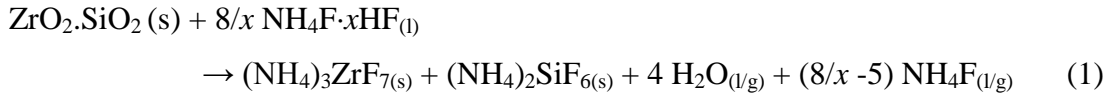
For reasons of efficiency, cost-effectiveness, and environmental friendliness, a dry processing route for PDZ is preferred. Candidates are treatment with elemental fluorine,

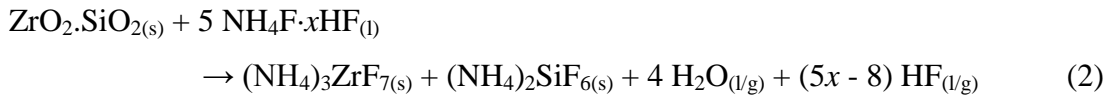anhydrous hydrogen fluoride, or $NH_4F \cdot xHF$. This article reports results achieved with the latter compound.

The reaction of $NH_4F \cdot xHF$ 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 $(NH_4)_3ZrF_7$ and $(NH_4)_2SiF_6$ 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_3 (Kinsman and Hanney, 1995). The ammonium fluorosilicate compound decomposes at a lower 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_4 can be described by the chemical reactions below:
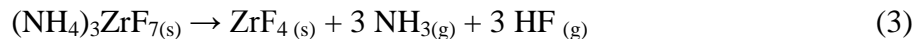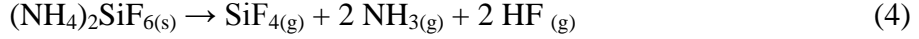
For $0 \leq x \leq 8/5$:

$$ZrO_2.SiO_2\,(s) + 8/x\ NH_4F \cdot xHF_{(l)}$$
$$\rightarrow (NH_4)_3ZrF_{7(s)} + (NH_4)_2SiF_{6(s)} + 4\ H_2O_{(l/g)} + (8/x - 5)\ NH_4F_{(l/g)} \qquad (1)$$

For $x > 8/5$:

$$ZrO_2.SiO_{2(s)} + 5\ NH_4F \cdot xHF_{(l)}$$
$$\rightarrow (NH_4)_3ZrF_{7(s)} + (NH_4)_2SiF_{6(s)} + 4\ H_2O_{(l/g)} + (5x - 8)\ HF_{(l/g)} \qquad (2)$$

The product NH_4F, which may be gas or liquid, decomposes thermally to form gaseous ammonia and hydrogen fluoride while silicon tetrafluoride decomposes to gaseous products as well:

$$(NH_4)_3ZrF_{7(s)} \rightarrow ZrF_{4\,(s)} + 3\ NH_{3(g)} + 3\ HF_{\,(g)} \qquad (3)$$

$$(NH_4)_2SiF_{6(s)} \rightarrow SiF_{4(g)} + 2\,NH_{3(g)} + 2\,HF\,_{(g)} \tag{4}$$

The two reaction equations assume that only the HF is involved in the dissolution of the oxides.The reagent and product phases are dependent on the temperature regime one is working in. In general it is preferred to have the ammonium acid fluoride as a liquid to prevent mass transfer problems. Therefore, the upper and lower temperature bounds are the melting and decomposition temperature of the acid fluoride, which are determined by the value of x.

2.   Experimental

PTFE containers each containing about 10 g of $NH_4F \cdot HF$, $NH_4F \cdot 1.5HF$ and $NH_4F \cdot 2HF$ respectively were heated to the desired temperature for roughly one hour. Samples of 1 g (>94 %) plasma-dissociated zircon were weighed and the mass recorded. PDZ, prepared according to the method (Nel, 1995), was added to the heated ammonium acid fluoride and lightly shaken/stirred for the duration of t at several time intervals between 5 s and 60 min. To quench the reaction, a boric acid solution was added to the reaction mixture at time t, after which the reaction mixture was rinsed with water to remove water-soluble reaction products. The remainder of the reaction mixture was dried, weighed and the exact mass of unreacted feedstock material was determined. The experiment was repeated at different reaction temperatures (T $\geq$ 135 °C for $NH_4F \cdot HF$, T $\geq$ 40 °C for $NH_4F \cdot 1.5HF$, and T $\geq$ 20 °C $NH_4F \cdot 2HF$).

3.   Results and discussion

3.1   Reaction model

The chemical-reaction controlled, shrinking-particle model (Levenspiel, 1999) was assumed due to the spherical nature of the particles. For this model it is assumed that all plasma-dissociated zircon particles have an initial radius R, and radius r at reaction time t. This assumption is supported by the straight line fits that are obtained when plotting the integral reaction model against time (section 3.2).

The fluid-solid reaction, where A_{fluid} represents the molten $NH_4F \cdot xHF$ and B_{solid} the PDZ to be fluorinated, is given by:

$$A_{fluid} + bB_{solid} \rightarrow products \qquad (3)$$
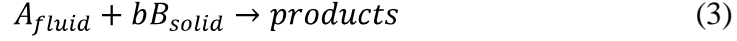
The rate of fluorination is assumed directly proportional to the available surface area of the plasma-dissociated zircon particles, therefore:

$$-\frac{1}{4\pi r^2}\frac{dN_B}{dt} = bk''C_A \qquad (4)$$

With k'' the rate constant and C_A the concentration of HF (C_{HF} hereafter, and taken as first order) in the liquid phase, which is directly proportional to the value of x in $NH_4F \cdot xHF$. After relating the molar change to the particle radius, integration yields:

$$r - R \ = -\ \frac{bk''C_{HF}}{\rho_B}\ t \qquad (5)$$

The fractional conversion $(1 - \alpha)$ is equal to the ratio of the particle volume at time t to the initial volume, therefore:

$$1 - \alpha^{1/3} = 1 - \frac{bk''C_{HF}}{R\rho_B}\ t \qquad (6)$$

A plot of $1 - \alpha^{1/3}$ against t should therefore result in a straight line with slope $-\frac{bk''C_{HF}}{R\rho_B}$. The values for k'' can accordingly be calculated for the different isothermal temperatures.

Differentiation of Equation (6) gives a rate expression of the form:

$$\frac{d\alpha}{dt} = -\frac{bk''C_{HF}}{R\rho_B} 3 \ 1 - \alpha^{\ 2/3} \qquad (7)$$

which is simply the well-known solid-state kinetics expression for a shrinking particle. (Khawam and Flanagan, 2006), where $f\ \alpha\ =\ 1 - \alpha^{\ 2/3}$ is the kinetic function that describes the reaction mechanism and $k\ T$ the Arrhenius constant:

$$k\ T\ = \frac{3bC_{HF}}{R\rho_B} k'' = Ae^{-E_a/RT} \qquad (8)$$

with A the pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature. Values for $k(T)$ are calculated by determining the slope of $1 - \alpha^{\ 1/3}$ against time (Equation 7) for a given temperature, and the kinetic parameters A and E_a are determined from an Arrhenius plot, along with k'', from the known system parameters.

3.2   Data analysis

When PDZ is reacted with ammonium bifluoride ($x = 1$) at temperatures above its melting point, conversion of more than 95% is achieved within reasonably short reaction periods as can be seen in Figure 2. Complete conversion of PDZ is also achieved with the higher x-value acid fluorides (Figures 3 and 4) at much lower temperatures, but at a significant time cost.
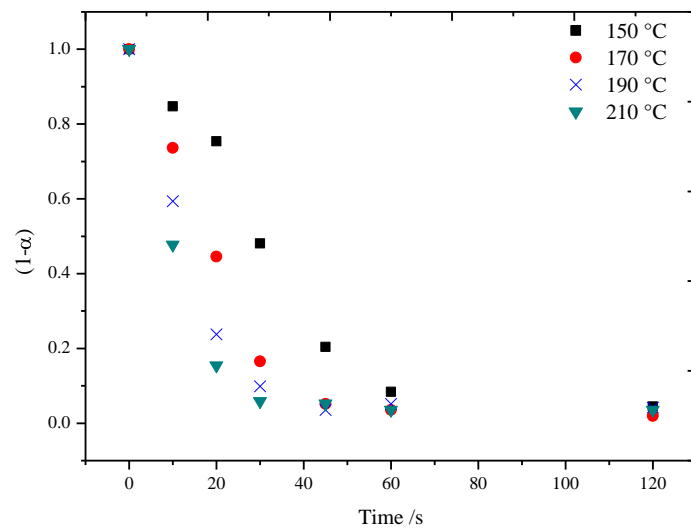
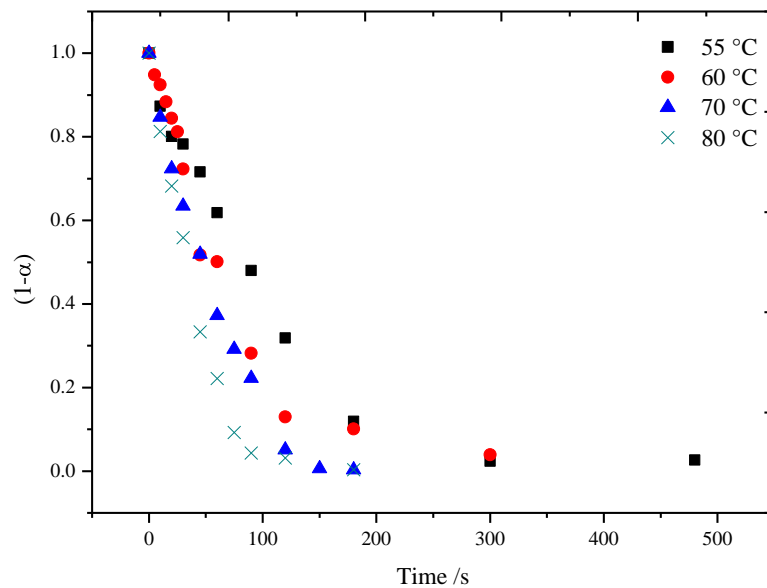**Figure 2** Conversion of plasma-dissociated zircon with NH$_4$F·HF at different temperatures.

Figure 3 Conversion of plasma-dissociated zircon with NH$_4$F·1.5HF at different temperatures.

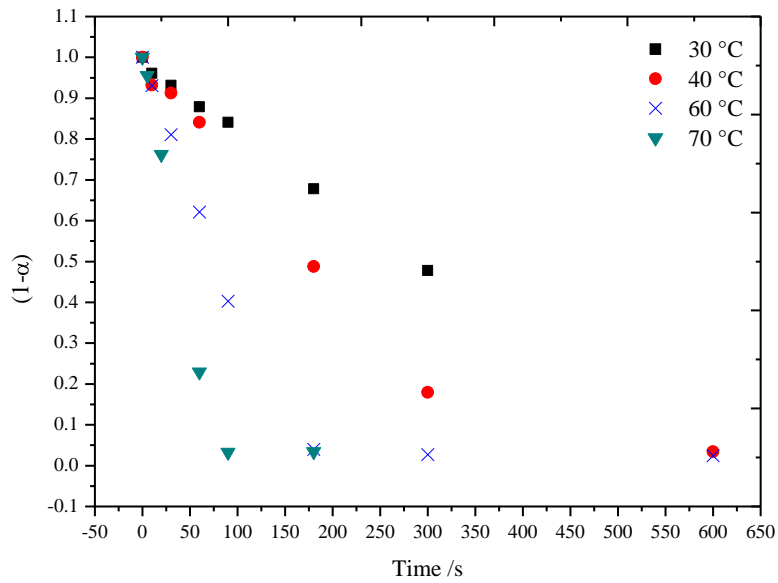**Figure 4** Conversion of plasma-dissociated zircon with $NH_4F \cdot 2HF$ at different temperatures.

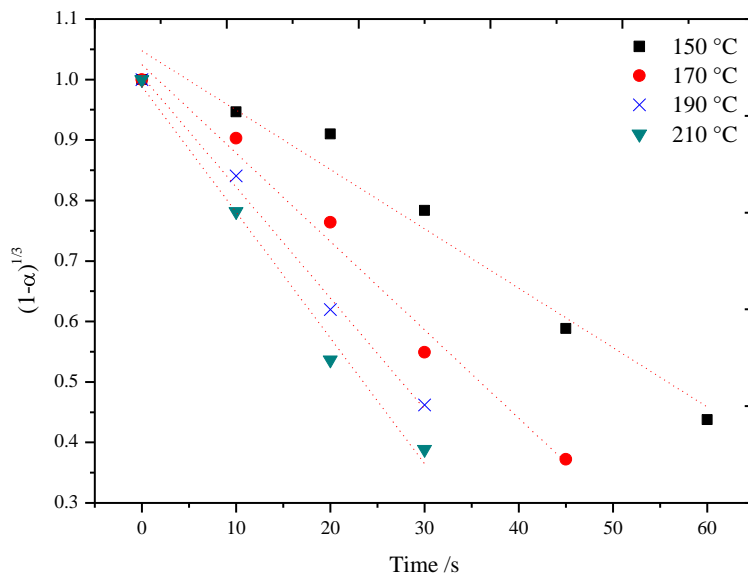**Figure 5** Plot of $(1-\alpha)^{1/3}$ vs time for the reaction of plasma-dissociated zircon with $NH_4F \cdot HF$.

Plots of $(1-\alpha)^{1/3}$ vs t, for each are shown on Figures 5, 6 and 7 with the corresponding slopes, $k(T)$ and rate constant k'' in Table 1. The good correlation with linearity of these plots, support the shrinking particle model initially assumed. Values in italics were linearly extrapolated.
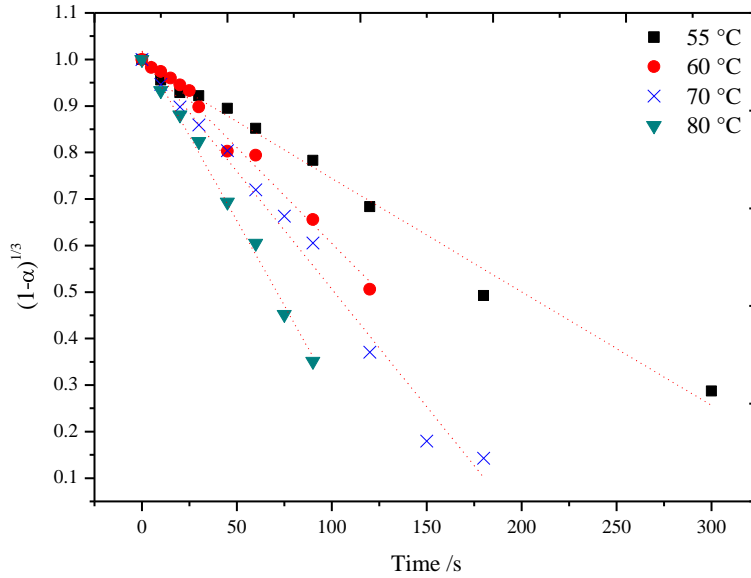

Figure 6 Plot of $\alpha^{1/3}$ vs time for the reaction of plasma-dissociated zircon with $NH_4F \cdot 1.5HF$

Table 1 *$k(T)$ and k'' values obtained* $(1-\alpha)^{1/3}$ vs t plots.

| Temp /°C	k	k''	Temp /°C	k	k''	Temp /°C	k	k''
55	*-0.0019*	*0.0006*	55	-0.0027	0.0004	30	-0.0007	0.0001
60	*-0.0022*	*0.0007*	60	-0.0041	0.0006	40	-0.0012	0.0002
70	*-0.0027*	*0.0009*	70	-0.0053	0.0008	60	-0.0026	0.0004
80	*-0.0033*	*0.0011*	80	-0.0073	0.0010	70	-0.0076	0.0011
150	-0.0098	0.0032	*150*	*-0.0591*	*0.0084*	150	-0.0717	0.0074
170	-0.0146	0.0047	*170*	*-0.0924*	*0.0132*	170	-0.1207	0.0131
190	-0.0184	0.0059	*190*	*-0.1389*	*0.0198*	190	-0.1942	0.0221
210	-0.0208	0.0067	*210*	*-0.2020*	*0.0289*	210	-0.3003	0.0358
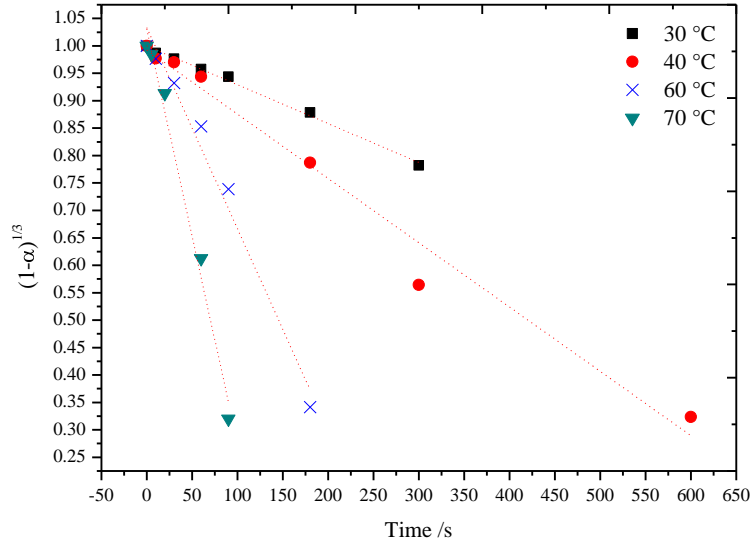
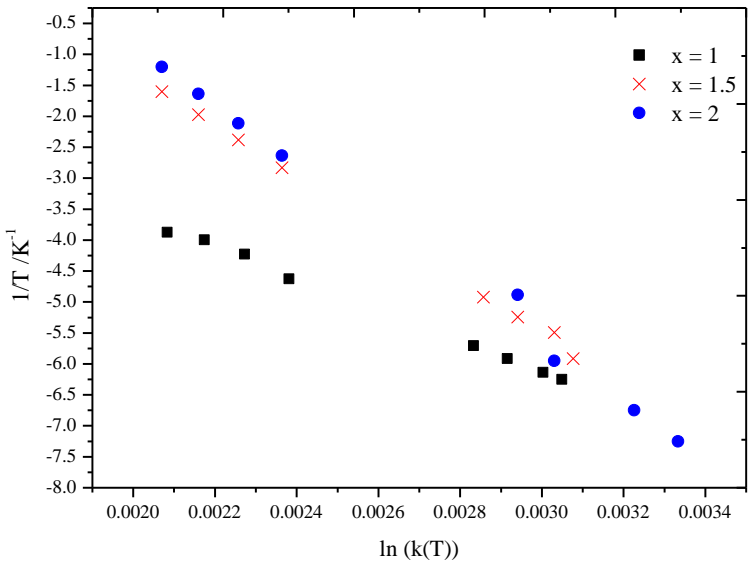**Figure 7** Plot of $\alpha^{\frac{1}{3}}$ vs time for the reaction of plasma-dissociated zircon with $NH_4F \cdot 2HF$

Figure 8 Arrhenius plots for the reaction of plasma dissociated zircon and $NH_4F \cdot xHF$.

Table 2   Kinetic constants, and linear fit correlation of $(1-\alpha)^{1/3}$ vs t, for the dissolution if PDZ in $NH_4HF \bullet xHF$.

	$x = 1$	$x = 1.5$	$x = 2$
E_a (kJ.mol^{-1})	20.97	34.80	46.70
A (s^{-1})	4.21	1171	88212
R^2	0.96	0.96	0.95

The calculated E_a values are 21 kJ.mol^{-1} for $NH_4HF \cdot xHF$ when $x = 1$, 35 kJ.mol^{-1} for $x = 1.5$ and 47 kJ.mol^{-1} for $x = 2$.
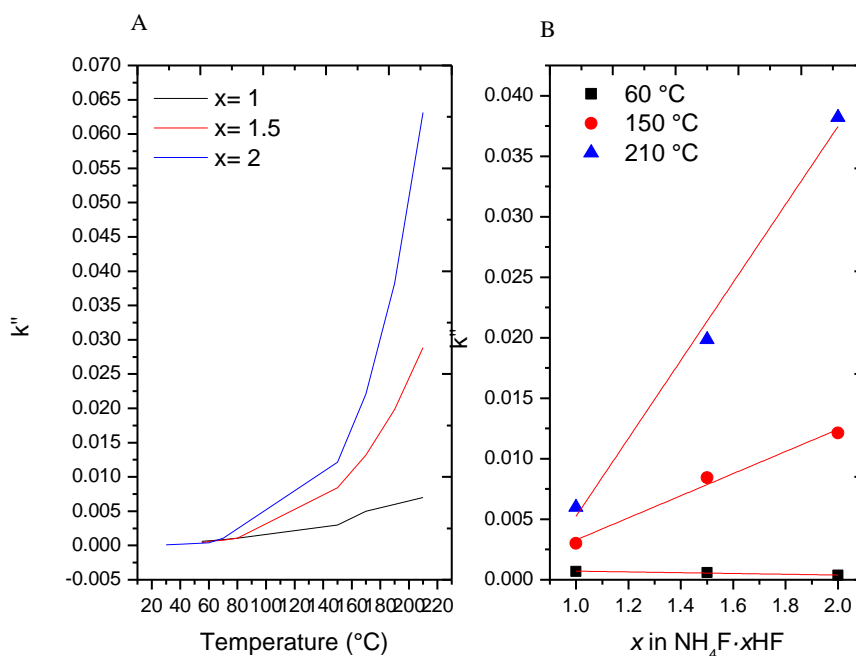

Figure 9 k'' related to A) temperature and B) value of x

By relating the value of k'' to temperature for different concentrations (Figure 9), it is seen that an exponential relationship exists between the value of k'' and temperature, but linear with respect to x in $NH_4HF \cdot xHF$ which indicates that the dependence on concentration is not first order as initially assumed.

Specific concentration dependence constants are given in table 3.

Table 3 Dependence of k'' on temperature at different values of x.

Value of x (in $NH_4HF.xHF$)	$k'' = ae^{bT}$	
	a	**b**
1	3.87	1.38
1.5	2.81	2.22
2	2.35	2.67

It is clear that an increase in x, which results in increasing molar concentration of HF, improves (speeds up), the reaction kinetics. This not only confirms that the reaction is limited by the availability of HF in the bulk solution, but also defines the exact relation thereof.

Considering the effect of x on k'' at different temperatures, it is seen that at 60 ℃, an increase in x has negligible effect on the value of k'' (table 4). At higher temperatures (150 and 210 °C) the linear increase with increasing value of x, indicates that the reaction is no longer limited by temperature and only the molar concentration of HF.

Table 4 Linear dependence of k'' on the value of x at different temperatures, with m the slope and c the intercept.

Temperature (°C)	$k''=mT + c$	
	m	**c**
60	0.000	0.001
150	0.009	-0.006
210	0.032	-0.027

4. Conclusion

The reactions of ammonium bifluoride with a variety of metal oxides are described in the literature. In this paper we pin down the exact kinetic parameters for different values of x in the general formula $NH_4F \cdot xHF$ when the compound is used to digest plasma dissociated zircon. With an increase in the value of x a linear increase in the value of k'' is observed at a given temperature, while at a specific value of x the kinetics is exponentially dependent on the temperature.

Activation energy for the digestion reaction is 21, 35 and 47 kJ.mol^{-1} for the different values of x respectively.

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