

Microwave digestion of zircon with ammonium acid fluoride: Derivation of kinetic parameters from non-isothermal reaction data

T.N. Nhlabathi ^a, J.T. Nel ^a, G.J. Puts ^b, P.L. Crouse ^{b,*}

^a The South African Nuclear Energy Corporation Ltd. (NECSA), P.O. Box 582, Pretoria, 0001, South Africa

^b Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa

ARTICLE INFO

Article history:

Received 31 July 2012

Received in revised form 15 August 2012

Accepted 16 September 2012

Available online 20 September 2012

Keywords:

Zircon

Microwave digestion

Ammonium acid fluoride

Kinetics

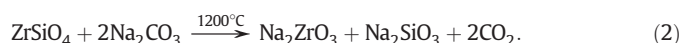
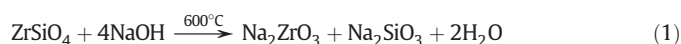
ABSTRACT

Zircon is notoriously inert. Aggressive processing methods such as alkaline fusion are conventionally used to extract zirconium values from the mineral. In this study results are presented with respect to microwave digestion of zircon using ammonium acid fluoride ($\text{NH}_4\text{F} \cdot 1.5\text{HF}$). Two distinct experimental methods were used. In the first method the reaction was followed in the temperature range of 100 to 200 °C, for a full reaction period of 60 min at each temperature. The second method comprised successive digestion periods interrupted by washing and re-introduction of fresh acid fluoride at a series of reaction temperatures varying between 120 and 240 °C. Complete digestion was achieved with the latter technique. The kinetics is shown to be controlled by product-layer diffusion. The two data sets were combined to derive consistent temperature-dependent kinetic parameters. A facile numerical technique for extracting these parameters from the experimental data is used.

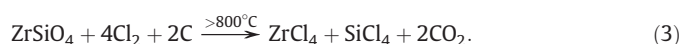
© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Zircon is chemically extremely inert (Wilks et al., 1974). The mineral is usually processed using relatively aggressive conditions, such as alkaline smelting with NaOH at 600 °C, or with Na_2CO_3 at 1200 °C (Stevens, 1986):



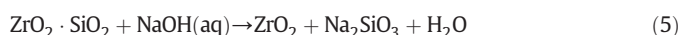
Separation of the sodium zirconate from the sodium silicate is achieved by dissolution in water, filtration, and precipitation. Alternatively zirconium tetrachloride is produced by carbo-chlorination of zircon at > 800 °C according to Bidaye et al. (1999):



Depending on the temperature, CO can also form in reaction (3). ZrCl_4 and SiCl_4 are separated by distillation. ZrCl_4 serves as a starting material for the manufacture of the metal and its alloys, as well as several zirconium chemicals.

Zircon can also be made chemically reactive by dissociation in a plasma tail-flame at > 1700 °C, producing so-called plasma-dissociated zircon

(PDZ, $\text{ZrO}_2 \cdot \text{SiO}_2$). This material is essentially microcrystalline zirconia particles embedded in an amorphous silica matrix. The amorphous silica can be selectively removed using a concentrated NaOH solution, or completely dissolved using aqueous HF (Williamson and Evans, 1979; Wilks et al., 1972; McPherson and Shafer, 1985; Nel, 1999):



H_2ZrF_6 and H_2SiF_6 are separated by evaporative crystallization. The crystallization also serves as a purification step for H_2ZrF_6 . Pure ZrO_2 can be produced from H_2ZrF_6 by steam pyrolysis:



PDZ can alternatively be subjected to dry fluorination using anhydrous HF (Nel, 1997):



We here extend the work reported recently (Nel et al., 2011) in which results pertaining to the microwave digestion of zircon with ammonium acid fluoride (AAF) were presented. It was shown that complete dissolution could be achieved if the unreacted zircon is intermittently removed from the digestion vessel, washed with water, and re-introduced into the system with fresh AAF. The rate limiting step was tentatively identified as product-layer diffusion, and effective

* Corresponding author. Tel.: +27 12 420 2856; fax: +27 12 420 5048.

E-mail address: philip.crouse@up.ac.za (P.L. Crouse).

diffusion constant derived on the assumption of a linear contribution to the reaction time by the heating and cooling steps. Here we introduce a more correct method for extraction of the kinetic data from what is essentially a non-isothermal system, and introduce new data pertaining to the case where the product is not subjected to repeated washing cycles.

2. Experimental

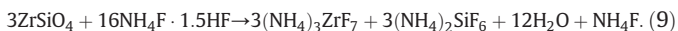
2.1. Chemicals and apparatus

Prime grade zircon (d_{50} particle size 125 μm) obtained from Namakwa Sands was used. Ammonium acid fluoride (AAF, $\text{NH}_4\text{F} \cdot 1.5\text{HF}$) was obtained from Pelchem Ltd. HF (40%) and H_3BO_3 were from Merck and were of analytical grade. All chemicals had a purity of >99%. A CEM Mars 5 programmable microwave unit was used for the experimental work. The system is capable of delivering a maximum power of 1600 W at a frequency of 2450 MHz. The sample carousel allows for up to twelve digestion vessels to be mounted simultaneously, one of which is a control vessel for monitoring pressure and temperature. These data are used for feedback control of the reaction conditions. The carousel rotates slowly through 360° during processing. CEM XP-1500 PFA lined digestion vessels (100 mL) and caps were used in these experiments. The maximum recommended working pressure and temperature of the vessels are 5.5 MPa and 240°C respectively. In all cases temperature was controlled, and reactor pressure was monitored.

The residue was analyzed by FT-Raman spectrometry (Bruker Ram II) and XRD (Bruker A-D8 Advance), as reported by Nel et al. (2011).

2.2. Experimental procedures

It is assumed that the reaction between zircon and $\text{NH}_4\text{F} \cdot 1.5\text{HF}$ proceeds according to:



AAF and ammonium fluoride, as well as the two ammonium fluorometallates, $(\text{NH}_4)_3\text{ZrF}_7$ and $(\text{NH}_4)_2\text{SiF}_6$, are totally soluble in water (Hala, 1989; Frayret et al., 2006). The fractional conversion, α , is thus readily obtained by washing, filtering, and drying the zircon residue after time t . The fractional conversion α is defined as the ratio of the residual mass m_{Residue} and the initial mass m_0 .

A starting mass of 0.5 g zircon was used for each set of experiments. This was mixed with 5 g of $\text{NH}_4\text{F} \cdot 1.5\text{HF}$ in the microwave vessel. Assuming that the reaction proceeds according to Eq. (9), this represents a roughly 5:1 excess based on AAF. The vessel was capped and placed in the microwave system for the desired time at a selected temperature setting. After completion, the vessel was cooled to room temperature, uncapped, and the reaction stopped by addition of 50 mL of 3% boric acid (H_3BO_3) solution to neutralize the remaining free and bound HF. The reaction proceeds according to Eqs. (10) and (11), with the formation of water-soluble HBF_4 and NH_4BF_4 :



The reaction mixture was centrifuged and the supernatant liquid decanted. The solid residue was washed with water and propanol, dried at 80°C for 3 h and weighed.

Two distinct experimental procedures were employed. In the first case (Procedure 1), the samples were digested for full reaction times (excluding heating and cooling times) of 10, 20, 30, and 60 min for the reaction temperatures 100, 120, 140, 160, 180, and 200°C .

Thus for each reaction temperature four samples were used, and for each of these data points an initial and final value of α was obtained. In the second case (Procedure 2) one sample was used for each of the reaction temperatures 120, 140, 160, 180, 200, 220, and 240°C . The reaction temperatures 100, 120, 140, 160, 180, 200, 220, and 240°C correspond to reactor pressure values of 15, 20, 27, 30, 32, 37, 39, and 45 bar respectively. For each temperature the sample was removed after ten minutes and the residual mass fraction determined after washing and drying as described above. The same sample was then re-introduced into the digestion vessel, and treated again. These cycles were repeated with a ten minute extension of reaction time up to a maximum of 60 min (total digestion time per series 260 min).

3. Results and discussion

The experimental results are given in Table 1 and Table 2 for Procedures 1 and 2 respectively. In both cases an increase in temperature clearly increases the rate of conversion of zircon. For Procedure 1 where no washing of the residue was performed, a minimum α value of 0.69 was obtained. This corresponds to 30% conversion only. For Procedure 2 about 30% ($\alpha=0.70$) of the zircon was converted at 120°C after 285 min, while >99% ($\alpha=0.007$) conversion was achieved at 240°C , the highest temperature investigated.

A number of kinetic models are possible for fluid–solid reactions (Levenspiel, 1999). Based on our previous analysis and, more importantly, the fact that washing of the product layer is required for full conversion, we only consider the ash-layer diffusion control model here. For the general solid–fluid reaction



the rate expression is given by (e.g. Levenspiel, 1999)

$$3\alpha^{2/3} - 2\alpha = 1 - \frac{t}{\tau} \quad (13)$$

with

$$\tau = \frac{\rho_s r_0^2}{6bM_s D_e c}. \quad (14)$$

Table 1
Fractional conversion data for Procedure 1.

Time (min)	100 °C α	120 °C α	140 °C α	160 °C α	180 °C α	200 °C α
0	1	1	1	1	1	1
10	0.97	0.92	0.91	0.83	0.84	0.81
20	0.97	0.93	0.88	0.84	0.81	0.75
30	0.94	0.93	0.87	0.81	0.76	0.72
60	0.95	0.89	0.82	0.77	0.69	0.69

Table 2
Fractional conversion data for Procedure 2, i.e. with intermittent washing and addition of fresh $\text{NH}_4\text{F} \cdot 1.5\text{HF}$.

Cumulative digestion time (min)	120 °C α	140 °C α	160 °C α	180 °C α	200 °C α	220 °C α	240 °C α
0	1	1	1	1	1	1	1
22.5	0.933	0.927	0.873	0.843	0.743	0.637	0.667
55.0	0.847	0.847	0.767	0.653	0.553	0.533	0.340
97.5	0.820	0.787	0.690	0.553	0.380	0.360	0.187
150.0	0.773	0.750	0.583	0.367	0.307	0.290	0.073
212.5	0.733	0.703	0.477	0.253	0.167	0.163	0.047
285.0	0.700	0.640	0.403	0.130	0.120	0.093	0.007

Download English Version:

<https://daneshyari.com/en/article/214124>

Download Persian Version:

<https://daneshyari.com/article/214124>

[Daneshyari.com](https://daneshyari.com)