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## INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

## Autoclave Breakdown of Zircon with Ammonium Fluorides

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Abstract-Autoclave breakdown of zircon with ammonium fluorides was studied.

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Zircon is one of the main mineral sources of zirconium materials, but the technology of its breakdown and processing is still labor-consuming, and much efforts are made to improve it.

The classical industrial methods of breaking down zirconium concentrates are sintering with fluosilicates and chlorination. Numerous studies summarized in [1] were devoted to zircon fluorination; however, it did not gain industrial application. The fluoride technology allows the scheme of the zirconium product processing to be reduced considerably, but high cost and corrosive behavior of HF and  $F_2$ , and also SiF<sub>4</sub> liberation restrain industrial application of these reagents.

In this study we examined the autoclave breakdown of zircon with ammonium fluorides.

Unlike fluorine and hydrogen fluoride, ammonium fluorides are very convenient to use, as these are solid crystalline substances under normal conditions. Ammonium fluorides can be obtained from metal fluorides by the action of ammonia water, which is the basis for conversion and recycling of ammonium fluorides.

Ammonium fluoride is known to react slowly with zircon [2, 3]. At temperatures below 240°C, the reaction rate is negligible and the degree of breakdown is unsatisfactory for the industrial use, whereas at higher temperatures ammonium fluoride evaporates with decomposition.

Here we report new data on the zircon breakdown with ammonium fluoride and hydrofluoride.

The essence of the method consists in the reaction of zircon with ammonium fluoride or hydrofluoride under isochoric conditions (in an autoclave), after which the reaction products are separated by sublimation to give zirconium tetrafluoride and dioxide. The advantage of ammonium fluorides over other fluorinating agents consists in their convenient physicochemical properties allowing their regeneration and recycling.

The experiments were carried out with zircon samples from Tugan deposit of Tomsk oblast.

The reactions of zircon with ammonium fluoride and hydrofluoride were studied under isochoric conditions in a 100 cm<sup>3</sup> stainless steel autoclave. A weighed portion of zircon with a grain size of 0.074 mm was placed in the autoclave together with a weighed portion of ammonium fluoride taken in a 20% excess in relation to the stoichiometric amount calculated for the reaction

$$ZrSiO_4 + 13NH_4F = (NH_4)_3ZrF_7 + (NH_4)_2SiF_6 + 8NH_3$$
  
+ 4H<sub>2</sub>O.

The autoclave was heated to 150, 200, 250, 300, 350, and 400°C and kept at these temperatures for 0.5, 1, 2, and 4 h.

After opening the autoclave, its content was transferred into a crucible and calcined for 30 min at 400°C to remove by sublimation unchanged  $NH_4F$ and formed  $(NH_4)_2SiF_6$ . The residue in the crucible was a mixture of unchanged  $ZrSiO_4$  and  $NH_4ZrF_5$ , to which 5 ml of concentrated sulfuric acid was added, and the mixture was kept until  $H_2SO_4$  vapor disappeared. Zirconium in the form of  $ZrOSO_4$  solution was leached with water from the formed cake, converted to zirconium dioxide, and weighed to determine the degree of conversion.

The same procedure was used to study the reaction of ammonium hydrofluoride with zircon

$$2\text{ZrSiO}_4 + 13\text{NH}_4\text{F} \cdot \text{HF} = 2(\text{NH}_4)_3\text{ZrF}_7 + 2(\text{NH}_4)_2\text{SiF}_6$$
  
+  $3\text{NH}_3 + 8\text{H}_2\text{O}.$ 



The data on the kinetics of zircon breakdown with ammonium fluoride are given in Fig. 1, which contains two series of curves: the first corresponds to temperatures below ammonium fluoride boiling point and the second, to elevated temperatures.

The standard mathematical treatment of the kinetic data showed that the curves for 150, 200, and 250°C are described with an adequate accuracy by Gray–Weddington's, and the curves for 300, 350 and 400°C, by Crank–Ginstling–Brounshtein's equation.

The rate equation for the range 150-250°C is

$$\alpha = 1 - [1 - 10^{-3} \exp(-17000/RT)t]^3.$$

The activation energy  $E_A$  is 17 kJ mol<sup>-1</sup>, which corresponds to the diffusion control, the preexponential factor  $k_0 = 10^{-3} \text{ s}^{-1}$ , and the gas constant R = 8.31.



**Fig. 1.** Kinetic curves for the reaction of ammonium fluoride with zircon under isochoric conditions. ( $\alpha$ ) Degree of conversion degree and ( $\tau$ ) time; the same for Fig. 2. Temperature, °C: (1) 150, (2) 200, (3) 250, (4) 300, (5) 350, and (6) 400.

The rate equation for the range 300-400°C is

$$1 - 1/3 \alpha (1 - \alpha)^{1/3} = \exp(-5500/RT) t.$$

The activation energy  $E_A = 55 \text{ kJ mol}^{-1}$ , which corresponds to the kinetic control, the preexponential factor  $k_0 = 1 \text{ s}^{-1}$ , and the gas constant R = 8.31. Material streams and material balance were calculated in accordance with Scheme 1.

Scheme 1 clearly illustrates the breakdown of zircon with ammonium fluoride and the formation of complexes followed by their hydrolysis and ammonium fluoride regeneration. Uniqueness of ammonium fluorides consists in the fact that their melt is the most powerful fluorinating agent reacting with zircon to form zirconium and silicon complex fluorides. Zirconium tetrafluoride and ammonium hexafluorosilicate are easy to separate by sublimation. After separation, the fluorides are subjected to hydrolysis with ammonia. Ammonium fluoride is regenerated, and oxides are precipitated from the solution. Unlike ammonium fluoride melt, its solution is inert and does not react with oxides.

The experimental dependences of the conversion  $\alpha$  on time and temperature for the breakdown of zircon with ammonium hydrofluoride are given in Fig. 2. The kinetic curves are linearized most accurately by Yander's equation

 $\alpha = 1 - \{1 - [6.6 \exp(-54000/RT)\tau]^{1/3}\}^3.$ 

The preexponential factor is  $k_0 = 6.6 \text{ s}^{-1}$ , and the activation energy calculated from the Arrhenius equation is  $E_A = 54 \text{ kJ mol}^{-1}$ , which indicates that the process is kinetically controlled and temperature





exerts a decisive effect on its rate. Scheme 2 of material streams in the breakdown of zircon with ammonium hydrofluoride is given below.

The above-given experimental data allow us to suggest the optimal process parameters: with  $NH_4F$ ·HF, the conversion higher than 95% is reached at 300°C within 1.5 h and at 400°C, within less than 0.5 h [4].

When  $NH_4F$  was used, an elevated pressure was developed in the autoclave. The heating of ammonium fluoride is known to result in its thermal dissociation into ammonia and hydrogen fluoride, which increases the total pressure in the system [5].

The pressure of the mixture of HF and  $NH_4F$  vapors calculated by the Mendeleev–Clapeyron equation considerably exceeds the actual pressure owing to the condensation of the mixture of hydrogen fluoride and ammonia at a temperature below 240°C and also owing to considerable deviations of the behavior of this mixture from that of an ideal gas to which theoretical calculations are applicable.

To determine the real pressure which is developed under the considered conditions, we have carried out special experiments.

The temperature dependence of the vapor pressure was studied for two substances: ammonium fluoride and hydrofluoride. In a 100 cm<sup>3</sup> autoclave, 10 g of salt was placed, and the system was sealed and gradually heated to 350°C with continuous monitoring of the pressure with an MTP-1M manometer. The plots of the vapor pressure of ammonium fluoride and hydrofluoride are given in Fig. 3. Apparently, the use of ammonium fluoride at high temperatures is not appropriate because high pressures arise and hence more sophisticated equipment is required; therefore, the use of ammonium hydrofluoride is the most efficient. As follows from Fig. 3, the vapor pressure of ammonium hydrofluoride at 300°C does not exceed 45 atm, which allows its use in the technology of the zircon breakdown with ammonium hydrofluoride. A considerable experience of using high-pressure devices in the industrial synthesis of ammonia and in the transportation of natural gas has been accumulated.

The temperature of  $300^{\circ}$ C is optimal for implementation of the process, as relatively low temperature will not cause strong corrosion of the instrumentation even at a long reaction time (4 h).

A distinctive feature of the zircon breakdown with ammonium hydrofluoride is the complete regeneration



**Fig. 2.** Kinetic curves for the reaction of ammonium hydro-fluoride with zircon. Temperature,  $^{\circ}$ C: (1) 250, (2) 300, (3) 350, and (4) 400.

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**Fig. 3.** Dependence of vapor pressure *P* of (1) ammonium fluoride and (2) ammonium hydrofluoride on temperature *T* under isochoric conditions in 100 cm<sup>3</sup> of air.

of ammonium fluoride, which makes the process economically attractive and environmentally safe.

The formed ammonium fluosilicate sublimes at temperatures above 320°C and is removed from the mixture [6].

Heating to  $300^{\circ}$ C removes unchanged ammonium fluoride from the mixture. As the temperature is increased,  $(NH_4)_2$ ZrF<sub>6</sub> decomposes to zirconium tetra-fluoride, and ammonia and hydrogen fluoride are liberated.

The overall process of ammonium fluoride breakdown of zircon is shown in Scheme 3.





In the suggested scheme, the number of operations is minimized and complete recycling of the reagents is provided. Among disadvantages of the scheme is certain complexity of the instrumentation of the main process, ammonium fluoride breakdown of zircon, which is caused by the buildup of high pressure under isochoric conditions. The corrosive action of ammonium fluoride on stainless steel can be reduced by adding sodium fluoride [7]; however, the use of sodium fluoride will pose a problem of its regeneration and removal from the products.

## CONCLUSIONS

(1) Optimal parameters of zircon breakdown with ammonium fluoride and hydrofluoride in an autoclave under isochoric conditions were found. In the case of ammonium hydrofluoride, the 95% decomposition at 300°C is reached within 1.5 h, and a pressure of 45 atm is developed in the system.

(2) The overall scheme of the cycle of zircon breakdown with the regeneration of ammonium fluoride and production of zirconyl hydroxide was suggested.

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