INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

# Interaction of Baddeleyite with Sodium Nitrate and Nitrite

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Received February 27, 2012

**Abstract**—Features of baddeleivte concentrate decomposition by interaction with sodium nitrate and nitrite were researched as well as those of hydrolytic and acid decomposition of resulting cakes.

DOI: 10.1134/S1070427212070026

Baddeleyte, natural zirconium(IV) oxide, is chemically very stable. Baddeleyite concentrates (BC) are produced in Russia by JSC "Kovdor GOK" according State Standard TU 1762-003-00186759-2000 and used without any chemical processing in production of refractories, glazes, etc. For production of zirconium compounds the BC zirconium should be converted into the solution. Methods of fusing with potassium bifluoride or chlorination in the presence of a carbon reductant, which are applied to the decomposition of zircon that is similar in chemical properties, have several disadvantages. Due to this fact the search for alternative methods of processing BC, which is currently the only Russian source of raw materials of zirconium, is relevant.

For obtaining  $Na_2ZrO_3$  almost total interaction of a mixture BC with soda is reached at 1100–1200°C [1]. The high temperature of the interaction has caused certain difficulties at further cake processing as noted below.

It is shown that sodium metazirconate  $Na_2ZrO_3$  can be obtained by fusion with NaOH at 550–650°C, but due to the high cost of alkali and formation of "alkali mist" the process has been recognized as low-tech [1].

In this paper we studied the patterns of interaction of BC with low-melting compounds of sodium: sodium nitrate and nitrite. It was suggested that a liquid reagent allows reducing the decomposition temperature of BC, developing methods for production of compounds of zirconium using reagents containing sodium in circulation.

Information on the interaction of NaNO3 alloy with

metal oxides is limiting. In examination of NaNO<sub>3</sub> interaction with chemically stable  $Al_2O_3$  formation of sodium aluminate was in a temperature range of 790–870°C. Information on an  $Al_2O_3$  binding termination and the process mechanism is contradictory [2–4]. It was confirmed that NaNO<sub>3</sub> is decomposed according to the following reactions

$$2NaNO_3 = 2NaNO_2 + O_2, \tag{1}$$

$$2NaNO_2 = Na_2O + NO + NO_2.$$
(2)

At first it was suggested that sodium aluminate formation is associated with the interaction of Al<sub>2</sub>O<sub>3</sub> approximately equally with NaNO<sub>2</sub> and Na<sub>2</sub>O resulted in the following reactions

$$2NaNO_2 + Al_2O_3 = 2NaAlO_2 + NO + NO_2, \qquad (3)$$

$$Na_2O + Al_2O_3 = 2 NaAlO_2.$$
(4)

Later it was concluded that the reaction with sodium oxide is main and that with sodium nitrite is of only a small significance.

### EXPERIMENTAL

We examined an interaction of baddeleyite and synthetic zirconium(IV) oxide with NaNO<sub>3</sub> and NaNO<sub>2</sub>, and also hydrolytic and acid decomposition of the resulted cakes based on Na<sub>2</sub>ZrO<sub>3</sub>.

Studying NaNO<sub>2</sub> consisted in the fact that in the baddeleyite interaction with NaNO<sub>3</sub> must be released nitrogen oxides which is captured by an aqueous solution of an alkali reagent (e.g., soda) with formation of mixture NaNO<sub>3</sub> and NaNO<sub>2</sub> according to reaction

$$2NO_2 + Na_2CO_3 = NaNO_3 + NaNO_2 + CO_2.$$
(5)

In the study we used BC ground to  $\leq$ 40 µm (PB-KhO grade) of a composition (wt %): 99.3 ZrO<sub>2</sub> + HfO<sub>2</sub>, 0.05 Fe<sub>2</sub>O<sub>3</sub>, 0.29 SiO<sub>2</sub>, 0.07 SO<sub>3</sub>, 0.03 MgO, 0.038 P<sub>2</sub>O<sub>5</sub>, 0.05 TiO<sub>2</sub>, 0.07 CaO, 0.8 Nb<sub>2</sub>O<sub>5</sub>, 0.16 Ta<sub>2</sub>O<sub>5</sub>; a specific radioactivity 26 Bq g<sup>-1</sup>, zirconium(IV) oxide with specific surface area 18 m<sup>2</sup> g<sup>-1</sup> (an average size of particles 0.74 µm), formed by calcination of zirconium(IV) hydroxide at 900°C; NaNO<sub>3</sub> and NaNO<sub>2</sub> (chemically pure grade).

Open crucibles made of porcelain and alundum with the mixture were calcined within a certain time at a preset temperature in a muffle furnace. As a rule, friable cakes easily extracted from the crucible were resulted. A small amount of adhering cake was separated after exposure to the acid solution. Phase composition of cakes was investigated by X-ray phase analysis (XPA). The cakes were leached with solutions of nitric or hydrochloric acid. The degree of decomposition of BC was assessed by a mass fraction of the cake not dissolved in the acid and content of of zirconium in the solution. These results tend to coincide. The compositions of solutions obtained after



**Fig. 1.** Variation weight  $\Delta m$  (%) vs. heat processing temperature *T* (°C) for (*1*) NaNO<sub>2</sub> and (*2*) NaNO<sub>3</sub>.

leaching the cakes were determined by X-ray, chemical, and other analytical methods.

Previously we examined dependences of weight variation of  $NaNO_2$  and  $NaNO_3$  on temperature of thermal processing (Fig. 1).

As follows from data on Fig. 1, the weight of  $NaNO_2$ at a temperature of 630–730°C increases, while the weight of  $NaNO_3$  begins to decrease markedly at 650–790°C. The increase in the weight of  $NaNO_2$  indicates the formation of nitrate by the reaction

$$NaNO_2 + 0.5O_2 = NaNO_3.$$
 (6)

This is confirmed by X-ray analysis of the products of thermal treatment of  $NaNO_2$  in the air (Fig. 2), showing the increase in the content of  $NaNO_3$  :  $NaNO_2$  with increasing the temperature of thermal treatment as well as by published data [5].

Though in theory variation in the weight according to reaction (6) should reach 23.3%, in practice, it was much lower. This is explained by the evaporation of sodium nitrate (nitrite).

Indeed, already at 636°C the equilibrium pressure of NaNO<sub>3</sub> vapor is equal to 316 Pa (2.4 mm Hg), the vapor mainly consists of monomeric molecules, and the fraction



**Fig. 2**. X-Ray patterns of sodium nintrate thermally processed for 2 h at different temperature. (*I*) Intensity, (2 $\theta$ ) Bragg angle (deg). *T* (°C): (*a*) 400, (*b*) 500, (*c*) 600, (*d*) 700. (*I*) NaNO<sub>2</sub>, (*2*) NaNO<sub>3</sub>.

of dimer molecules is 3-5% [6].

Table 1 shows the values of the equilibrium pressure of NaNO<sub>3</sub> vapor calculated by extrapolation of a dependence found in [6]. As can be seen from data in Table 1 with increasing temperature the loss of sodium nitrate due to its evaporation must increase rapidly.

A slight decrease in the weight change may occur as a result of the interaction of sodium nitrate (nitrite) with a crucible material, when should be released oxygen and nitrogen oxides in proceeding the reaction (3) and(or)

$$2NaNO_3 + Al_2O_3 = 2NaAlO_2 + NO_2 + NO + O_2.$$
 (7)

For establishing the interaction mechanism between BC and NaNO<sub>3</sub> the mixture containing NaNO<sub>3</sub> in the amount of 120–130% of the stoichiometrically required for the formation of metazirconate was studied by differential thermogravimetry (DTG; NETZSCH STA 409 PC/PG). DTG data are shown in Fig. 3.

Endothermic effect at 277.6°C is associated with a transformation of  $\alpha$ -NaNO<sub>3</sub>  $\rightarrow \beta$ -NaNO<sub>3</sub> at 319.5°C with melting of  $\beta$ -NaNO<sub>3</sub>. The exothermic peak at 413.8°C, probably, is due to impurities present in the BC (burning out of residues of flotation reagents).

The slight decrease in the weight is observed in a temperature range of 560–600°C indicating an onset of the BC interaction with NaNO<sub>3</sub>.

The interaction takes place mainly in the temperature range of 640–860°C. A number of small peaks in this temperature range indicates limitations arising from a diffusion penetration of molten sodium nitrate to the grains of baddeleyite coated with reaction products. An endothermic effect at 955.3°C close to the boiling point of NaNO<sub>3</sub> (Table 1) is probably due to the completion of the sublimation of NaNO<sub>3</sub>. Apparently, the complex nature of changes in temperature in the range 700–881°C is determined by a competition of simultaneously occurring processes of interaction between components of the mixture and evaporation of NaNO<sub>3</sub>.

The loss of weight equal to 47% (Fig. 3) notes that the interaction has proceeded according the following reaction

$$ZrO_{2} + 2.66NaNO_{3} = Na_{2}ZrO_{3} + 0.66NaNO_{3}\uparrow$$
$$+ 2NO\uparrow + 1.5O_{2}\uparrow.$$
(8)

If sodium nitrate is decomposed with the formation

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**Table 1.** Equilibrium pressure of NaNO<sub>3</sub> vapor at different temperature

	Pressure of the vapor		
<i>I</i> , C	Ра	Hg mm	
700	1991	15.1	
800	10620	80.7	
900	42560	323	
971	105	760	

of sodium oxide by the reaction

$$ZrO_{2} + 2.66NaNO_{3} = Na_{2}ZrO_{3} + 0.33Na_{2}O + 2.66NO\uparrow + 1.49O_{2}\uparrow,$$
(9)

then the weight decrease will be 41.1%.

The excess of NaNO<sub>3</sub> is evaporated completely in the case of a small weighted portion of the mixture (loading weight 0.2 g) used during the DTG analysis.

In practice the evaporation degree depends on the values of mixture loading, temperature *T*, and time of thermal processing  $\tau$ .

Experimental data on sintering of BC with sodium nitrate and nitrite are listed in Table 2. It is seen that the interaction is observed already at 700°C, decreases in the range of 850–900°C, and is hampered at higher temperatures. By additional experiments we found that an increase in the time of the thermal processing over 3 hours virtu-



**Fig. 3**. Curves of TG and DTG of the BC + NaNO<sub>3</sub> mixture in an amount 133% in term of the stoichiometrically required for Na<sub>2</sub>ZrO<sub>3</sub>. ( $\Delta m$ ) Loss of weight, %, (*T*) temperature, °C.

Experiment Weighted portion of		NaNO <sub>3</sub> or NaNO <sub>2</sub> , $\%$ in term		Sodium residue	Loss of Na- trium	$ZrO_2$ recovery into solution,	
110.	BC, g	required	of stoichoimetrically required $T$ , °C $\tau$ , h rel %		%	%	
Sodium nitrate							
1	5	100	700	2	65.2	_	2.6
2	5	100	750	2	65.2	-	4.1
3	5	100	770	3	53.6	-	19.1
4	5	100	800	2	49.3	-	22.3
5	10	120	800	2	53.0	-	37.5
6	5	120	800	3	33.3	3.2	46.0
7	5	120	850	2	30.1	6.4	50.1
8	5	120	850	3	24.5	8.0	54.0
9	5	100	900	2	32.6	3.9	52.0
10	20	120	900	3	28.6	7.9	64.0
11	20	120	950	3	29.3	6.2	54.5
·			Sodium nitrit	e			
1	5	100	700	2	75.0	-	5.8
2	5	100	750	2	70.1	-	7.4
3	5	100	770	3	67.8	-	11.1
4	5	120	800	2	47.8	-	28.4
5	5	120	800	3	35.8	9.1	42.0
6	5	120	850	2	37.3	7.6	57.5
7	5	120	850	3	37.3	7.6	60.8
8	5	120	900	2	37.3	7.6	64.0
9	20	120	900	3	37.3	7.6	64.0
10	5	120	950	2	34.3	10.6	60.6
11	5	150	950	3	34.3	10.6	63.8

Table 2. Experimental data in sintering BC with sodium nitrate and nitrite

ally did not increase the degree of decomposition of BC. Moreover, no changes in the degree of decomposition occurred at the repeat thermal processing with an additional introduction of sodium-containing reagent. In theory at complete transformation in  $Na_2ZrO_3$  or  $Na_2O$  in the cake an amount of the residue of the loaded sodium in the case of  $NaNO_3$  is 36.5%; for  $NaNO_2$ , 44.9%. As can be seen from Table 2 for sodium nitrate in



Fig. 4. Diffraction pattern of cake obtained in thermal processing at 180°C of mixture containing 133% NaNO<sub>3</sub> in tern of of the stoichiometrically required. (1) monoclinic  $ZrO_2$ , (2) Na<sub>2</sub>ZrO<sub>3</sub>.

experiment nos. 1–5 the amount of the residue exceeded this value indicating the presence in the cake of unreacted NaNO<sub>3</sub>, while in experiment nos. 6–10 that was less than this value due to the increasing sublimation of NaNO<sub>3</sub> at high temperatures. Similar results were observed when using NaNO<sub>2</sub>: sodium loss occurred even during the heat treatment at 800°C for 3 h. At small weighted sample portions of the mixture the highest degree of decomposition of BC was observed at 850–900°C for 3 h and almost no depended on the type of a reagent used for the decomposition of BC.

According to the XPA in the cakes the formation of new phases are usually not observed, as X-ray amorphous  $Na_2ZrO_3$  was resulted. Only during the sintering of the enlarged weighted portion of the mixture containing 133% NaNO<sub>3</sub> from the stoichiometrically required, we found the formation of crystalline  $Na_2ZrO_3$  (Fig. 4).

We compared the dependence of the degree of decomposition on temperature of 40  $\mu$ m BC and zirconium(IV) oxide. The sintering was conducted for 3 h (the content of Na NO<sub>3</sub> 120% from the stoichiometrically required). The experimental data (Fig. 5) show that in sintering under the same conditions an enlargement of particles of materials based on zirconium(IV) oxide from 0.74 to 40  $\mu$ m reduces the degree of formation of Na<sub>2</sub>ZrO<sub>3</sub>.

The experimental data allow concluding that the reaction rate is controlled by diffusion of a liquid opening reagent through a barrier layer of refractory Na<sub>2</sub>ZrO<sub>3</sub> formed on the surface of grains of baddeleyite.

The slight increase in the degree of decomposition of

BC was reached with the help of an increase in the mixture weight and consumption of NaNO<sub>3</sub>. Thus, a degree of opening of 72.4% is reached by the thermal processing at 800°C for 4 h of the weighted portion of the mixture containing 100 g of BC with NaNO<sub>3</sub> consumption 133% from stoichiometrically required.

The higher degree of decomposition of BC ( $\approx 95\%$ ) can be obtained in the case of its grinding to a particle size  $\leq 0.75 \,\mu$ m that is hardly economically viable. Return of not decomposed part of the concentrate to the circulation is more appropriate. Because it is easy to implement, the degree of decomposition equal to 72.4% reached in the integrated experiment at 800°C and for 4 h of the interac-



Fig. 5. Degree of decomposition D (%) of baddeleyite and zirconium(IV) oxide vs. sintering temperature T (°C). (1) BC grains of 40 µm size, (2) ZrO<sub>2</sub> particles of average size 0.74 µm.

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tion is acceptable for practical use.

Transition of Zr(IV) in a solution of the cakes can be made by dissolving Na<sub>2</sub>ZrO<sub>3</sub> in acids. Further purification and recovery of Zr(IV) by extraction from nitric acid environment is possible as well as deposition of Zr(IV) in the form oxochloride or basic sulfate from hydrochloric acid environment [7–9].

The amount of acid to dissolve  $Na_2ZrO_3$  was defined in term of stoichiometry and conditions for further recovery of Zr(IV) from solution. The basic zirconium sulfate is precipitated at low pH of the solution, so for this purpose it is necessary to decompose the cake at a slight excess of acid. Extraction of Zr(IV) from nitrate solutions is performed at pH 6.5. Use of more concentrated hydrochloric acid is possible with zirconium oxochloride recovery. Data on the dissolution of the cake washed with water are shown in Fig. 6. It implies that the sufficiently complete leaching occurs for 1 h and only slightly depends on the concentration and type of acid. In re-processing no more than 2–4% Zr(IV) passed additionally in solutions.

We found that impurities of niobium(V), tantalum(V), scandium(III), which are a isomorphic part of the structure of baddeleyite, pass along with zirconium (IV) in solution. In the not decomposed residue their content corresponds to that in the original concentrate. Niobium(V), tantalum(V), silicon(IV) in dilute chloride and nitrate solutions are mainly in colloidal form and in aging of the solutions they are precipitated: the precipitate composition (wt%) is 20–30 ZrO<sub>2</sub>, 0.2–0.25 Fe<sub>2</sub>O<sub>3</sub>, 50–55 SiO<sub>2</sub>, 0.2–0.3 TiO<sub>2</sub>, 0.3 CaO, 10–13 Nb<sub>2</sub>O<sub>5</sub>, 4.5–5.0 Ta<sub>2</sub>O<sub>5</sub>.

To reduce the acid consumption and obtaining of the solution of sodium hydroxide which, as mentioned above, can be used for the absorption of nitrogen oxides



**Fig. 6.** Kinetic curves of leaching Zr(IV) by solution of (1, 2) 8 N HNO<sub>3</sub>, (3) 6 N HNO<sub>3</sub>, (4) 3 N HCl. ( $\alpha$ ) recovery of Zn(IV), %);( $\tau$ ) leaching time, h. *T*, °C: (1, 3, 4) 60; (2) 85.

**Table 3.** The effect of the solution volume on the degree of hydrolysis of the  $Na_2ZrO_3$  cake

g : l	NaOH content in aqueous phase, g l <sup>-1</sup>	Sodium extracted in water phase, %	
1:1	220	43.6	
1:2	116	45.9	
1:2.5	104	51.5	
1:5	52	51.5	
1:10	28	55.5	

released in sintering, water pre-treatment of the cake is recommended [1].

In the case of the hydrolytic decomposition of  $Na_2ZrO_3$  synthesized at 1100–1200°C by the interaction of soda with BC, it was found that at 90°C for 4 h a complete transition of sodium in solution was provided. However, in the solid phase along with zirconium hydroxide there was monoclinic zirconium dioxide which is not soluble in mineral acids. The share of zirconium in the acid-insoluble form reached 40%. To avoid the formation of the acid-insoluble zirconium, hydrolysis should be carried out for 5 min with separating from  $Na_2ZrO_3$  only 0.5 mol of sodium (25% used to regenerate sodium) [1].

The effect of the temperature and treatment time on the degree of hydrolysis in aqueous leaching of the product obtained by sintering BC with NaNO<sub>3</sub> at 900°C



Fig. 7. Degree of hydrolysis G (%) vs. leaching time  $\tau$  (h) of cake of sodium zirconate. T, °C: (1) 20, (2) 50, (3) 80.

is shown in Fig. 7. The leaching occurred at s : l = 1 : 10. The concentration of alkali in the solutions was 30–35 g L<sup>-1</sup>. As can be seen from Fig. 7, the growth in the leaching temperature increases the degree of leaching and reduces the time of hydrolysis. There was good correlation between the amounts of alkali passed into a solution of and acid-soluble zirconium. Thus, on hydrolytic processing of cakes obtained at a lower temperature a significant amount of the acid-soluble zirconium were not observed under the studied conditions.

For use alkali in recycling its maximum concentration is the most suitable, which is achieved by reduction in a volume of the leaching solution and use of countercurrent leaching. Table 3 shows data on the 40°C hydrolytic leaching of the product obtained by sintering at 800°C. In assessing of the recovery the loss of alkali caused by sublimation in the course of sintering was not taken into account.

Data of Table 3 demonstrate that hydrolysis of the cake even at 40°C allows producing a solution containing 220 g L<sup>-1</sup> of NaOH. A tenfold growth in s : 1 ratio increased the recovery of sodium in the solution only by 27 rel %. The more complete recovery of alkali is reached by the countercurrent leaching or increase in the hydrolysis temperature.

It is noticed that the filtration rate of the pulp of acid leaching changes without affecting the extraction of  $ZrO_2$ in the case of variation of the temperature of the water leaching. At the high temperature of water leaching the acid pulp is almost unfiltered. The most favorable conditions are 50°C temperature with an exposure of the pulp.

Thus, BC interacts with sodium nitrate (nitrite) without the formation of sodium oxide as intermediate product. In heating in the air sodium nitrite transforms into nitrate. In the process sodium nitrate is partially vaporized that should be taken into account on designing the equipment and choice of the mixture composition. The optimal tem-

<sup>a</sup> We used densities of solids.

perature range of the interaction is 800-900°C; the time, 3 h. In this case, as a rule, X-ray amorphous Na<sub>2</sub>ZrO<sub>3</sub> is resulted. The increase in the excess of sodium nitrate up to 133% from the stoichiometrically required contributes to the partial formation of crystalline Na<sub>2</sub>ZrO<sub>3</sub> which is difficultly soluble in mineral acids.

For reaching the virtually acceptable degree of decomposition of BC it is advisable to use a concentrate of PB-KhOM grade with particle size of 5–7  $\mu$ m, which is produced by JSC "Kovdor GOK." Nitrogen oxides released in the course of the sintering may be captured by an alkaline or soda solution, and the yielded mixture of sodium nitrate and nitrite was used in the feedback for the decomposition of BC. Articles made of alundum (corundum) under the studied conditions are of fairly corrosion resistance.

Use of sodium nitrite results in slightly higher values than use of sodium nitrate despite transformation of nitrite into nitrate occurs in heating in the air.

This allows suggestion that there is another reason that affects the efficiency of the process. Indeed, the bulk density of BC is about 3 g cm<sup>-3</sup>. Therefore, in each 1 dm<sup>3</sup> of the crucible volume there are 0.666 kg of BC and 0.333 dm<sup>3</sup> of free space. Table 4 shows the degree of filling of voids of BC powder using stoichiometric amounts of sodium nitrate and nitrite. A volume of pores in the loaded solids should be sufficient for filling by the melt. Otherwise, after melting of the reagent its part is located above the layer of BC, and an interaction of this part with BC is practically impossible since there is no mixing.

Comparison of data of Tables 2 and 4 shows that the efficiency of decomposition is in opposition to the degree of filling the pores. This confirms the suggestion. Since in melting a volume of liquid phase increases, then the use of sodium nitrate is even more difficult. It is therefore advisable to use sodium nitrate in an amount, which is less than stoichiometrically required, separating and

Compound	Density, <sup>a</sup> kg dm <sup>-3</sup>	Stoichiometrical consumption		Share of loaded sodium compounds
		weight, kg	volume, dm <sup>3</sup>	that fit in pores
NaNO <sub>3</sub>	2.257	1.38	0.611	54.3
NaNO <sub>2</sub>	2.168	1.07	0.494	67.6

Table 4. Share of loaded sodium compounds (stoichiometrical consumption) that can be placed in voids of BC loaded

returning into circulation not decomposed portion of the concentrate.

Improving the efficiency of decomposition of BC in its grinding is controlled not only by increasing the surface interaction, reducing the diffusion path, but also by a decrease in the bulk density, and, as a consequence, by a growth in an amount of liquid sodium nitrate in the pores of loaded BC.

As the enlargement of the process facilitates a decrease in the share of distilled NaNO<sub>3</sub> the optimal ratio of components in the original mixture should be determined by a size and geometry of crucibles used.

## CONCLUSIONS

(1) It was shown that the interaction of baddeleyite with sodium nitrate occurs at temperatures above 640°C directly without preliminary decomposition of sodium nitrate to sodium nitrite or oxide. In heating in the air sodium nitrite before the interaction with baddeleyite is transformed into sodium nitrate. A growth in interaction temperature increases both the rate of the reaction between reagents and degree of sublimation of sodium nitrate. The optimal temperature range of the interaction is 800–900°C and time is 3 hours.

(2) Strontium zirconate formed on the surface of baddeleyite grains is, as a rule, X-ray amorphous and hampers the diffusion penetration of the molten sodium nitrate to the baddeleyite grains.

(3) Due to hydrolytic decomposition of X-ray amorphous strontium zirconate over 70% of bound sodium in the form of hydroxide goes into the solution and can be used for the absorption of nitrogen oxides released during the interaction of baddeleyite with sodium nitrate

and nitrite.

#### ACKNOWLEDGMENTS

This work was supported by the Program for Basic Research of Russian Academy of Sciences "Creation of new products from mineral and organic materials."

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