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Abstract

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ON THE REVERSIBILITY OF THE REACTION OF BETA-SPODUMENE WITH POTASSIUM SULFATE

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In the course of studying the interaction of spodumene with sulfates of alkali metals (Me_2SO_4), it was established (^{1}) that the pronounced ability of the β-modification of this mineral to enter, at high temperatures, into reaction with various salts is usually not characterized by a tendency toward decomposition of the mineral into a number of phases with the formation of soluble aluminates and silicates. As a result of the interaction of β-spodumene with Me_2SO_4, proceeding under many experimental conditions as a solid-phase process, only one new mineral formation insoluble in water arises; along with it, Li_2SO_4 is obtained with an impurity, mainly Na_2SO_4, due to the isomorphous sodium contained in the spodumene. It is precisely this circumstance that makes β-spodumene a convenient starting material for experimental mineralogy. Thus, by sintering β-spodumene with K_2SO_4, Rb_2SO_4, and Cs_2SO_4, we synthesized, respectively, leucite, rubidium aluminosilicate, and pollucite (^{1}) of composition $Me[AlSi_2O_6]$. At the present time, complete identification of these synthetic aluminosilicates has been carried out ($^{2-5}$). Only in the case of the interaction of β-spodumene with Na_2SO_4 was destruction of the mineral, vitrification of the mass, and, ultimately, cessation of the reaction observed.

The formation of synthetic aluminosilicates also takes place (^{1}) in the interaction of α-spodumene with Me_2SO_4; however, it proceeds through the intermediate stage of the $\alpha \to \beta$ transition of spodumene, which requires an increased supply of heat (^{6}).

In the synthesis of aluminosilicates of alkali metals from β-spodumene, according to x-ray investigation ($^{1,\ 3-5}$), a temperature of 900—950° proved sufficient, and only for complete completion of the reaction (the production of entirely single-phase products) was it deemed expedient to carry out sintering at 1000—1050°.

From the practice of the sulfate method of processing spodumene, based on sintering this mineral with K_2SO_4 at 1050—1100°, it is also well known that temperature affects the degree of extraction of lithium into sulfate, i.e., in this case, the completeness of the conversion of β-spodumene into leucite. Of no less importance is the consumption of K_2SO_4 at the sintering stage. Although, in estimating it, the content of Li_2O in spodumene concentrates is usually taken into account, this estimate is empirical in character. Since quantitative data on the degree of simultaneous extraction of sodium from spodumene are lacking, the technological calculations are, in essence, not connected with the principal reaction that determines the mechanism of interaction of the mineral with K_2SO_4. In many cases, when working with standard raw material, in preparing the charge one simply uses a weight ratio between the components equal to 1 : 1 or close to it.

For further study of the reaction of interaction of spodumene with K_2SO_4, it was of interest to estimate the consumption of the reagent both in connection with the extraction of the principal element (lithium) and of the accompanying element (sodium). Indeed, if

For the article by E. V. Plyushchev, p. 584

(Figure: Figure 1)

Fig. 1. Debyegrams: **a** –initial β-leishite; **b** –β-spodumene (standard); **c** – synthetic β-spodumene

For the article by V. S. Babkin and L. S. Kozachenko, p. 591.

(Figure: Figure 1)

Fig. 1. Shock wave ahead of the front of a turbulent flame in a rough tube

(Figure: Figure 2)

Fig. 2. Formation of the combustion mechanism with ignition at the tube walls in a mixture of 25% H_2 + 21.5% O_2 + 53.5% N_2

If spodumene were a purely lithium mineral, then the sintering reaction of it with K_2SO_4 could be represented as follows:

$$\mathrm{Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + K_2SO_4 = Li_2SO_4 + K_2O \cdot Al_2O_3 \cdot 4SiO_2}. \tag{1}$$

In reality, spodumene contains a variable amount of sodium, and therefore the principal reaction determining the mechanism of interaction of the mineral with K_2SO_4 should be represented in general form by the equation:

$$\mathrm{(Li, Na)_2O \cdot Al_2O_3 \cdot 4SiO_2 + K_2SO_4 = (Li, Na)_2SO_4 + K_2O \cdot Al_2O_3 \cdot 4SiO_2}. \tag{2}$$

In order to trace the nature of the extraction of lithium and sodium from spodumene, experiments were carried out at various ratios of the reaction components and over a wide temperature range. The starting material was β-spodumene containing 5.44% Li_2O and 3.20% Na_2O (1). The procedure, with respect to preparation of the charge, its sintering, aqueous treatment of the sinters, and analysis of the solutions, was analogous to that described earlier (^{2}).

The duration of sintering in all cases was three hours. The results obtained in the analysis of solutions from the stage of aqueous treatment of the sinters are presented in Table 1. In it, the consumption of K_2SO_4 for the sintering reaction, amounting to 20, 40, 60, 80, and 100% relative to the weight of β-spodumene, is expressed as percentages of that theoretically required by reaction (1) in comparison with the consumption according to reaction (2). The calculated data for reaction (2) are shown in parentheses.

Table 1

Data on the interaction of β-spodumene with potassium sulfate

Temperature of interaction, °C	62.5 (50), Li_2O	62.5 (50), Na_2O	125 (100), Li_2O	125 (100), Na_2O	187.5 (150), Li_2O	187.5 (150), Na_2O	250 (200), Li_2O	250 (200), Na_2O	312.5 (250), Li_2O	312.5 (250), Na_2O
	K_2SO_4 consumption for reaction (1) or (2) (in percent of theory); passed into solution (in percent of the amount originally in the mineral)									
700	traces	–	–	–	traces	traces	1.68	2.84	2.74	4.69
800	–	–	3.02	traces	4.82	4.38	6.74	7.83	8.19	9.83
900	6.15	traces	22.16	12.02	42.18	20.93	58.16	30.56	69.11	38.12
950	8.02	2.50	30.24	16.52	48.23	27.54	65.02	39.06	77.99	46.96
1000	9.42	6.94	36.51	23.90	59.12	40.04	77.30	50.34	89.11	61.07

Temperature of interaction, °C	62.5 (50), Li_2O	62.5 (50), Na_2O	125 (100), Li_2O	125 (100), Na_2O	187.5 (150), Li_2O	187.5 (150), Na_2O	250 (200), Li_2O	250 (200), Na_2O	312.5 (250), Li_2O	312.5 (250), Na_2O
1050	11.87	10.08	38.56	26.49	63.10	43.48	79.48	55.03	95.20	65.25
1100	14.04	11.15	49.13	32.62	73.40	45.94	88.05	59.36	96.24	70.33

As is evident from Table 1, as lithium passes into the soluble phase, sodium also passes into it; this transfer increases sharply beginning at 900°, when, as a result of the interaction of β-spodumene with K_2SO_4, the formation of leucite is observed in the reaction products (^{1,2}). However, the relative amount of sodium extracted into the soluble phase gradually lags behind the amount of lithium extracted from spodumene. At a K_2SO_4 consumption of 250% relative to that required by reaction (2), practically complete extraction of lithium from spodumene is achieved, with simultaneous significant, but incomplete, extraction of sodium. Part of the latter is retained by the leucite formed during sintering. Thus, the main portion of the K_2SO_4 consumed is used for complete extraction of lithium, and a certain amount is lost in the accompanying extraction of sodium, which it does not appear possible to prevent.

The nature of the influence of excess K_2SO_4 on the degree of lithium extraction suggests the reversibility of the reaction between β-spodumene and K_2SO_4 at high temperatures. The simplest way to test this assumption appeared to be an attempt to carry out the reverse synthesis of β-spodumene from leucite. For this purpose, sintering was performed on a sample of natural leucite ($K_2O = 20.73$; $Na_2O = 0.37$; $Al_2O_3 = 23.38$; $SiO_2 = 55.46$ wt. %) with lithium sulfate at ratios of 1 : 1 and 1 : 2 by weight (which amounted respectively to 340 and 680%) at temperatures of 800, 900, and 1000° for two and three hours. The procedure was completely analogous to that used···

···in the synthesis of leucite (^{1}, ^{2}). After washing out all soluble salts, the residues of the sinters were subjected to X-ray phase analysis. In all residues the presence of β-spodumene was detected; moreover, the residues obtained as a result of experiments carried out at 900 and 1000° were single-phase, i.e., they consisted of β-spodumene; leucite was absent from them.

One of the residues, obtained at 1000° and with a ratio of the reaction components equal to 1 : 1, was studied in more detail. Silicate analysis found (wt. %): 7.97 $\mathrm{Li_2O}$; 27.38 $\mathrm{Al_2O_3}$; 64.63 $\mathrm{SiO_2}$. Calculated for $\mathrm{Li[AlSi_2O_6]}$ (wt. %): 8.04 $\mathrm{Li_2O}$; 27.40 $\mathrm{Al_2O_3}$; 64.56 $\mathrm{SiO_2}$. The mean refractive index $n' = 1.519 \pm 0.003$; the polymorphism characteristic of leucocite was absent. The interplanar spacings and intensities found from the powder photograph were in good agreement with data recently obtained for β-spodumene (^{7}). Figure 1 presents Debye patterns of the initial leucite, of β-spodumene obtained from natural α-spodumene by calcining it at 1100° for 6 h, and of synthetic β-spodumene obtained from leucite. Thus, the fact of synthesis of β-spodumene from leucite under the action of Li_2SO_4 on the latter is established; this serves as proof of the reversibility of the main reaction of the sulfate method for processing spodumene. This reaction can evidently be characterized by the following equation:

$$2\beta\text{-Li}[AlSi_2O_6] + K_2SO_4 \overset{Q_{\text{cal}}}{\rightleftarrows} 2\alpha\text{-K}[AlSi_2O_6] + Li_2SO_4. \qquad (3)$$

Let us note that an analogous route for the synthesis of β-spodumene starting from pollucite $Cs[AlSi_2O_6] \cdot nH_2O$ and Li_2SO_4 does not achieve the objective, which indicates the high strength of the bonds in the compound $Cs[AlSi_2O_6]$.

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REFERENCES CITED

[1] V. E. Plyushchev, DAN, 124, 642 (1959). [2] V. E. Plyushchev, ZhPKh, 32, 1413 (1959). [3] V. E. Plyushchev, Yu. P. Simanov, I. V. Shakhno, ZhNKh, 3, 2133 (1958). [4] V. E. Plyushchev, Zap. Vsesoyuzn. min. obshch., 88, 152 (1959). [5] V. E. Plyushchev, Nauchn. dokl. Vyssh. shk., ser. khim. i khim. tekhnol., No. 2, 284 (1959). [6] G. G. Urazov, V. E. Plyushchev, I. V. Shakhno, DAN, 113, 361 (1957). [7] V. E. Plyushchev, Yu. P. Simanov, I. V. Shakhno, DAN, 125, 334 (1959).

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