Hydrothermal Treatment of Fluor-phlogopite.—Hydrothermal Treatment of Agglomerate Mass of Synthetic Mica Crystals to Facilitate Separation of Individual Crystals

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The method now used to produce synthetic mica is to cool a melt having a chemical composition of fluor-phlogopite with small amounts of fluorides and silicates. The cooled mass thus obtained is composed of crystals of fluor-phlogopite with small amounts of glassy substance and fluorides between the mica crystals[1]. The glassy substance binds mica crystals together and makes them difficult to separate from one another.

Further, a thin glass film adhering to the crystals makes them harder and less flexible than natural mica. The quality of mica crystals is often damaged when crystals are separated forcibly.

In order to separate the individual mica crystals more easily and to obtain soft and flexible crystals, agglomerates of synthetic fluor-phlogopite were treated hydrothermally with electrolyte solutions.

Experimental

Samples used were agglomerates of crystals obtained by cooling melts having the following chemical compositions:

I. $3.59\,MgO,\ 0.60\,Al_2O_3,\ 3.00\,SiO_2,\ 0.70\,K_2SiF_6$
$=K_{1.17}Mg_{3.00}Al_{1.00}Si_{3.09}O_{9.52}F_{3.51}$
$=1.14KMg_3AlSi_3O_{10}F_2+0.13K_2SiF_6+0.16MgSiF_6$
$+0.01MgF_2+0.06AlF_3$

II. $0.50K_2O,\ 1.88MgO,\ 1.13MgF_2,\ 0.50Al_2O_3,$
$3.00SiO_2$
$=KMg_3AlSi_3O_{9.88}F_{2.24}$
$=0.80KMg_3AlSi_3O_{10}F_2+0.15MgF_2$
$+0.05KAlSi_3O_8$ (POM2)[1]

All of these agglomerates contained small amounts of glassy substance and fluorides.

Small pieces of the agglomerate mass, together with an aqueous solution of electrolyte, were placed in an autoclave and heated for one or two days at a temperature within the range 150 to 350°C. The ease of separating individual crystals and the flexibility of separated crystals were tested qualitatively. The fluorine content of the original and treated samples was determined and the weight decrease at various temperatures was measured by a thermobalance. The ease of separation is evaluated by grades A_0, A, B and C. Grade A means that the separation is as easy as that of natural muscovite; grade C is the same as that of untreated agglomerate; grade B is between A and C, and A_0 is better than A.

Results

1) Treatment with sodium hydroxide solution.—(*a*) *Effects of concentration of solution and of period of treatment.*—Results of experiments are given in Table I.

TABLE I

Sample No. 1—fluorine content 13.9%, Temperature of treatment: 350°C.

Experiment	No. 1	No. 2	No. 3	No. 4	No. 5
Condition for treatment					
Concn. of NaOH solution (N)	0	0.5	1.0	2.0	2.0
Period (hr.)	24	24	24	24	48
Properties of the product					
Ease of separation	C	B	B	A	A
F content (%)	13.5	13.7	13.0	11.2	8.6
Percentage decrease of F	3	1	7	19	38
W. loss between 600° and 850°C (%)	0.0_7	0.1_0	0.1_1	0.1_8	0.3_1

Sample No. 1 contained free fluorides and had a larger fluorine content than that of pure fluor-phlogopite with the theoretical content of 9.04%. Treatment with tap water for 24 hr. at 350°C had no effect of making separation easier. Treatment with

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1) a) T. Noda and S. Sugiyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **46**, 1082 (1943).
b) T. Noda, *J. Am. Ceram. Soc.*, **38**, 147 (1955).

TABLE II

Sample No. 1—fluorine content 13.9%, Temperature: 350°C, Period: 48 hr.

Experiment	No. 5	No. 6	No. 7	No. 8
Treating solution	2N NaOH	0.95 mol. NaF / 1·2N NaOH	5.1 mol. $KF \cdot 2H_2O$ / 1·2N NaOH (= 4.3 mol. KF / 1·1.7N NaOH)	0.27 mol. Na_2SiF_6 / 1·2N NaOH
Properties of product				
Ease of separation	A	A	A_0	A
F content (%)	8.6	11.2	10.0	12.7
Percentage decrease of F	38	19	28	9
W. loss between 600° and 850°C(%)	0.3_1	—	0.1_9	0.2_5

0.5 N sodium hydroxide had a weak effect, and that with a more concentrated solution had a stronger effect. Products of experiments Nos. 4 and 5 separated easily and the separated crystals were flexible. The more concentrated the solution and the longer the period of treatment, the greater the decrease of the fluorine content in the product. Temperature-weight loss

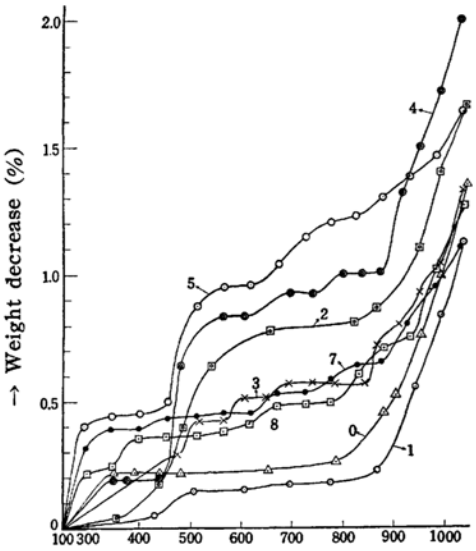


Fig. 1.

curves of these products are given in Fig. 1. The curve for the untreated mass is designated No. 0. In these curves, four stages of weight decrease can be observed, i. e. between 100° and 300°C, between 450° and 550°C, between 600° and 850°C and above 850°C. An agglomerate mass of fluor-phlogopite often occludes gas and carbon. The weight decrease between 100° and 300°C may be due to the evolution of gas and the combustion of carbon. Fluor-phlogopite gradually decomposes and liberates fluorine when heated to above 850°C[2]. These phenomena were verified by the steps of weight decrease observed in the curve of the untreated mass. The glassy substance and fluorides may be changed into hydroxides by these hydrothermal treatments and therefore the weight decrease between 450°C and 550°C is probably due to the decomposition of hydroxides. The weight decrease between 600° and 850°C is related to the dehydration of hydroxyl-phlogopite[3]. It can therefore be concluded that hydrothermal treatments at 350°C with sodium hydroxide solution did produce hydroxides and only the long treatment (No. 5) with concentrated solution changed a part of the fluor-phlogopite into hydroxyl-phlogopite[4].

(*b*) *Effects of addition of fluoride to treating solution.*—As described above, the hydrothermal treatment with sodium hydroxide solution resulted in the change of fluor-phlogopite into hydroxyl-phlogopite. If some equilibrium exists between alkali hydroxide and fluor-phlogopite, such as

$$\text{F-phlogopite} + 2OH^- \rightleftarrows \text{OH-phlogopite} + 2F^-,$$

the hydration of fluor-phlogopite may be suppressed or decreased by the addition of the fluoride ion to the treating solution. Experiments carried out on these lines are given in Table II.

That an addition of fluoride to the solution decreases the percentage decrease of fluorine content of the treated product seems reasonable. The observed decrease in fluorine content of treated products may be due to dissolution of fluoride

2) a) T. Noda and K. Aoki. *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **51**, 7 (1948).
b) T. Noda and T. Matsushita, ibid., **51**, 83 (1948).
3) H. S. Yoder and H. P. Eugster, *Geochim. Cosmochim. Acta*, **6**, 157 (1954).
4) T. Noda and Rustum Roy, *Am. Mineral.*, **41**, 929 (1956).

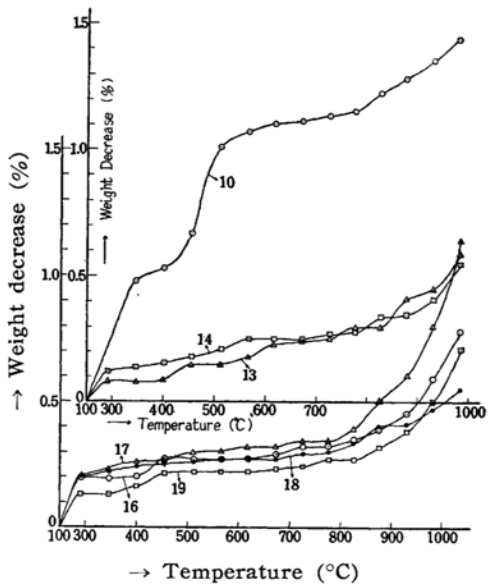
TABLE III

Experiment	No. 9	No. 10	No. 11	No. 12	No. 13	No. 14
Conditions for treatment						
Treating soln.	2N KOH	2N KOH	$\frac{5.31\text{mol. } KF\cdot 2H_2O}{1\cdot 2N \text{ KOH}}$ $\left(=\frac{4.46 \text{ mol. KF}}{1\cdot 1.68N \text{ KOH}}\right)$	$\frac{3.19\text{mol. } KF\cdot 2H_2O}{1\cdot 2N \text{ KOH}}$ $\left(=\frac{2.86 \text{ mol. KF}}{1\cdot 1.80N \text{ KOH}}\right)$	$\frac{2.13\text{mol. } KF\cdot 2H_2O}{1\cdot 2N \text{ KOH}}$ $\left(=\frac{1.98 \text{ mol. KF}}{1\cdot 1.86N \text{ KOH}}\right)$	$\frac{1.06\text{mol. } KF\cdot 2H_2O}{1\cdot 2N \text{ KOH}}$ $\left(=\frac{1.02 \text{ mol. KF}}{1\cdot 1.93N \text{ KOH}}\right)$
Period of treatment (hr.)	12	24	24	24	24	24
Properties of product						
Ease of separation	A	A	A	A	A	A
F content (%)	8.2	7.7	9.2	9.3	9.3	8.7
Percentage decrease of F	41	45	34	33	33	37
W. loss between 600° and 850°C (%)	—	0.1_6	—	—	0.1_4	0.1_0

originally occluded in agglomerate mass. Product No. 7 which was treated with a solution containing 1.7 mol. sodium hydroxide and 4.3 mol. potassium fluoride per liter gave the greatest ease of separation (grade A_0) even though fluor-phlogopite crystals of the product were not changed into hydroxyl-phlogopite.

2) Treatment with potassium hydroxide solution.—(*a*) *Optimum concentration of potassium fluoride.*—Sample No. 1 having a fluorine content of 13.9% was used. It seems probable that sodium ion replaces some potassium ion of fluor-phlogopite when sodium hydroxide solution is used as a treating solution. Therefore, the use of potassium hydroxide is prefer able to sodium hydroxide as a treating solution. Treatment with 2N solution of sodium hydroxide gave the best results for easing separation, but for the reason already given, 2N solution of potassium hydroxide was used in the following experiments. Experimental results obtained in using 2N potassium hydroxide with the addition of various amounts of potassium fluoride are given in Table III.

It can be seen in Table III that the effect of potassium hydroxide solution was stronger than that of sodium hydroxide solution. Fluorine contents of the products of experiments Nos. 11, 12 and 13 were nearly equal to the theoretical value of 9.04%, but those of experiments Nos. 9, 10 and 14 were less than this value. Temperature-weight loss curves of these products are shown in Fig. 2. The product of experiment No. 10 gave 0.40% of the weight decrease between 450° and 550°C



→ Temperature (°C)

Fig. 2.

which corresponds to the decomposition of hydroxides, whereas the products of experiments Nos. 13 and 14, in which potassium fluoride was added to the treating solution, gave a negligible decrease of weight in the same temperature range. The weight decrease between 600° and 850°C was 0.16% for the product of experiment No. 10 and that of the products of experiments Nos. 13 and 14 was about 0.1%. These results indicate that both the formation of hydroxides and the hydration of fluor-phlogopite with hydrothermal treatment were suppressed by the addition of fluoride to the treating solution. The concentration of 1.5 to 2mol.

TABLE IV

Concn. of KF: 2.1 mol. per liter, Temp. of treatment: 350°C, Period of treatment: 24 hr.

Experiment	No. 15	No. 16	No. 17	No. 18	No. 19	No. 20
Concn. of KOH(N)	2	1	0.5	0.25	0.125	0
Properties of product						
Ease of separation	A	A	A	A	B	B
F content (%)	9.4	12.2	12.5	9.3	10.2	10.7
Percentage decrease of F	33	12	10	33	27	23
W. loss between 600° and 850°C(%)	—	0.1_0	0.1_3	0.1_0	0.0_8	—

potassium fluoride per liter was necessary in order to suppress the hydration of fluor-phlogopite in the treatment with 2 N potassium hydroxide.

(*b*) *Optimum concentration of potassium hydroxide.*—Sample No. 1 having a fluorine content of 13.9 % was used. In the experiments described above the concentration of potassium hydroxide was fixed at 2 N. Table IV shows the results of experiments carried out with potassium hydroxide solution of various concentrations, 2.1 mol. potassium fluoride being added per liter to every treating solution.

A solution containing 2.1 mol. potassium fluoride and no potassium hydroxide had some effect and a concentration of 0.5 N potassium hydroxide with 2.1 mol. potassium fluoride per liter was sufficient to facilitate separation. Curves shown in Fig. 2 indicate no hydration of fluor-phlogopite for these experiments.

(*c*) *Effect of temperature.*—All experiments hitherto described were carried out at 350°C. When the temperature of treatment is high, the working pressure is consequently high and from a practical standpoint, it is desirable to work with as low temperatures and under as low pressures as possible for the accomplishment of easy separation. Results of experiments using a dilute solution 0.5 N and a concentrated solution (10 N) are given in Table V.

Experiments with 0.5 N potassium hydroxide gave an effect of easing separation when they were carried out at 300°C or above, while in experiments using 10 N potassium hydroxide, treatment at 250°C or above was sufficient to give a good effect. Therefore, the temperature of treatment was fixed at 300°C and the effect of concentration was investigated in experiments given in Table VI.

TABLE V

Period of treatment: 24 hr.
Sample No. 2 having a fluorine content of 9.3% was used.

Temperature of treatment (°C)	350	300	250	200	150
Concn. of KOH					
0.5 N	B	B	C	C	C
10 N	A_0	A	A	C	C

It was found that a solution of 0.25 N potassium hydroxide with 2.1 mol. potassium fluoride per liter was sufficiently strong for easy separation with the treatment at 300°C, as it was with treatment at 350°C.

3) Treatment with acid and salt solutions.—Effects of using acids and some salt solutions as treating solutions for hydrothermal treatment of fluor-phlogopite were investigated because Saito, one of the present authors, had found that hydrothermal treatment of synthetic asbestos with solutions of acids, alkalies or some salts gave easy separation of fiber crystals. Experimental results are given in Table VII.

Treatments with 10 N potassium carbonate solution or with more concentrated solutions gave good results, those with less concentrated solutions had less effect and that with 1 N solution had no effect. Treatments with mixed solutions of 8.4 N potassium carbonate and various concentrations of potassium hydroxide gave the same results as those with mixed solutions of 2.1 N potassium fluoride and various concentrations of potassium hydroxide, as given in Table VI, i. e. treatments with 0.25N potassium hydroxide or more concentrated solutions gave good results. This means that in both cases potassium hydroxide played the main role.

Treatments with hydrochloric acid gave good results when 0.125 N or more concentrated solutions were used. Treatment with potassium hydrogen sulfate gave the best results among those with bisulfate, bicarbonate and biphosphate of potassium.

Fluorides were found to have a suppressing effect on hydration of fluor-phlogopite, and experiments Nos. 27′ to 31′ show that

TABLE VI

Sample No. 1 having a fluorine content of 13.9% was used.
Temp. of treatment: 300°C, Concn. of KF: 2.1 mol. per liter, Period of treatment: 24 hr.

Experiment	No. 21	No. 22	No. 23	No. 24	No. 25	No. 26
Concn. of KOH(N)	2	1	0.5	0.25	0.125	0.0625
Properties of product						
Ease of separation	A	A	A	A	B	B
F content (%)	9.5	13.7	11.0	10.8	10.4	11.7
Percentage decrease of F	32	1	21	23	25	16
W. loss between 600° and 850°C(%)	0.0_7	0.0_5	0.1_7	0.0_6	0.0_8	0.0_7

TABLE VII

Condition I: Temp.: 250°C, Period: 24 hr., except on special notice.
Condition II: Temp.: 350°C, Period: 48 hr.

Experiment	Condition	Treating soln.	Ease of separation
No. 1′	I	11.6N K_2CO_3	A_0
2′	I	10.0N K_2CO_3	A
3′	I	8.4N K_2CO_3	B
4′	I	4.7N K_2CO_3	B
5′	I	1.0N K_2CO_3	C
6′	I	3.0N KOH 8.4N K_2CO_3	A
7′	I	2.0N KOH 8.4N K_2CO_3	A
8′	I	1.0N KOH 8.4N K_2CO_3	A
9′	I	0.5N KOH 8.4N K_2CO_3	A
10′	I	0.25N KOH 8.4N K_2CO_3	A
11′	I	0.125N KOH 8.4N K_2CO_3	C
12′	I	0.0625N KOH 8.4N K_2CO_3	B
13′	I	0.25N HCl	A
14′	I	0.125N HCl	A
15′	I(12 hr.)	0.125N HCl	C
16′	I	0.0625N HCl	B
17′	I	0.0312N HCl	B
18′	I	0.0156N HCl	B
19′	I	0.0078N HCl	C
20′	I	0.125N HCl 4.7N KCl	B
21′	I	0.125N HCl 2.35N KCl	B
22′	I	2.2N $KHSO_4$	A_0
23′	I	1.5N $KHSO_4$	C
24′	I	0.7N $KHSO_4$	C
25′	I	3.0N $KHCO_3$	B
26′	I	2.9N KH_2PO_4	B
27′	I	7.4N KF	A
28′	I(12 hr.)	7.4N KF	B
29′	I	6.2N KF	C
30′	I	5.0N KF	C
31′	II	2.4N KF	A_0
32′	II	H_2O	C

potassium fluoride itself can ease separation of mica crystals.

Crystals treated with acid solutions were found to be harder and less flexible than those treated with alkaline solutions. It seems that the difference in these physical properties of products depends on the different actions of acid and alkali on glassy substance in the agglomerate mass. Alkali reacts on glass to make the silicic acid component of the glass soluble or to accelerate devitrification of the glass, thus decreasing the strength of the glass to bind mica crystals. The dissolution and the devitrification of the glass help the treating solution to penetrate further into the agglomerate mass and react on glass in deep places of the mass. The milk-white substance produced by devitrification of glass which exists between mica crystals in treated agglomerates, was separated easily when the crystals were split from the mass.

Acid reacts on glass to dissolve basic components of glass and leaves the silicic acid component undissolved. The silicic acid skeleton thus produced may prevent penetration of the treating solution into shallow spaces, such as interstices between cleavage planes of mica crystals. This

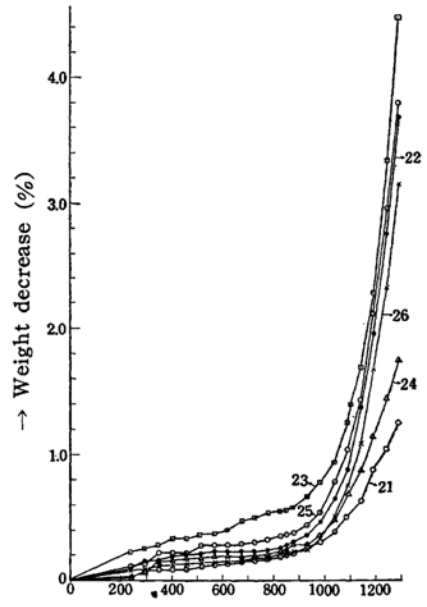


Fig. 3.

makes separation of glassy substance in the acid-treated mass more difficult than separation of glass in the alkali-treated mass and the split crystals from the acid-treated mass are somewhat harder and less flexible than those from the alkali-treated mass.

Hydrothermal treatment for easy separation was much more effective on agglomerates of well developed crystals than on those of small crystals because treating solution penetrates much more easily into the mass along plate crystals than through the mass of irregularly arranged small crystals.

Percentage decreases of fluorine content of the mass treated with potassium carbonate, potassium hydrogen sulfate or hydrochloric acid were found to be smaller than those of the mass treated with alkali by the measurement of fluorine content and temperature-weight loss curve of these products.

4) Investigation on treated mica crystals. — (*a*) *Vacuum test.* — Vacuum characteristics of split mica crystals of untreated synthetic fluor-phlogopite, of products of experiments Nos. 1 to 8 and natural phlogopite were measured. Specimens used for the measurement were washed with ethylalcohol, rinsed with distilled water and dried at 120°C for 1 hr. The specimens were placed in a silica glass tube pumped to a pressure of 1×10^{-5} mmHg. Then the specimens were put into a hot place in the vessel maintained at a definite temperature, and the change of pressure of the vessel was measured. Fig. 4a shows the volume of gas evolved from the specimens when heated. Results of the measurements on specimens which were first outgassed by heating in a high vacuum (1×10^{-5} mmHg) are shown in Fig. 4b. The glassy substance adhering to untreated crystals contains minute amounts of carbon and gas. Hydrothermal treatment decreases the amount of glass adhered. This is why treated crystals evolved smaller amounts of gas than the untreated crystals at temperatures lower than 800°C. Specimen No. 5, which was treated with 2 N sodium hydroxide for 48 hr. and was expected to contain hydroxyl-phlogopite, increased the gas evolution rapidly at about 950°C in the same way as natural phlogopite did. It is worthy of note that specimen No. 7, which was treated with 1.7 N sodium hydroxide in the presence of 4.3 mol. potassium fluoride per liter, evolved the smallest amount of gas among specimens tested.

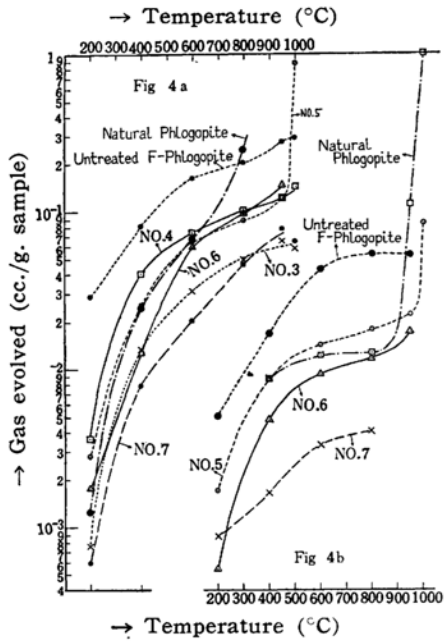


Fig. 4.

(*b*) *X-ray powder diagram.*—It can be said from the experimental results described above that the main part of the original fluor-phlogopite remained unchanged by hydrothermal treatment, although a small part of the mica changed to hydroxyl-phlogopite. X-ray powder photographs taken by using a camera of 114.6 mm. diameter gave no difference between untreated and treated micas. However, by using a Norelco X-ray Geiger counter goniometer, weak extra peaks adjacent to (00*l*) of fluor-phlogopite were detected in the X-ray powder diagram of treated mica which was found to have a weight loss between 600° and 850°C. This means that a small amount of hydroxyl-phlogopite exists in the specimen because these extra peaks correspond to (00*l*) of hydroxyl-phlogopite[4].

Summary and Conclusion

Agglomerates of synthetic mica crystals were treated hydrothermally with alkali, acid and salt solutions in order to ease the separation of mica crystals which are bonded together by glassy substance.

(1) Among treatments with sodium hydroxide solutions of the concentration from 0.5 to 2 N at 350°C for 24 hr., that with 2 N sodium hydroxide facilitated greatly the separation of mica crystals.

A small amount of fluor-phlogopite probably changed to hydroxyl-phlogopite and hydroxides were produced by the hydrothermal treatment.

(2) The hydration of fluor-phlogopite and the formation of hydroxide were suppressed by the addition of fluorides in the treating solution. It was found that the presence of 1.5 mol. potassium fluoride per liter of treating solution was effective for the suppression.

(3) Among treatments with potassium hydroxide solution in the presence of 2 mol. potassium fluoride per liter solution at 350°C for 24 hr., that with 0.25 N or more concentrated solution of potassium hydroxide was effective for easing separation of mica crystals. Potassium fluoride itself was found to be effective for easy separation.

(4) It was necessary to keep the temperature at 250°C or above in the treatment with 10 N potassium hydroxide and 300°C or above in the treatment with 0.5 N potassium hydroxide in order to obtain a good result.

(5) Treatments with potassium hydroxide solution in the presence of 2 mol. potassium fluoride per liter solution at 300°C for 24 hr. were as effective as those with the same solution at 350°C.

(6) Among treatments with solutions of various concentrations of potassium carbonate or potassium carbonate and potassium hydroxide at 250°C for 24 hr., 10 N or more concentrated potassium carbonate solution was effective as a treating solution and in a mixed solution of potassium carbonate and potassium hydroxide the latter played the main role.

(7) Among treatments with solutions of various concentrations of hydrochloric acid or hydrochloric acid and potassium chloride at 250°C for 24 hr., 0.125 N or more concentrated hydrochloric acid solution was effective as a treating solution and the presence of potassium chloride had no effect.

(8) Among treatments with potassium hydrogen sulfate, potassium hydrogen carbonate and potassium dihydrogen phosphate, that with potassium hydrogen sulfate was most effective and the smallest necessary concentration of the treating solution was 2 N.

(9) A solution of 7 N potassium fluoride or a more concentrated one was effective as a treating solution at 250°C for 24 hr.

(10) Split crystals from the mass treated with alkali and potassium fluoride solutions were flexible and those treated with acid were harder and less flexible than the former. The difference of the effects of acid and alkali was interpreted as the difference of their action on binding glass.

(11) Hydrothermal treatment for easy separation was much more effective on agglomerates of well developed crystals than on those of small crystals because the treating solution penetrates easily into the mass along plate crystals.

(12) Investigation of X-ray powder diagram of treated products revealed that the main part of fluor-phlogopite crystals remained unchanged and only a small amount of original mica changed to hydroxyl-phlogopite by treatments with strong alkali solutions. This observation was in good agreement with the experimental results deduced from the observed decreases of fluorine contents and temperature-weight loss curves of treated products.

(13) It was found that split crystals from a treated mass evolved less gas than those from an untreated mass because of the low content of adhering glass in the former. Split crystals which contained a small amount of hydroxyl-phlogopite began to evolve gas at about 950°C.

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