EXPERIMENTAL HYDROTHERMAL ALTERATION OF K-FELDSPAR IN ALUMINUM SULPHATE SOLUTION

(2) EFFECT OF CHEMICAL CONDITION AND PARTICLE SIZE

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INTRODUCTION

Natural potash feldspar (orthoclase perthite) is used as starting materials and is altered in aluminum sulphate solution under hydrothermal condition. The purpose of the present study is to make clear the effect of chemical condition and particle size in process of alunitization. Some chemical data on alteration process are described in this paper.

TECHNIQUE

Each specimen was reacted with aluminum sulphate-aqueous solution in the test-tube-type bomb, under varying time and concentration. The 2.5 grams of sample and 10–25 milliliters of aluminum sulphate solution were sealed in the bomb. The running temperature was fixed at 200°C and pressure was controlled at 14–75 kg/cm². The size fraction of 100–250 (–) mesh was used for the experiment. The specimens were X-rayed after the hydrothermal treatment to determine mineral phase. Starting material and alteration products were examined by chemical analysis to observed the chemical behavior in process of alunitization.

EFFECT OF CONCENTRATION OF REACTION SOLUTION

In the present experiment, 2.5 grams of starting material (minus 250 mesh) and 25 milliliters of aluminum sulphate solution were used. Concentration of reaction solution was regulated to be 1% and 5%.

Identification of the phases was based on the X-ray diffraction patterns. In the aluminum sulphate solution environment, the mineral phases of starting material change to form alunite (Abe, *et al.*, 1970). As for the specimen No. 12 (200°C, 260 hours, 1% solution), peaks of orthoclase lower and the peaks of alunite ((012)·(015)·(021)) begin to appear. With the

Table 1. Chemical compositions of alteration products

	10	11	12	13	14	15	16	17	18
SiO ₂	61.69	61.01	60.48	56.43	55.23	53.46	52.09	48.95	47.24
Al ₂ O ₃	18.35	18.65	18.82	20.12	20.86	21.04	21.20	22.17	23.43
Na ₂ O	3.24	3.18	3.02	3.12	2.84	2.57	2.72	2.58	2.57
K ₂ O	11.12	10.98	10.82	10.07	9.29	8.88	9.54	8.61	8.20
SO ₃	2.31	2.40	2.98	5.35	6.79	7.60	7.92	9.05	9.71
H ₂ O(±)	3.01	3.21	3.41	4.44	4.70	7.22	6.79	8.12	9.03
Total	99.72	99.43	99.53	99.53	99.71	100.77	100.26	99.48	100.18

Numbers (10-18) are the same as in Table 1 of preceding paper (Abe, *et al.*, 1970)

specimen No. 6 (200°C, 260 hours, 5% solution), the peaks of orthoclase are observed slightly and the most part comes to be occupied by the diffraction patterns of alunite. Intensity of main peaks of alunite increases by increase in concentration.

SiO₂

Leaching value of SiO₂ is greater for the higher concentration. SiO₂ decreases from 13.60% (200°C, 50 hours) to 19.14% (200°C, 260 hours) in 5% solution runs. Especially at the early stage of running time (until 50 hours) SiO₂ decreases rapidly (Fig. 1-A). In 1% solution environment, SiO₂ decreases from 3.57% (200°C, 50 hours) to 4.78% (200°C, 260 hours). In this environment, slight decreases (1.21%) of SiO₂ is observed between 50 hours and 260 hours (Table 1).

Al₂O₃

A comparison of the results from the 5% solution run with those of 1% solution run shows a clear trends toward concentration. In 1% solution environments, Al₂O₃ indicate a relatively low value (Fig. 1-B). Al₂O₃ increases from 0.11% (200°C, 50 hours) to 0.28% (200°C, 260 hours). But it increases with increased concentration. Al₂O₃ increases from 2.75% (200°C, 50 hours) to 3.84% (200°C, 260 hours) in 5% solution environments.

Na₂O

The alkali content in alteration products decreases by increase in concentration of reaction solution. In 1% solution environments, Na₂O decreases from 0.36% (200°C, 50 hours) to 0.58% (200°C, 260 hours). In 5% solution runs, Na₂O decreases from 0.74% (200°C, 50 hours) to 1.28% (200°C, 260 hours) compared with that of starting materials (Fig. 2).

Fig. 1. Variation curves for concentration of solution. Open circle; starting material, solid circle; alteration product.

Fig. 2. Variation curves for concentration of solution.

K_2O

The leaching value of K_2O is greater than that of Na_2O . In 1% solution runs, K_2O leaches from 0.58% (200°C, 50 hours) to 0.88% (200°C, 260 hours), and in 5% solution environments from 2.33% (200°C, 50 hours) to 4.15% (200°C, 260 hours).

 SO_3

The SO_3 content tends to increase with increased concentration of reaction solution. In 1% solution runs, SO_3 increases from 2.31% (200°C, 50 hours) to 2.98% (200°C, 260 hours). In 5% solution runs SO_3 increases from 7.91% (200°C, 50 hours) to 11.20% (200°C, 260 hours) compared with that in initial environment (Fig. 2).

EFFECT OF VOLUME IN REACTION SOLUTION

For this hydrothermal treatment, 2.5 grams of starting materials (minus 250 mesh) and 10 milliliters or 25 milliliters of aluminum sulphate solution (5%) were sealed in test-tube bombs. This was reacted at 200°C and varying time. The samples were analysed before and after the hydrothermal treatment to determine the behavior of leaching and increment of chemical composition in the course of the reaction.

 SiO_2

SiO_2 decreases maximally 19.14% (200°C, 260 hours) in 25 milliliters runs. In contrast with 25 milliliters runs, SiO_2 decreases from 8.83% (200°C, 50 hours) to 11.80% (200°C, 260 hours) in 10 milliliters runs. Difference of leaching value is 4.77–7.34% as compared with those of 10 milliliters and 25 milliliters treatments (Fig. 3).

 Al_2O_3

In 25 milliliters runs, Al_2O_3 increases from 2.75% to 3.84% compared with that of starting materials. Al_2O_3 increases from 1.58% (200°C, 50 hours) to 2.50% (200°C, 260 hours) in 10 milliliters treatments.

 $Na_2O \cdot K_2O$

The alkali content in alteration product decreases as shown in Figure 4. In the 10 milliliters treatments, Na_2O leaches from 0.48% (200°C, 50 hours) to 1.03% (200°C, 260 hours) and K_2O decreases from 1.63% (200°C, 50 hours) to 2.82% (200°C, 260 hours). The leaching value of alkali is smaller than that in 25 milliliters treatments (Fig. 4).

 SO_3

As shown in Figure 4, SO_3 increases from 5.35% (200°C, 50 hours) to 7.60% (200°C, 260 hours). The increment value of SO_3 is smaller compared with that in 25 milliliters treatments.

Fig. 3. Isovolumetric variation curves for SiO_2 and Al_2O_3 .

Fig. 4. Isovolumetric variation curves for Na_2O , K_2O and SO_3 .

EFFECT OF PARTICLE SIZE

In this case 2.5 grams of orthoclase perthite and 25 milliliters of aluminum sulphate solution (5%) were reacted. Particle size of starting materials is regulated to be 100–150 mesh and minus 250 mesh. Fine grained specimens are generally more ready to be alunitized than coarser grained specimens under the same conditions of hydrothermal treatments, although compositional difference between them is small.

 SiO_2

SiO_2 decreases from 13.17% (200°C, 50 hours) to 18.02% (200°C, 260 hours) in coarse grained (100–150 mesh) specimens. In the fine grained (minus 250 mesh) specimens, leaching value of SiO_2 is much the same as in the coarse grained specimens (Fig. 5).

 Al_2O_3

In the coarse grained specimens, Al_2O_3 increases from 2.66% (200°C, 50 hours) to 4.89% (200°C, 260 hours) compared with that of starting materials. In this case, an increment value of Al_2O_3 is larger than that of fine grained specimens under the same conditions of hydrothermal environments.

 $\text{Na}_2\text{O} \cdot \text{K}_2\text{O}$

The alkali contents decrease in alteration product, and leaching value of alkali is larger in the fine grained specimen than in the coarse grained one. In the coarse grained specimens Na_2O decreases from 0.88% (200°C, 50 hours) to 1.03% (200°C, 260 hours) and K_2O decreases from 2.16% (200°C, 50 hours) to 3.50% (200°C, 260 hours) compared with that of original materials.

Fig. 5. Variation curves for particle size. A: 100–150 mesh, B: 250(–) mesh

Fig. 6. Variation curves for particle size. A: 100–150 mesh, B: 250(–) mesh

SO₃

In the coarse grained specimens, SO₃ increases from 7.92% (200°C, 50 hours) to 9.71% (200°C, 260 hours) compared with that of fresh orthoclase perthite. In the fine grained specimens, an increment value of SO₃ is 7.91–11.20% (Fig. 6).

GEOLOGICAL APPLICATION AND DISCUSSION

Alunite is typically distributed with a close relation to mineralization in the volcanogenic sulphur ore deposits. Alteration chemistry of the Abuta mine (Abe, 1962), which is most typical sulphur deposit in Japan is as follows. That is SiO₂ decreases in alunite zone (Fig. 7). These leaching silica may be removed to silica mineral zone. In the present hydrothermal treatment, SiO₂ decreases compared with that of starting material, and this tendency is not connected with the chemical condition and particle size. Al₂O₃ shows a trend of increase in the alunite zone as compared with the silica mineral zone near the sulphur ore body (Fig. 7). In the hydrothermal study, Al₂O₃ increases with the elevated temperature, higher concentration and in larger volume of reaction solution. K₂O increases in weight percentage in the alunite zone of

Fig. 7. Diagram showing variation of chemical composition in wall-rock of the Abuta mine.

M: montmorillonite zone, K: kaolinite zone, S: silica mineral zone, A: alunite zone, Sa: saponite zone, Or: original rock, O: ore body, A·B·C·D: hanging wall side, E·F·G·H·I: foot wall side. (grams of oxides in cubic meter). (After Abe, 1962)

natural alteration aureole. Na_2O and K_2O show the trend of decrease throughout the other alteration mineral (chalcedonic quartz, opal, α -cristobalite, kaolinite, halloysite, montmorillonite) zones. But, in the hydrothermal experiments, alkali decreases with elevated temperature, in higher concentration and finer particle size. It is probable that alkali leached in the solution side recombine with Al^{3+} , SO_4^{2-} and H_2O during the hydrothermal alteration process. SO_3 and $\text{H}_2\text{O}(\pm)$ show increasing values in the alunite zone that enclose the sulphur deposit. In the present study, SO_3 and $\text{H}_2\text{O}(\pm)$ contents tend to increase with increasing temperature, in higher concentration of reaction solution and in finer grained specimens.

The same chemical behavior as in the artificial alteration process is shown to cause the increment or decrease in chemical elements as observed in the altered zone enclosing the sulphur deposit. Mainly by such chemical reaction, the rearrangement and alteration of rock-forming minerals were progressively repeated. Accordingly, such complicated alteration and mineral assemblage as is now observed may have been formed (Abe and Takeuchi, 1967; Takeuchi and

Abe, 1967). The long and frequent interaction between acidic hydrothermal solution and the country rocks must have caused the increment and/or decrease in chemical elements. And then alkali, as the elements leached out from the country rocks, combined with SO_4^{2-} and H_2O primarily contained in the ascending solution and excess Al^{3+} , formed alunite as alteration mineral. At the area nearest to the paths of acidic hydrothermal solution, almost all elements are leached out, and in this area residual or leached silica arranges to form the silica mineral zone.

The chemical behavior of the elements observed in the laboratory is very similar to that investigated in nature. Much more work must be done to determine the nature of the chemical environment under hydrothermal conditions.

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摘 要

硫酸アルミニウム溶液によるカリ長石の熱水変質実験 (2) 溶液条件および粒度の影響

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カリ長石と硫酸アルミニウム溶液を熱水条件下で反応させ、得られた明礬石化変質産物の化学組成変化を検討した。

溶液濃度 (1% および 5%) および容量 (10ml および 25ml) の、変質度合に及ぼす影響は大きい。出発物質の粒度差 (100-150mesh および 200(-) mesh) は組成変化に対して強い影響を与えない。人工変質による化学的な溶出・付加の material balance は、虻田硫黄鉱床における alteration chemistry のそれと酷似する。