Leaching of Andesite in Acid Media

By Hiroshi KAMIYA

(Received June 2, 1960)

" Leaching " is a term often used in geology. There is little geochemical study on the leaching process of rocks.

In many epithermal deposits such as sulfur, iron sulfide, opal and alunite ores, the original host rocks have been altered with acid leaching and other processes, and transformed into various altered zones.

Leaching action of surface and ground waters takes part in weathering processes at ordinary temperature and pressure.

As a result, it is important to investigate under natural conditions the behavior of chemical elements, which are abundant in the host rocks as constituents of rock-forming minerals, in order to consider the mechanism of weathering and the alteration of host rocks in the zone of oxidation.

In the study on the behavior of chemical elements, the concept " mobility " has been introduced by many investigators. The relative mobility of some elements in hydrothermal condition has been established by Bakhmutov[1]. Moreover, in weathering processes including leaching, migration and fixation of constituents of the host rocks by actions of ground and surface waters, their mobilities have been discussed[2].

Mobility defined in this way is affected by pH and oxidation-reduction potentional of the environments and many other factors.

Elements may move not only as ions, but as colloids or detrial fragments of original minerals. The movement of the elements as emanation, moreover, may take place, where volcanic gasses take part in the formation of altered rocks.

The above-mentioned discussions are based on no theory or experiments but on field data and observations, as well as on the analysis of natural substances.

The initial processes of both alteration and weathering are chemical and physical decompositions of rocks. Concerning this, solubility of rocks and minerals in water has been measured[3-5].

The present experiment was carried out to investigate what mobility the constituents of rock-forming minerals have, as mainly ions in various acid media in the presence of a sufficient quantity of air.

It is the aim of this study to obtain quantitative data on a leaching action which may play a serious role in weathering and alteration of rocks in the zone of oxidation.

---

[1] L. A. Bakhmutov, *A Translation of Geokhimiya*, No. 1, 83 (1958).

[2] D. H. Anderson and H. E. Hawkes, *Geochim. et Cosmochim. Acta*, **14**, 204 (1958).

[3] M. D. Dorfman, *A Translation of Geokhimiya*, No. 5, 537 (1958).

[4] D. Carroll and H. C. Starkéy, *Geochim. et Cosmochim. Acta*, **16**, 83 (1959).

[5] L. K. Yakhontova, *A Translation of Geokhimiya*, No. 1, 95 (1958).

Experimental

Sample.—Like other sulfur deposits, various kinds of altered rocks consisting of secondary minerals, such as opal, alunite and kaoline, were found around sulfur ore bodies of Ogushi Mine in Gumma Prefecture.

It has been recognized there that one of the original host rocks thus hydrothermally altered is augite hypersthene-andesite. The least altered andesite was powdered to 150∼200 meshes and used for the present leaching experiment. The chemical composition and mode of the andesite are shown in Tables I and II.

TABLE I. CHEMICAL COMPOSITION OF ANDESITE

Constituent	Content (%)
SiO_2	55.8
Al_2O_3	18.8
FeO	4.1
Fe_2O_3	3.4
MgO	3.8
CaO	7.5
Na_2O	2.1
K_2O	1.0
H_2O (−)	3.0
H_2O (+)	1.4
Total	100.9

TABLE II. VOLUME PERCENTAGE OF THE CONSTITUTENTS OF THE ANDESITE

Phenocryst	Plagioclase	38
	Hypersthene	9
	Augite	8
	Magnetite	5
Groundmass		33
Alteration product		7
Total		100

Equipment.—A polyethylene 500 ml. bottle, which contained 200 ml. of leaching acid or water to suspend the powdered sample, was placed on a water bath. This leaching bottle was fitted with a two-hole rubber stopper carrying a polyethylene tube of 5 mm. diameter attached to a flow-meter of air through a washing bottle and reached nearly to the bottom of the leaching bottle so that the leaching acid or water in it would be well stirred by the introduction of air, and also carrying a condenser connected to an aspirator.

For all equipment polyethylene was used because glass could introduce silica and sodium.

Procedure.—The flow of air was regulated with the aspirator so that the air would be bubbled through the solution at the rate of 2 l. per minute.

As its temperature was raised up to approximately 90°C, 2 g. of the powdered sample was suspended in it. The leaching experiments were carried out at 90±3°C.

After 5 min., 30 min., 1, 2 and 3 hr. from addition of the sample, the treatment was stopped immediately, and the leachates were centrifuged and analyzed.

For this experiment were used 0.1, and 0.01, 0.001 N sulfuric acids and distilled water.

Analytical Method.—The leachates were analyzed for silica, aluminum, iron, calcium, magnesium, sodium and potassium which are abundant in the rock.

1) *SiO_2*.—Silica was determined colorimetrically by a molybdenum blue method which would determine only dissolved silica, but no colloidal silica.

2) *Fe.* — Colorimetric estimation of total iron was carried out by reduction of all the iron to ferrous state, using hydroxylamine, and then by measurement of transmittance of a red color developed with α, α'-dipyridyl. Ferrous iron was determined by adding α, α'-dipyridyl with no reducing agents, reading the transmittance and comparing with a calibration curve. Ferric iron was determined by difference from the sum of the two.

3) *Al.*—Total iron and aluminum was detemined by back titration of a small excess of EDTA with a standard zinc sulfate solution using dithizone as an indicator after addition of sodium acetate buffer. Then, aluminum was determined from the amount of total iron and aluminum after deducting the amount of iron obtained by colorimetric method.

4) *Ca and Mg.*—Total calcium and magnesium were determined by titrating with EDTA in the presence of Eriochrome Black T at pH 10 after removal of iron and aluminum. Next calcium was determined by titration with EDTA using NANA* indicator in strong alkaline solution, and finally the amount of magnesium was calculated by subtracting the amount of calcium from the combined amount.

5) *Na and K.* — Sodium and potassium were determined by means of flame photometry.

Results and Discussion

Leaching of Seven Constituents.—The amounts of seven constituents, SiO_2, Al, Fe, Ca, Mg, Na and K leached out of 2 g. sample with sulfuric acid or water at 5 min., 30 min., 1, 2 and 3 hr., respectively, after starting the leaching are arranged in Table III. They are plotted against time in Fig. 1.

As change in pH of the leaching media might have an influence on the leaching, it was desirable to keep the pH of them constant and to maintain the original leaching conditions. However, the experiment under pH-constant condition was not carried out, because the use of buffer solutions, for instance, would make it difficult to detect small amount of constituents leached out of the rock and have an effect on the leaching. Ranges from initial to final pH of the leaching acid or water are given in Fig. 1.

Among the constituents leached, only silicon

---

* NANA is a commercial name which has chemical formula of 2-hydroxy-1-(2'-hydroxy-4'-sulfo-1-naphthylazo)-3-naphthoic acid.

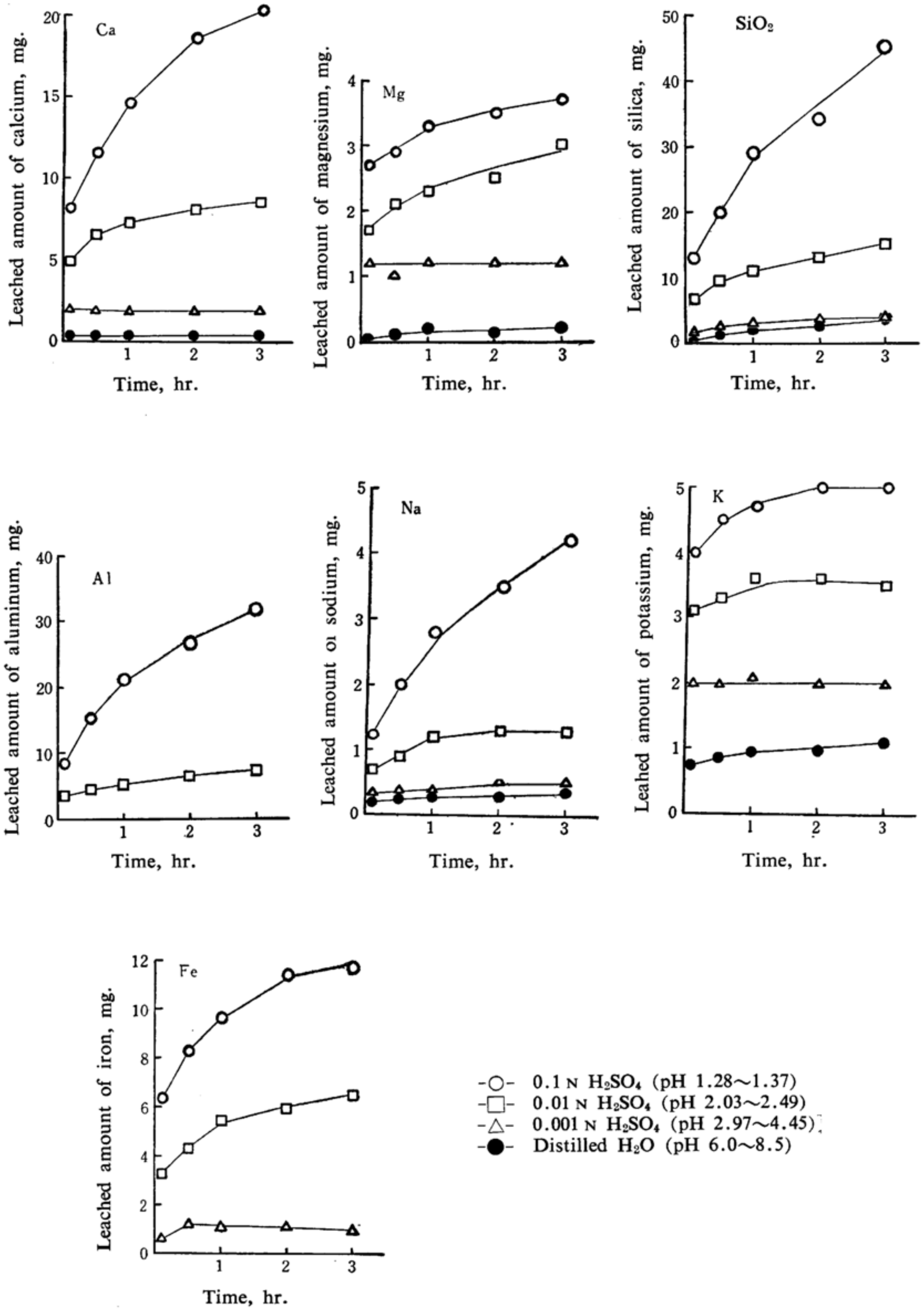

Fig. 1. Leaching-curve of seven constituents plotted against time.

TABLE III. SEVEN CONSTITUENTS LEACHED OUT OF 2 g. POWDERED SAMPLE WITH 200 ml. SULFURIC ACID AND WATER

	Time	Na (mg.)	K (mg.)	Ca (mg.)	Mg (mg.)	Fe^{2+} (mg.)	Fe^{3+} (mg.)	Al (mg.)	SiO_2 (mg.)	pH
0.1 N-H_2SO_4 (pH 1.28)	5 min.	1.2	4.0	8.2	2.7	5.6	0.7	8.5	13	1.31
	30 min.	2.0	4.5	11.6	2.9	6.3	2.0	15.2	20	1.33
	1 hr.	2.8	4.7	14.6	3.3	6.4	3.3	21.2	29	1.34
	2 hr.	3.5	5.0	18.5	3.5	7.8	3.6	26.5	34	1.35
	3 hr.	4.2	5.0	20.2	3.7	8.5	3.2	31.6	45	1.37
0.01 N-H_2SO_4 (pH 2.03)	5 min.	0.7	3.1	4.9	1.7	3.2	<0.1	3.4	6.5	2.20
	30 min.	0.9	3.3	6.5	2.1	4.1	0.2	4.4	9.5	2.28
	1 hr.	1.2	3.6	7.2	2.3	5.3	<0.1	5.2	11	2.35
	2 hr.	1.3	3.6	8.0	2.5	5.7	0.2	6.6	13	2.42
	3 hr.	1.3	3.5	8.5	3.0	6.2	0.2	7.3	15	2.49
0.001 N-H_2SO_4 (pH 2.97)	5 min.	0.35	2.0	2.0	1.2	0.67	<0.05	0.2	1.6	3.89
	30 min.	0.37	2.0	1.9	1.0	1.1	0.1	0.2	2.6	4.33
	1 hr.	0.40	2.1	1.8	1.2	1.0	0.1	0.3	3.0	4.37
	2 hr.	0.43	2.0	1.8	1.2	1.1	<0.05	0.2	3.9	4.42
	3 hr.	0.42	2.0	1.8	1.2	0.9	0.1	0.3	4.0	4.45
Distilled H_2O (pH 6.0)	5 min.	0.21	0.75	0.3	<0.1	<0.05	—	0.1	0.6	7.4
	30 min.	0.24	0.87	0.2	0.1	<0.05	—	0.1	1.4	7.7
	1 hr.	0.28	0.95	0.2	0.2	<0.05	—	0.2	2.2	8.2
	2 hr.	0.28	0.97	0.3	0.1	<0.05	—	0.2	2.8	8.5
	3 hr.	0.34	1.1	0.3	0.2	<0.05	—	0.2	3.6	8.5

is represented as SiO_2, because it would be leached in the form of oxide[6].

As shown in Fig. 1, time of leaching, generally, tends to increase the amount of constituents leached. The leaching is very rapid for an initial stage of the experiment, but becomes retarded gradually later, as the concentration of constituents in the leachate appears to approach the limit of their solubility in the leaching acid or water.

The lower pH of the leaching media is, the larger initial leached amount and its increment are. At a high pH of the leaching media such as 0.001 N sulfuric acid and distilled water, time of leaching hardly increases the initial leached amount of several constituents.

The rock contains both ferrous and ferric irons. There existed more ferrous than ferric iron in the leachate of 0.1 N sulfuric acid, and in the leachate of 0.01 N and 0.001 N sulfuric acids and distilled water ferric iron was hardly detected. As the leached ferrous iron might be oxidized to ferric state by bubbled air, it should not be concluded that all the ferric iron in the leachate came only of one kind in the rock. Therefore, the leaching curve of total iron is drawn without a distinction between ferric and ferrous irons in Fig. 1.

With 0.001 N sufuric acid the leaching of iron proceeds during the first 30 min. of the experiment, but prolongation of it decreases its amount in the leachate. This decrease may be caused by reprecipitation of iron once leached owing to an increase of pH.

Initial Leaching.—As already described, the initial leaching is very rapid. A considerable amount of constituents was leached out of the rock even during the first 5 min. of experiment.

Each straight line, which is drawn through the first two points representing the leached amount at 5 and 30 min. on the curves given in Fig. 1, does not pass through the origin, but intercepts the axis of the leached amounts. The value of this interception may be thought to correspond to the initial leached amount. In 0.1 N sulfuric acid, for example, this amount of potassium reached 80 per cent of its amount leached up to the end of the experiment.

The initial leaching ratio, that is, the ratio of the initial leached amount of each constituent, obtained in this way, to its content in the original rock was calculated. In Fig. 2 these ratios are plotted against initial pH of the leaching acid or water used for the experiment.

Fig. 2 shows that the initial leaching ratio of every constituent decreases with an increase of pH. The ratio of potassium is the largest among the constituents under the experimental conditions, that is, at pH range 1 to 6. On the contrary, that of silica is the smallest. The ratio of sodium belongs to a rather small

---

[6] H. Mukaiyama, *Min. Geol.*, 4, 195 (1954).

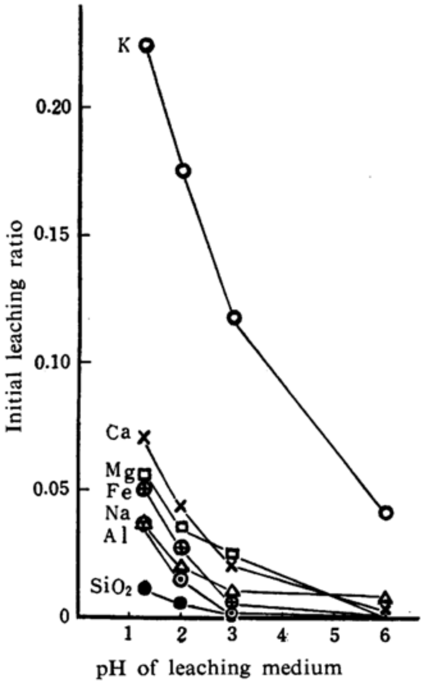

Fig. 2. Relation between initial leaching ratio and pH of leaching medium.

group at low pH, but is large next to that of potassium at pH 6.

Above pH 3 the ratios of aluminum and iron are much the same to that of silica.

Increasing Rate of Leached Amount. — The leaching of the constituents out of the rock proceeds at a certain increasing rate, whereupon it becomes gradually retarded.

During three hours of the leaching experiment an average increment per hour of the amount of each constituent excepting the initial leached amount was obtained from the curve in Fig. 1. This increasing rate expresses an average slope of the curve which passes through the five points corresponding to the amount leached at each time.

The ratio of this rate to the content of each constituent in the rock was calculated and plotted against the intermediate value of initial and final pH of the leaching acid or water in Fig. 3.

With an increase of pH, the increasing ratio defined in this way has the same tendency to decrease as the initial leaching ratio has. However, the increasing rate of several constituents is too small to be recognized in 0.001 N sulfuric acid and distilled water. In general, the leaching of all the constituents out of the rock is retarded at high pH. For this reason a small increasing rate need not be discussed in detail.

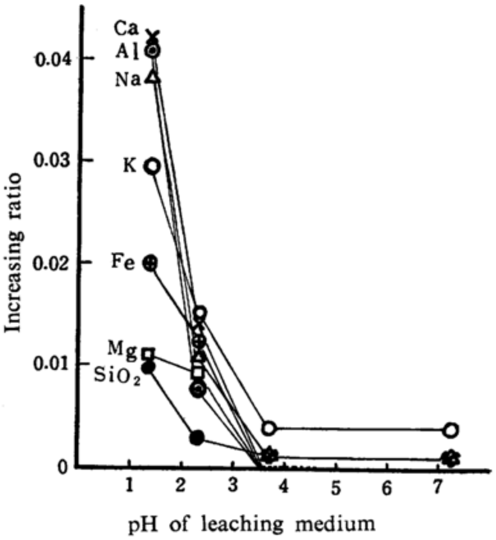

Fig. 3. Relation between increasing ratio and pH of leaching medium.

The curves of the increasing ratio in Fig. 3 differ somewhat from the curves of the initial leaching ratio in Fig. 2.

At pH 1 calcium, aluminum and sodium refer to a group of large ratio, next to which are potassium and iron. The ratio of magnesium and silica are small at this pH. Raising of pH changes the order of the ratios at pH 1. At pH 2 aluminum, which has a large ratio at pH 1, belongs to a group of smaller ratio, and on the other hand potassium is the top of them. Magnesium has less difference of the ratio than other constituents at pH range 1 to 2.

A Comparison between Initial Leaching Ratio and Increasing Ratio.—In Table IV are given the following ratios of each constituent at pH's 1 and 2.

$$\frac{\text{Increasing ratio (shown in Fig. 3)}}{\text{Initial leaching ratio (shown in Fig. 2)}}$$

Table IV shows that the leaching of potassium is very rapid at an initial stage but becomes retarded soon, that is, the average slope of its leaching curve is less steep than the other constituents in Fig. 1, and that on the contrary

TABLE IV. INCREASING RATIO/INITIAL LEACHING RATIO

	Na	K	Ca	Mg	Fe	Al	SiO_2
0.1 N-H_2SO_4	1.1	0.1	0.6	0.2	0.4	1.1	0.9
0.01 N-H_2SO_4	0.6	0.1	0.3	0.3	0.4	0.5	0.6

the increasing rate of sodium, aluminum and silica is superior to the initial leaching.

As a result, every constituent has a characteristic initial leaching ratio and increasing ratio which may depend on mineral composition of the rock or other factors.

The least mobility of silica in the present experiment agrees in Shimada's conclusion that action of sulfuric acid could cause aluminum, iron etc. originally present in rocks to be removed leaving silica to form siliceous rocks(7).

Though a leaching process of rocks would be very complicated under natural conditions, the effect of pH on it is the most important one of many environmental factors.

The writer wishes to express his indebtedness to Professor K. Noguchi for having been good enough to read this manuscript, to Dr. T. Sudo for helpful advice and encouragement and to Dr. J. Ossaka and Mr. M. Ichikuni for help and advice with regard to the analytical techniques. His acknowledgement is also due to the staff of the Ogushi Mine for help in the collection of specimens.

Department of Chemistry
Faculty of Science
Tokyo Metropolitan University
Setagaya, Tokyo

---

7) K. Shimada, *J. Chem. Soc. Japan. Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 263 (1959).