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journal or publication title	鹿児島大学理学部紀要. 地学・生物学
volume	18
page range	55-70
別言語のタイトル	アルカリ処理による乱された“シラス”安定化の実験的研究
URL	http://hdl.handle.net/10232/00009978

EXPERIMENTAL STUDY ON THE STABILIZATION OF THE DISTURBED "SHIRASU" BY MEANS OF THE ALKALI-TREATMENT

By

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(Received July 8, 1985)

Abstract

The "Shirasu", pumice flow in a narrow sense, prevailing over South Kyushu, Japan, is characterized essentially by the presence of the welded texture. When the development is moving in the "Shirasu" regions, the appearance of the disturbed "Shirasu" whose original welded texture is fractured can not be avoided. For the purpose of the stabilization of the disturbed "Shirasu", keeping the disaster prevention in mind, more than one hundred experiments were carried out under various different conditions; the artificial production of crystalline minerals, which play a role of cementing material to fill intergranular spaces existing among fractured grains, from volcanic glass of the disturbed "Shirasu" was investigated by means of the alkali-treatment. As a result, it was apparently proved that it is possible to produce artificially crystalline minerals of zeolite group, such as nosean, Na-chabazite, K-chabazite, Na-P zeolite and analcime, from volcanic glass by means of a comparatively simple alkali-treatment on a laboratory scale. Among the alkali-treatments, the (NaOH+NaAlO₂)-treatment was most effective; nosean was produced.

Introduction

The so-called "Shirasu" is defined to be pumice flow in a narrow sense or pyroclastic flow in a broad sense those which prevail over South Kyushu, Japan, and came from caldera volcanoes as "nuée ardente" (ŌBA et al., 1967). Thus, the "Shirasu" pumice flow has also been used for the explanation in occasion instead of the "Shirasu" (ŌBA et al., 1980, 1983). The "Shirasu" or "Shirasu" pumice flow are characterized by the presence of the welded texture. That is, they are weakly welded ones. A major portion of the welded texture consists of volcanic glass, which plays a role to fill intergranular spaces among major and minor minerals and to make mineral grains bind with one another. For such a reason, naturally, they have a comparatively large physical stability (ŌBA, 1973; ŌBA et al., 1980). They are, in general, gradationally changed into the strongly welded ones, i. e., welded tuff (ŌBA, 1973).

The technical terms "Shirasu", primary "Shirasu" which is the non-weathered and

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fresh "Shirasu" of which the natural ground is composed (ŌBA et al., 1972), and disturbed "Shirasu" whose original welded texture was fractured by man-work (ŌBA, 1973; ŌBA et al., 1980), have widely been used in the fields of soil mechanics, civil engineering, disaster prevention, pedology and industrial utilization in Japan. The appearance of the disturbed "Shirasu" can not be avoided in areas where the development such as a housing land construction is moving in the "Shirasu" or "Shirasu" pumice flow regions. It is reasonable that the disturbed "Shirasu" whose original welded texture was fractured is physically unstable in comparison to the primary "Shirasu" whose welded texture is preserved.

The results obtained from microscopic observation, X-ray diffraction and differential thermal analysis clearly show that none of clay mineral such as aluminium hydrosilicate is contained in the non-weathered and fresh "Shirasu", i. e., the primary "Shirasu" (ŌBA, 1973; ŌBA et al., 1980). This fact means that cementing materials are not present, but intergranular spaces only are present among grains of fractured materials when the primary "Shirasu" was fractured once. In addition, most grains of volcanic glass are the vesiculated ones, and, naturally, they contain much bubbles. These facts demonstrate how the disturbed "Shirasu" is liable to become loose right away when it is encountered with the running water (ŌBA, 1973; ŌBA et al., 1980). When the disturbed "Shirasu" is saturated by water, therefore, it becomes loose immediately, and causes not only the landslide, but also the rush-down in a form of fluid. This is the reason why the so-called "Shirasu disaster" of unusual patterns repeatedly took place mainly at portions of the disturbed "Shirasu" at places where works such as a housing land development were carrying on in the "Shirasu" or "Shirasu" pumice flow regions in every heavy rain seasons in the past.

For the purpose of the stabilization of the disturbed "Shirasu", keeping the disaster prevention in mind, a series of experimental work was carried out under various different conditions. Major attention will be given in this paper to: the experimental methods and conditions possible to produce artificially crystalline minerals to play a role of cementing material, which fills intergranular spaces existing among grains of major and minor constituent minerals of the disturbed "Shirasu" and makes the grains bind with one another; and possibility of the application on the artificial production of crystalline minerals of zeolite group by means of the alkali-treatment for the stabilization of the disturbed "Shirasu".

Starting Materials and Experimental Methods

The "Shirasu" sample used for the experiments was collected from Aira "Shirasu" (ŌBA et al., 1976) or Aira "Shirasu" pumice flow and/or Aira "Shirasu" pumice flow deposit (ŌBA et al., 1980, 1983), i. e., Ito pyroclastic flow (ARAMAKI, 1965) which came from Aira caldera volcano locating at Kagoshima Bay, at Shiroyama Housing Land east of Gokoku-Jinja, Kagoshima City, South Kyushu, Japan. The following three groups were prepared as starting materials: (a) pulverized "Shirasu" samples after sieving under 0.147 mm of Tyler's standard sieve and drying at room temperature; (b) "Shirasu" sample sieved under 1.4 mm of Tyler's standard sieve after drying at room temperature; and (c) non-prepared

Table 1. Modal analysis (vol. %) of the starting material "Shirasu"

Volcanic glass	87.6 %
Plagioclase	6.8
Quartz	0.5
Hypersthene	0.7
Augite	0.2
Hornblende	0.2
Opaque minerals	3.9
Others	0.1

Analyst. K. Inoue. • Grain size 0.246~0.124 mm.

Cited from Ōba et al. (1980).

Table 2. Chemical analysis (wt. %) of the starting material "Shirasu"

SiO ₂	71.40 %
TiO ₂	0.25
Al ₂ O ₃	13.65
Fe ₂ O ₃	0.76
FeO	1.55
MnO	0.04
MgO	0.48
CaO	1.88
Na ₂ O	3.36
K ₂ O	2.70
H ₂ O+	3.40
H ₂ O-	0.62
P ₂ O ₅	0.05
Total	100.14

Analyst. H. Yamashita. Cited from Tomita et al. (1969).

"Shirasu" samples. Each group of the samples is called in convenience ; pulverized "Shirasu" samples, "Shirasu" samples sieved under 1.4 mm, and non-prepared "Shirasu" samples, respectively.

Modal and chemical analyses of the starting material "Shirasu" are given in tables 1 and 2. The "Shirasu" is composed in mineral composition of a large amount of amorphous volcanic glass and a small amount of plagioclase, quartz, hypersthene, augite and hornblende, and accompanied by magnetite, apatite and others. X-ray powder diffraction patterns for the starting material "Shirasu" is given in 1 on Figs. 1, 2, 3 and 4 for comparison. Only plagioclase and quartz were detected. Differential thermal analysis curve for the starting material "Shirasu" is shown in 1 on Fig. 5.

The samples were treated by alkali solutions ; 5 % NaOH aqueous solution, 5 % KOH aqueous solution, a mixture of 4 % NaOH aqueous solution and 4 % NaCl aqueous solution 1 : 1, and a mixture of 4 % NaOH aqueous solution and 4 % NaAlO₂ aqueous solution 1 : 1. Erlenmeyer flasks with Liebig-Graham condenser were used for boiling or warming of the starting materials. Water bathes with a thermostat were used for heating and warming of the starting materials so that 100°C or 50°C are kept in temperature. For the out-door test, the starting materials 3 or 4 Kg contained in 10 l polyethylene bucket were layed on the roof top of building for the exposure to the sunrays.

Starting materials, alkali solutions, temperatures and time or duration required for the treatment are tabulated in Table 4. The out-door test required a long time on the reason that it was winter season. The treated samples were followed by centrifugal separator, filtration and dressing, and then dried at room temperature, and, finally, examined by X-ray powder diffraction and differential thermal analysis.

Experimental results

Experimental results obtained under various different conditions are given in Table 4.

Table 3. X-ray powder diffraction data for the produced crystalline minerals of zeolite group in the pulverized "Shirasu" samples after the alkali-treatment

1 Na-chabazite			2 K-chabazite			3 Na-P zeolite			4 Analcime			5 Nosean		
hkl	d(Å)	I	hkl	d(Å)	I	hkl	d(Å)	I	hkl	d(Å)	I	hkl	d(Å)	I
101	9.50	s	101	9.35	m									
110	7.03	w	110	6.86	vw	110	7.08	m						
012	6.46	vw										110	6.42	vs
021	5.61	vw	021	5.54	vw				221	5.64	vs			
003	5.09	w	003	5.04	vw	200	5.01	w	220	4.87	m			
												200	4.46	vw
211	4.37	m	211	4.33	m									
						211	4.10	m						
122	3.91	w	122	3.87	w									
300	3.62	s		3.60	vw				321	3.66	m	211	3.66	vs
220	3.48	vw	220	3.44	vw				400	3.44	vs			
104			104											
						310	3.16	vs						
401	2.95	vs	401	2.93	vs				332	2.93	vs			
												310	2.81	s
410	2.62	vw	410	2.61	vw	321	2.68	m	431	2.69	m			
125	2.53	vw	125	2.51	vw	400	2.51	vw	521	2.51	m	222	2.57	s
232			232						440	2.43	w			
						411	2.36	vw				321	2.38	vw
						330								

CuK α = 1.5418Å. 1, 3 and 4: see No. 3, 4 and 6 in Table 4; 2: see No. 12 in Table 4; 5: see No. 21 in Table 4.

Treatment by NaOH Solution

Pulverized "Shirasu" samples after boiling:

Each 1 g of the pulverized "Shirasu" sample was totally immersed in 5 % NaOH solution 50 ml and boiled for 5, 10, 15, 20, 25 and 50 hours. As a result, Na-chabazite was detected in the treated samples after boiling for 10 and 15 hours, and both Na-P zeolite and analcime were recognized in the treated samples after boiling for 20, 25 and 50 hours (see No. 1-6 in Table 4). No any crystalline mineral, however, was recognized in the treated sample after boiling for 5 hours. X-ray powder diffraction patterns for the treated samples are given in Fig. 1. Its data for Na-chabazite and analcime are tabulated in Table 3. Differential thermal analysis curve showing the production of Na-chabazite, indicated by an endothermic peak at about 150°C, is shown in 2 on Fig. 5.

"Shirasu" samples sieved under 1.4 mm after heating at 100°C and 50°C:

Each 5 g of the "Shirasu" sample sieved under 1.4 mm was totally immersed in 5 % NaOH solution and heated at 100°C for 20, 30, 40 and 100 hours, and at 50°C for 20, 40, 60, 80 and 100 hours. As a result, both Na-chabazite and Na-P zeolite were identified in

(continued)

No.	Starting materials	Weight	Alkali solutions			Temperature	Time	Products
52	Non-prepared "Shirasu"	3-4 Kg	NaOH	5 %	Immersed	Out-door	15 days	None
53	"	"	"	"	"	"	30	"
54	"	"	"	"	"	"	45	"
55	"	"	"	"	"	"	60	"
56	"	"	"	"	"	"	75	"
57	"	"	"	"	"	"	90	"
58	"	"	"	"	"	"	105	"
59	"	"	"	"	"	"	120	"
60	"	"	KOH	"	"	"	15	"
61	"	"	"	"	"	"	30	"
62	"	"	"	"	"	"	45	"
63	"	"	"	"	"	"	60	"
64	Non-prepared "Shirasu"	3-4 Kg	KOH	5 %	Immersed	Out-door	75 days	None
65	"	"	"	"	"	"	90	"
66	"	"	"	"	"	"	105	"
67	"	"	"	"	"	"	120	"
68	"	"	NaOH NaCl	4 % 4 %	"	"	15	"
69	"	"	"	"	"	"	30	"
70	"	"	"	"	"	"	45	"
71	"	"	"	"	"	"	60	"
72	"	"	"	"	"	"	75	"
73	"	"	"	"	"	"	90	"
74	"	"	"	"	"	"	105	"
75	"	"	"	"	"	"	120	"
76	"	"	NaOH NaAlO ₂	4 % 4 %	"	"	15	"
77	"	"	"	"	"	"	30	"
78	"	"	"	"	"	"	45	"
79	"	"	"	"	"	"	60	"
80	"	"	"	"	"	"	75	"
81	"	"	"	"	"	"	90	"
82	"	"	"	"	"	"	105	"
83	"	"	"	"	"	"	120	"

Abbreviations.-S, Na-chabazite; K, K-chabazite; P, Na-P zeolite; A, analcime; N, nosean.

the treated samples after heating at 100°C for 30 and 40 hours, and both Na-P zeolite and analcime were recognized in the treated samples after heating at 100°C for 100 hours (see No. 22-30 in Table 4). However, none of crystalline mineral of zeolite group was detected in all the treated samples after heating at 50°C for any time and the treated samples after heating at 100°C for 20 hours.

Comparison of the relative intensities of peaks appeared on the X-ray powder diffraction patterns suggests that crystalline minerals produced in the "Shirasu" samples sieved under 1.4 mm after the NaOH-treatment and heating at 100°C for 30 and 100 hours correspond in amount to those in the pulverized "Shirasu" samples after the NaOH-treatment and boiling for 10 and 20 hours.

Non-prepared "Shirasu" samples after the out-door test:

Each 3 or 4 kg of the non-prepared "Shirasu" sample was fully immersed in 5 % NaOH solution and layed at the out-door, and then examined by X-ray powder diffraction for each 15 days. As a result, on any crystallin mineral such as zeolite was detected even after 120 days at most (see No. 52-59 in Table 4).

Treatment by KOH Solution

Pulverized "Shirasu" samples after boiling:

Each 1 g of the pulverized "Shirasu" sample was totally immersed in 5 % KOH solution 50 ml and boiled for 5, 10, 15, 20, 25 and 50 hours. X-ray powder diffraction patterns for the treated samples are given in Fig. 2. K-chabazite was identified in the treated samples after boiling for 20 hours or more, although none of crystalline mineral of zeolite group was detected in the treated samples after boiling for 5 and 10 hours (see No. 7-12 in Table 4). X-ray powder diffraction datum for K-chabazite is given in 2 in Table 3. Differential thermal analysis curve also shows the production of K-chabazite, indicated by an endothermic peak at about 145°C (see 3 on Fig. 5).

"Shirasu" samples sieved under 1.4 mm after heating at 100°C and 50°C:

Each 5 g of the "Shirasu" sample sieved under 1.4 mm was totally immersed in 5 %

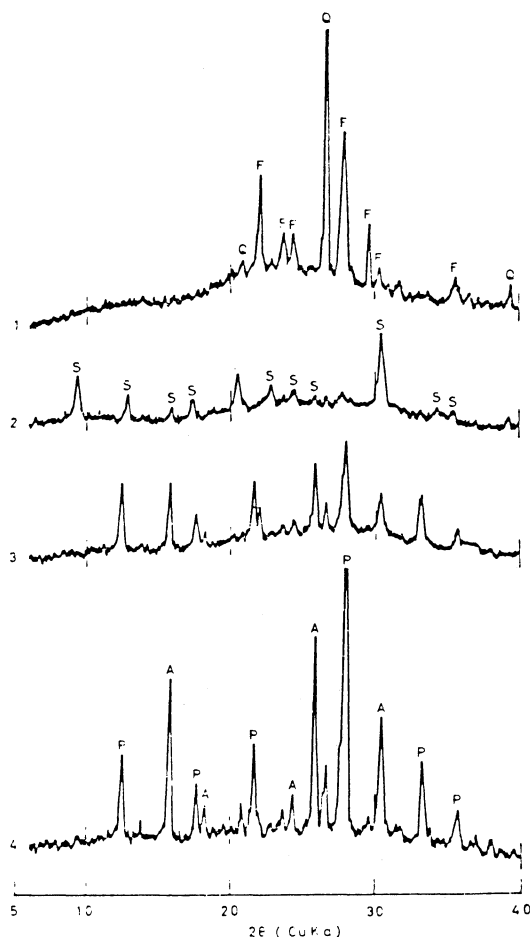


Fig. 1. X-ray powder diffraction patterns for the pulverized "Shirasu" samples treated by 5 % NaOH solution. 30 KV, 15 mA. 1, starting material "Shirasu"; 2, after boiling for 10 hs; 3, after boiling for 20 hs; 4, after boiling for 50 hs. Abbreviations.-F., plagioclase; Q, quartz; S, Na-chabazite; P, Na-P zeolite; A, analcime.

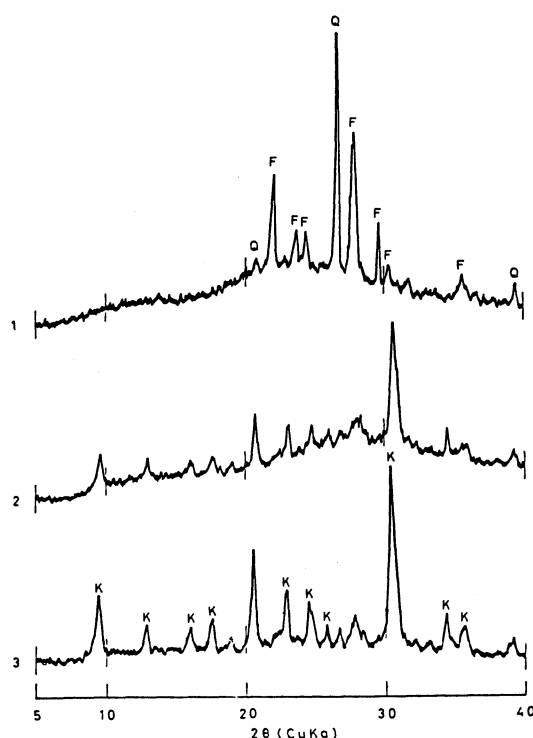


Fig. 2. X-ray powder diffraction patterns for the pulverized "Shirasu" samples treated by 5 % KOH solution. 1, starting material "Shirasu"; 2, after boiling for 20 hs; 3, after boiling for 50 hs. K, K-chabazite. The other abbreviations are the same as those in Fig. 1.

KOH solution and heated at 100°C for 20, 30, 40 and 100 hours, and at 50°C for 20, 40, 60, 80 and 100 hours. However, no any crystalline mineral of zeolite was recognized (see No. 31–39 in Table 4).

Non-prepared "Shirasu" samples after the out-door test:

Each 3 or 4 Kg of the non-prepared "Shirasu" sample was fully immersed in 5 % KOH solution and layed at the out-door, but no any crystalline mineral of zeolite was recognized even after 120 days (see No. 60–67 in Table 4).

Treatment by (NaOH + NaCl) Solution

Pulverized "Shirasu" samples after boiling:

Each 1 g of the pulverized "Shirasu" sample was totally immersed in a mixture of 4 % NaOH solution 25 ml and 4 % NaCl solution 25 ml and boiled for 5, 10 and 20 hours. X-ray powder diffraction patterns for the treated samples are given in Fig. 3. Both Na-chabazite and analcime were identified in the treated samples after boiling for 10 hours or more, although none of crystalline mineral of zeolite was detected in the treated samples after 5 hours boiling (see No. 13–15 in Table 4). Differential thermal analysis curve showing the production of analcime, indicated by a broad endothermic peak between 100°C

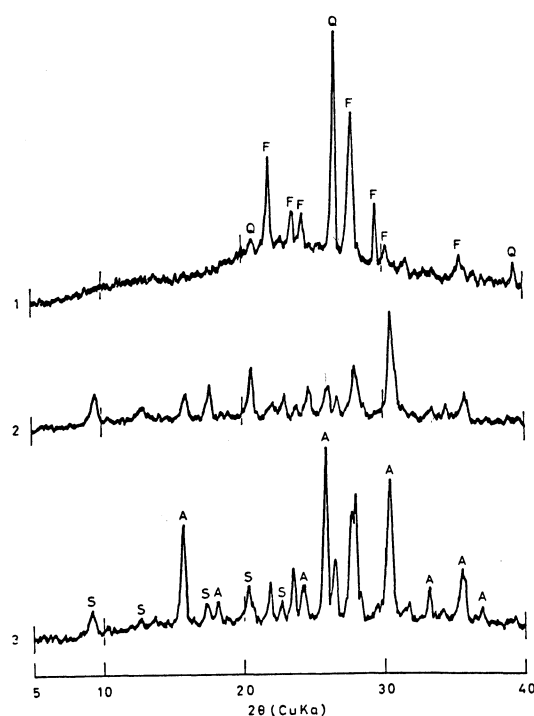


Fig. 3. X-ray powder diffraction patterns for the pulverized "Shirasu" samples treated by a mixture of 4 % NaOH solution and 4 % NaCl solution. 1, starting material "Shirasu"; 2, after boiling for 10 hs; 3, after boiling 20 hs.

Abbreviations are the same as those in Fig. 1.

and 200°C, is given in 4 on Fig. 5.

"Shirasu" samples sieved under 1.4 mm after heating at 100°C and 50°C:

Each 5 g of the "Shirasu" sample sieved under 1.4 mm was totally immersed in a mixture of 4 % NaOH solution 25 ml and 4 % NaCl solution 25 ml and heated at 100°C for 10, 20 and 40 hours, and at 50°C for 20, 40 and 100 hours. As a result, both Na-chabazite and analcime were identified in the treated samples after heating at 100°C for 20 hours or more, although none of crystalline mineral of zeolite was detected in the treated samples after heating at 50°C for any time and in the treated samples after heating at 100°C for 10 hours (see No. 40–45 in Table 4).

Non-prepared "Shirasu" samples after the out-door test:

Each 3 or 4 Kg of the non-prepared "Shirasu" sample was fully immersed in a mixture of 4 % NaCl solution 1 : 1 and layed at the out-door, but no any crystalline mineral of zeolite was recognized even after 120 days (see No. 68–75 in Table 4).

Treatment by (NaOH + NaAlO₂) solution

Pulverized "Shirasu" samples after boiling:

Each 1 g of the pulverized "Shirasu" sample was totally immersed in a mixture of 4 %

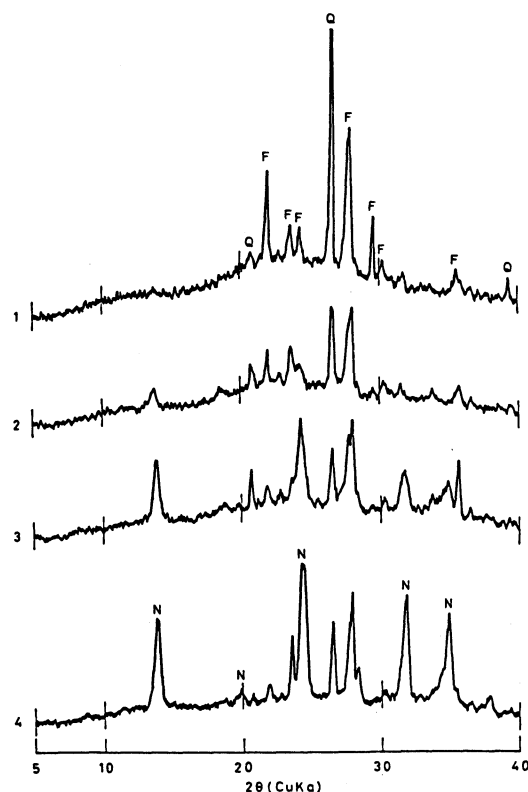


Fig. 4. X-ray powder diffraction patterns for the pulverized "Shirasu" samples treated by a mixture of 4 % NaOH solution and 4 % NaAlO₂ solution. 1, starting material "Shirasu"; 2, after boiling for 2 hs; 3, after boiling for 5 hs; 4, after boiling for 20 hs. N, nosean. The other abbreviations are the same as those in Fig. 1.

NaOH solution 25 ml and 4 % NaAlO₂ solution 25 ml and boiled for 1, 2, 3, 4, 5 and 20 hours. As a result, nosean was recognized in the treated samples after boiling for 2 hours or more, but none of crystalline mineral of zeolite was detected in the treated samples after boiling for one hour (see No. 16–21 in Table 4). X-ray powder diffraction patterns for the treated samples after boiling 2, 5 and 20 hours are given in Fig. 4. X-ray powder diffraction datum for nosean is given in 5 in Table 3. Differential thermal analysis curve showing the production of nosean, indicated by a broad endothermic peak between 100°C and 200°C, is given in 5 on Fig. 5.

"Shirasu" samples sieved under 1.4 mm after heating at 100° and 50°C:

Each 5 g of the "Shirasu" sample sieved under 1.4 mm was totally immersed in a mixture of 4 % NaOH solution 25 ml and 4 % NaAlO₂ solution 25 ml and heated at 100°C and 50°C for 10, 20 and 40 hours. As a result, the production of nosean was identified in all the treated samples (see No. 46–51 in Table 4).

Comparison of the relative intensities of peaks appeared on the X-ray powder diffraction patterns suggests that an amount of nosean produced in the treated "Shirasu"

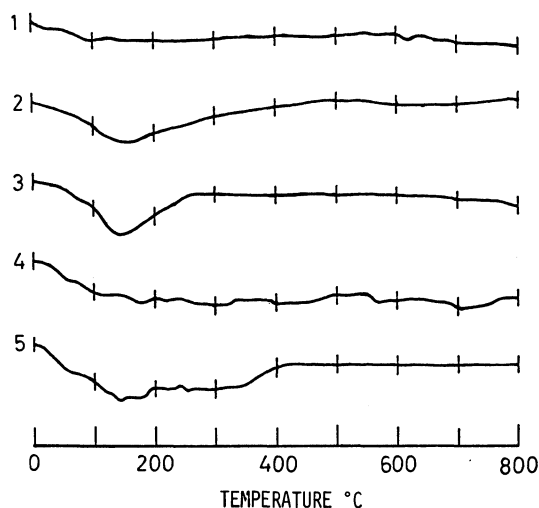


Fig. 5. Differential thermal analysis curves indicating the production of crystalline minerals of zeolite group in the pulverized "Shirasu" samples after the alkali-treatment. 1, curve without reaction peak in the starting material "Shirasu"; 2, curve with an endothermic peak at about 150°C indicating the production of Na-chabazite (see No. 2 in Table 4); 3, curve with an endothermic peak at about 145°C indicating the production of K-chabazite (see No. 9 in Table 4); 4, curve with a broad endothermic peak between 100°C and 200°C indicating the production of analcime (see No. 14 in Table 4); 5, curve with a broad endothermic peak between 100°C and 200°C indicating the production of nosean (see No. 17 in Table 4).

samples sieved under 1.4 mm after heating at 100°C for 10, 20 and 40 hours roughly corresponds to that of nosean in the pulverized "Shirasu" samples after boiling for 2, 5 and 20 hours.

Non-prepared "Shirasu" samples after the out-door test:

Each 3 or 4 Kg of the non-prepared "Shirasu" sample was fully immersed in a mixture of 4 % NaOH solution and 4 % NaAlO₂ solution 1 : 1 and layed at the out-door for 120 days at most. No any crystalline mineral of zeolite, however, was recognized in the treated samples (see No. 76-83 in Table 4).

Summary for the Experimental Results

The experimental results obtained under various different conditions will be summarized as follows.

Treatment by NaOH Solution

It is possible to produce artificially crystalline minerals belonging into zeolite group, such as Na-chabazite, K-chabazite, Na-P zeolite and analcime, in the pulverfzed "Shirasu" which was immersed in NaOH solution and boiled for 10 hours or more, and in the "Shirasu" sieved under 1.4 mm which was immersed in NaOH solution and heated at 100°C

for 30 hours or more, although no any chemical reaction was recognized in the non-prepared "Shirasu" which was immersed in NaOH solution and layed at the out-door for 120 days at most.

Treatment by KOH solution

K-chabazite alone is produced only in the pulverized "Shirasu" which was immersed in KOH solution and boiled for 15 hours or more, but no any crystalline mineral of zeolite group is produced under the other conditions. That is, the NaOH-treatment is much more effective than the KOH-treatment for the production of crystalline minerals of zeolite group under the same condition.

Treatment by (NaOH+NaCl) Solution

Na-chabazite and analcime are produced in the pulverized "Shirasu" which was immersed in a mixture of NaOH solution and NaCl solution 1 : 1 and boiled for 10 hours or more, and in the "Shirasu" sieved under 1.4 mm which was immersed in the same mixed solution and heated at 100°C for 20 hours or more ; while no any crystalline mineral of zeolite group is produced under the other conditions. Time required to produce crystalline minerals of zeolite group in the (NaOH+NaCl)-treatment is much shorter as compared to that in the NaOH-treatment in a case of the "Shirasu" sieved under 1.4 mm.

Treatment by (NaOH+NaAlO₂) solution

Nosean is produced in the pulverized "shirasu" which was immersed in a mixture of NaOH solution 1 : 1 and boiled for 2 hours or more, and in the "shirasu" sieved under 1.4 mm which was immersed in the same mixed solution and heated at 100°C and 50°C for 10 hours or more ; while no any crystalline mineral of zeolite group is produced in the non-prepared "Shirasu" which was immersed in the same mixed solution and layed at the out-door for 120 days at most. Time required to produce crystalline minerals of zeolite group by means of the (NaOH+NaAlO₂)-treatment is shortest among the other alkali-treatments if the produced mineral is regardless of kind of zeolite.

Supplemental Experiments by Means of the (NaOH+NaAlO₂)-Treatment

Throughout the whole experimental results, it became clear that the (NaOH+NaAlO₂)-treatment is most effective for the artificial production of crystalline minerals of zeolite group from the "Shirasu" material. Thus, supplemental experiments by means of the (NaOH+NaAlO₂)-treatment for the "Shirasu" samples were furthermore tried under various different conditions.

Starting materials, alkali solutions and experimental conditions for the supplemental experiments are tabulated in Table 5. Each "Shirasu" sample 1 g was put in Erlenmeyer flask and immersed totally in a mixture of 4 % NaOH solution 25 ml and 4 % NaAlO₂ solution 25 ml, and followed by the experimental conditions given in Table 5. Corked

Table 5. Supplemental experiments for the artificial production of nosean from the starting material "Shirasu" by means of the (NaOH + NaAlO₂)-treatment under various different conditions

No.	Starting materials* 1 g	Procedures	Duration at out-door	Products
1	Pulverized "Shirasu"	Not heated	15 days	None
2	"	Boiled 10 min	"	"
3	"	Boiled 20 min	"	"
4	"	Boiled 30 min	"	Nosean
5	"	Immersed in solution heated at 100°C	"	None
6	"Shirasu" sieved under 1.4 mm	Not heated	"	"
7	"	Boiled 10 min	"	"
8	"	Boiled 20 min	"	"
9	"	Boiled 30 min	"	Nosean
10	"	Immersed in solution heated at 100°C	"	None
11	Pulverized "Shirasu"	Not heated	30 days	"
12	"	Boiled 10 min	"	"
13	"	Boiled 20 min	"	Nosean
14	"	Immersed in solution heated at 100°C	"	None
15	"Shirasu" sieved under 1.4 mm	Not heated	"	"
16	"	Boiled 10 min	"	"
17	"	Boiled 20 min	"	Nosean
18	"	Immersed in solution heated at 100°C	"	None

* Starting materials were totally immersed in a mixture of 4 % NaOH Solution 25 ml and 4 % NaAlO₂ solution 25 ml.

flasks were layed at the out-door for the exposure to the sunrays. After 15 days and 30 days, the treated samples were examined by X-ray powder diffraction.

As a result, the production of nosean was recognized in both the pulverized "Shirasu" and the "Shirasu" sieved under 1.4 mm those which were boiled for 30 min. and layed for 15 days at the out-door and boiled for 20 min. and layed for 30 days at the out-door, while none of crystalline mineral of zeolite was detected under the other conditions (see No. 4, 9, 13 and 17 in Table 5). Comparison of the relative intensities of peaks appeared on the X-ray powder diffraction patterns suggests that the produced amount of nosean roughly corresponds to that of nosean in a case of the pulverized "Shirasu" after boiling for 2 hours.

Discussion

More than one hundred experiments in total number under various different conditions were carried out for the purpose of the stabilization of the disturbed "Shirasu". Major

efforts were given to the artificial production of crystalline minerals to play a role as cementing material in intergranular spaces existing among grains from volcanic glass.

As a result, it was apparently proved that it is possible to produce crystalline minerals of zeolite group easily from volcanic glass by means of a simple alkali-treatment. The mechanism of the artificial production of crystalline minerals of zeolite group from volcanic glass will be explained as follows: alkalis break the network linkage of Si (Al)-oxygen in volcanic glass and facilitate the rearrangement of ions toward new crystalline minerals (TOMITA et al., 1969). If only the artificial production of crystalline minerals of zeolite group is taken account, the (NaOH+NaAlO₂)-treatment will be most

Table 6. The shortest time or duration required to produce crystalline minerals of zeolite group from the starting material "Shirasu" under various different conditions

No.	Starting materlas	Weight	Alkali solutions			Temperature	Products	Time
1	Pulverized "Shirasu"	1 g	NaOH	5 %	50 ml	Boiled	S & P	10 hs
2	"	"	KOH	5 %	50 ml	"	K	15
3	"	"	NaOH NaCl	4 % 4 %	25 ml 25 ml	"	S & A	10
4	"	"	NaOH NaAlO ₂	4 % 4 %	25 ml 25 ml	"	N	2
5	"Shirasu" sieved under 1.4 mm	5 g	NaOH	5 %	50 ml	Heated at 100°C	S & P	30
6	"	"	NaOH NaCl	4 % 4 %	25 ml 25 ml	"	S & A	20
7	"	"	NaOH NaAlO ₂	4 % 4 %	25 ml 25 ml	"	N	10
8	"	"	"	"	"	Heated at 50°C	"	"
9	Pulverized "Shirasu"	1 g	"	"	"	Out-door after boiling 30 min	"	15 days
10	"Shirasu" sieved under 1.4 mm	"	"	"	"	"	"	"
11	Pulverized "Shirasu"	"	"	"	"	Out-door after boiling 15 min	"	30 days
12	"Shirasu" sieved under 1.4 mm	"	"	"	"	"	"	"

Abbreviations are the same as those in Table 4.

effective among the others.

No any crystalline mineral of zeolite group, however, could not be recognized in the non-prepared "Shirasu" samples after the alkali-treatment even if the treated samples were layed for 120 days at the out-door. This fact suggests that the qualitative conversion from volcanic glass into crystalline minerals of zeolite group through chemical reaction would be very slowly and gradually proceeded in the non-prepared "Shirasu" not on a scale of day, but on a scale of year.

The shortest hours or days possible to produce crystalline minerals of zeolite group from volcanic glass under various different conditions are summarized in Table 6. In No. 4 of Table 6, nosean is produced immediately after the time when the pulverized "Shirasu" sample was boiled for 2 hours or more ; and, in No. 9-12 of Table 6, it is produced slowly after the time when the pulverized "Shirasu" samples or the "Shirasu" samples sieved under 1.4 mm were boiled for 15 min. or 30 min. and layed at the out-door for 30 days or 15 days. If it is only taken account that cementing material is slowly produced to fill intergranular spaces existing among grains of the disturbed "Shirasu", No. 9-12 appear to be much better than No. 4.

The "Shirasu" material sieved under 1.4 mm, which was used for the experiments No. 10 and 12 in Table 6, occupies about 70 % in weight of the whole disturbed "Shirasu". Therefore, the artificial production of nosean from volcanic glass in No. 10 and 12 will be meaningful for the future application. In addition, sodium hydroxide and sodium alminate those which were used in the experiments No. 4 and No. 7-12 are very common and low cost, and they were used as a highly dilute mixed solution. Throughout the experimental results, it is also apparent that the production of crystalline minerals of zeolite group from volcanic glass by means of a mixed solution of sodium hydroxide and sodium alminate is accelerated under the presence of a highly dilute solution of sodium chloride, which seems to behave as a catalyst. This matter means that the sea water itself, in place of a highly dilute solution of sodium chloride, is available to be used as it is.

The discussion about the results obtained from the experiments No. 9-12 in Table 6 will be summarized as follows: when the disturbed "Shirasu" is added by a highly dilute alkali solution and heated for a comparatively short time, chemical reaction will take place between volcanic glass and alkalies, thus the conversion from volcanic glass into crystalline minerals of zeolite group will be slowly progressed as the time goes toward the stabilization of the disturbed "Shirasu".

Acknowledgements

Thanks are given to Kagoshima Prefectural Government, by which this work was financially supported in part.

References

- ARAMAKI, S. (1965): ^{14}C data at Ito pyroclastic flow, Aira caldera. *Earth Science (Chikyū Kagaku)*, no. 80, p.38 (in Japanese).
- ŌBA, N. (1973): Microstructure and physicochemical features of the "Shirasu". *Civil Construction Engineering (Sekō Gijutsu)*, **6**, p.67-72 (in Japanese).
- ŌBA, N., TOMITA, K., and YAMAMOTO, M. (1980): Physicochemical features of the "Shirasu" pumice flow deposits and its related landslides in South Kyushu, Japan. *Proceed. Intern'l Symposium on Landslides (ISL)*, New Delhi, 1980, **1**, p. 13-18.
- ŌBA, N., TOMITA, K., YAMAMOTO, M., ISTIDJAB, M., BADRUDDIN, M., SUDRADJAT, A. and SUHANDA, T. (1983): Geochemical comparison of volcanic products of Krakatau Group and Arira caldera-Sakurajima Volcano. Paper presented at Symposium on 100th Year Development of Krakatau and its Surroundings, August 23-27, 1983, Jakarta, Indonesia, 11 p., with 3 Figs.
- ŌBA, N., TOMITA, K., YAMAMOTO, M., ISTIDJAB, M., BADRUDDIN, M., SUDRADJAT, A., SUHANDA, T., KIYOSAKI, S., ISHII, T., NAKAMURA, J. and INOME, T. (1983): Geochemical comparison of the 1883 Krakatau pumice flow, Indonesia, and the Ata and Aira "Shirasu" pumice flows, Japan. *Rep. Fac. Sci., Kagoshima Univ.*, no. 16, p. 43-54.
- ŌBA, N., TSUYUKI, T., and EBHARA, H. (1967): Mineral and chemical compositions, and genesis of the Shirasu (I). *Jour. Japan. Assoc. Min. Petr. Econ. Geol.*, **58**, p. 81-97 (in Japanese with English abstract).
- ŌBA, N., YAMASHITA, H., and YAMAMOTO, M. (1972): Mineral and chemical compositions of the Secondary Shirasu. *Jour. Japan. Assoc. Min. Petr. Econ. Geol.*, **67**, p. 84-89 (in Japanese with English abstract).
- ŌBA, N., YAMAMOTO, M., TOMITA, K., and INOUE, K. (1980): Physicochemical features of the "Shirasu" and stability of the Filled Shirasu and the Weathered Shirasu. *Rep. Fac. Sci., Kagoshima Univ.*, no. 13, p. 1-9.
- TOMITA, K., YAMASHITA, H. and ŌBA, N. (1969): Artificial crystallization of volcanic glass to sodium and potassium form of chabazite at room temperature. *Jour. Japan. Assoc. Min. Petr. Econ. Geol.*, **60**, p. 25-34.