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THE CHARACTERIZATION OF ASR PRODUCTS AND ALKALIES IN CEMENT PASTE

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Summary:
The experiments of reactions between rocks and alkalies were made , and the influence of alkali cations to the reaction was investigated. It was recognized that sodium cation and potassium cation influence the reaction promotively. Also the character of ASR products was investigated by the cryoscopic method. From this experiment, adsorption of sodium cation to alkali silicate was suggested.

1. INTRODUCTION

In this paper , Two experiments were reported. The first experiment was the reaction of rocks with alkali-salt solution. In this experiment , the relation between the reaction and alkali cations was investigated. The second experiment was the reaction of rocks with sodium hydroxide solution . In this experiment , the character of ASR products was investigated.

2. SOME EXPERIMENTS ABOUT THE INFLUENCE OF ALKALI METAL CATION ON THE REACTION BETWEEN ROCKS AND ALKALIES

It was considered that the main part of the reaction between rocks and alkalies , was cut of a silaxane bond of Silicate , by an attack of hydroxyl anion.
In order to know the relation of the influence of alkali metal cation to the reaction, some experiments were carried out.

2.1 EXPERIMENTAL

Five kinds of rocks were used in this reaction experiment. The features of these rocks were showed in Table-1. A and B, were andesites. C was a chert, and D was a sandstone. E was also an andesete, but the most different point from other andesites; A and B , was that E was of montmorillonite-bearing rocks, and the other rocks were montmorillonite-free.
These rocks were crushed and their controlled grain sizes were from 0.15 to 0.30mm, these crushed rocks were washed by distilled water, and dried in an oven, and were used as rock samples in later reactions.
Tetramethylammonium hydroxide was chosen as an alkali agent for

the reaction. This alkali agent contain no alkali metal elements. There is a report which use this alkali in experiments of the expansion of mortar-bar(1). Solutions for the later reaction were made. The concentration of alkali was constant 1 mol/l , and the concentration of salt and kinds of salts were variegated. These solutions for reaction were mixed with the rock samples in Erlenmeyers made of fluorocarbon polymers, and were shaken (150rpm) in an incubator controlled in 80°C for 24hours. Cooling with ice was the first quenching of the reaction, and the second, filtration with a Buchner funnel, and the concentration of a liquid silicon layer was analyzed by atomic absorption.

Table-1 The outlines of rocks used in the experiments

Rock	Kind of rocks	Note
A	andesite	montmorillonite free
B	andesite	montmorillonite free
C	sandstone	montmorillonite free
D	chert	montmorillonite free
E	andesite	montmorillonite bearing

2.2 RESULT AND CONSIDERATION

The result of the reaction was showed in Fig-1. The condition of the reaction was that the alkali was 1M-tetramethylammonium hydroxiede and the salt was sodium chloride, and the concentration of salt was variegated from 0M to 2M.

There were two types of rocks in Fig-1. [Si] of one type of rock increases , as the concentration of salt in an alkali-salt solution increases. The other did not show a remarkable increase , as the concentration of salt in an alkali-salt solution increased. The former was mainly andesites which was montmorillonite-free,and its Sc values of ASTM C289 was high.

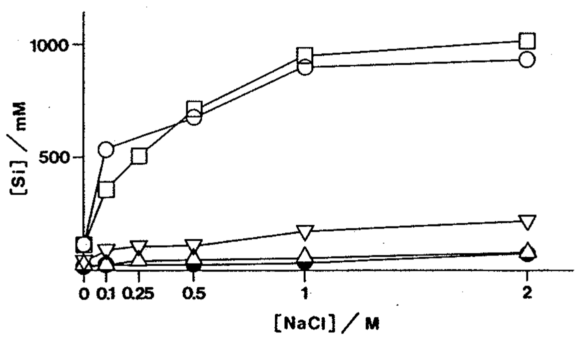

Fig-1 Concentrations of silicon in the reaction solution. Rocks was reacted with 1M-Me4NOH and NaCl solution. ○ is A, □ is B, ▽ is C, △ is D, ● is E.

The other was mainly chert, sandstone, and andesite which was montmorillonite-bearing. It was remarkable that those rocks which react well with sodium hydroxide solution did not produce so many values of [Si].

All the while , it has been said that sodium cation does not have a close relation with the mechanism of the solution of rocks, but have a close relation with the mechanism of expansion (1),(2). But this experiment suggested that there was some relation

between sodium cation and the mechanism of the solution of rocks.
The results of reactions between rocks and 1M-tetramethyammonium hydroxide with 1M-some kinds of salt were showed in Fig-2. The five kinds of salts were lithium chloride, sodium chloride, potassium chloride, cesium chloride , and tetramethyl-ammonium chloride . It may be said from Fig-2 that when the salt of the reaction solution was CsCl or Me_4NCl , [Si] , the reaction was almost same as if there was no salt This indicated these salts did not influence the reaction. But when the salt of the reaction solution was NaCl , [Si] , the reaction increased very much. This indicated that sodium cation promoted the influence of reaction. KCl was also recognized as having an influence on the reaction, but it was not such a remarkable influence in comparison with NaCl, and moreover, there were some rocks [Si] of the reaction solution that did not increase. On the contrary, when the salt was LiCl, [Si] of the reaction solution decreased in comparison with no-salt alkali. This suggested lithium cation influenced the reaction restrainedly.

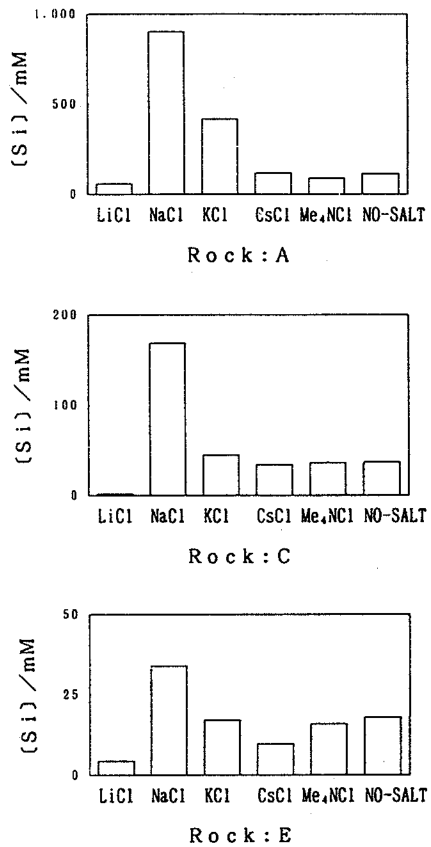

Fig-2 Concentrations of silicon in the reaction solution. Rocks was reacted with 1M-Me4NOH and salts.

3. EXPERIMENT ABOUT ASR PRODUCT

Some experiments of reactions between rocks and alkali (NaOH) were carried out, and the contain of ASR products was analized in order to investigate the character of ASR products.

3.1 EXPERIMENTAL

Seven kinds of rocks were used in these reaction experiments. The outlines of these rocks are showed in Table-2. These rocks were crushed and their grain size controlled from 0.15 to 0.30mm, these crushed rocks were washed by distilled water, and dried in an oven, and these were used as rock samples in the later reaction.
Sodium hydroxide was used as an alkali in the reactions. This alkali was considered as the main alkali in cement paste, and

it has been also used in ASTM C289.
The concentration of alkali in the reaction solution was constant in 1mol/l.
These solutions for the reaction were mixed with the rock samples in Erlenmeyers made of fluorocarbon polymers, and were shaken (150rpm) in an incubator controlled at 80°C for 24hours.
Cooling with ice was the first quenching of the reaction, and the second, filtration with Buchner funnel, and [Si], [Na], [K], [Al], [Mg], [Ca] of the liquid layer were analyzed by atomic absorption, and titration by EDTA was carried out in analyzing [Ca]. The freezing point of depression was measured, too.

Table-2 The outlines of rocks used in the experiments

Rock	Kind of rocks	Note
A	andesite	montmorillonite free
B	andesite	montmorillonite free
C	sandstone	montmorillonite free
D	chert	montmorillonite free
E	andesite	montmorillonite bearing
F	andesite	montmorillonite bearing
G	andesite	montmorillonite bearing

3.2 RESULT AND CONSIDERATION

The outlines of the result of these experiments were shown in Table-3. Andesites (montmorillonite-free) gave the reaction solution approximately 0.8mmol/l of [Si]. [Si] in the other kinds of rocks did not have so high a value, [Si] in rock C(chert) is approximately 0.1mmol/l, and [Si] in both D(sandstone) and E,F,G (andesites(montmorillonite-bearing)) was from 10 to 60mmol/l.
But there was a large difference of the concentration of sodium between these two type of rocks ; sandstone and andesites(montmorillonite-bearing). The difference was the concentration of sodium of the reaction solution.

Table-3 Concentrations of main elements in the reaction solution. The condition was 1N-NaOH , AGG/SOLN = 1(g/ml), 80degree, 24hr.

	[Si]	[Na]	[K]	[Al]	[Mg]	[Ca]	ΔT
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	℃
A	897	826	1.9	0.59	<0.05	0.18	1.1
B	826	818	1.3	0.44	0	0	1.15
C	52.5	913	1.5	5.71	0	0	3.2
D	114	922	0.5	1.78	0	0	3.1
E	61.1	753	2.2	3.2	0	0.28	
F	14.2	753	2.4	9.1	0	0.18	
G	15.8	722	1.7	5.6	0	0.03	

Before the reaction occurred, [Na] was 1.00 mol/l. Therefore [Na] in every rock was considered to decrease in their values. [Na] of rocks D and C was approximately 0.9 mol/l, so the remainding sodium, of about 0.1 mol/l, was considered to adsorb into the solid layer. And [Na] of andesite(montmorillonite-free) was about 0.8 mol/l or 0.85 mol/l, so the remainding sodium was about 0.1 mol/l or 0.15 mol/l.
On the other hand, [Na] values of andesites(montmorillonite-bearing) was about from 700mmol/l to 760mmol/l, therefore it was considered that the sodium amount from 240 to 300mmol/l absorbed into the solid layer. This was considered to indicate a high cation exchange capacity of montmorillonite
Comparing the concentration of these two element, [Si] and [Na], the concentrations of another elements were little.
A little aluminium was found in the reaction solution of sandstone sample and andesite(montmorillonite-bearing) , which had aluminium in their flames.
Potassium was very little, and Magnesium could not be found in any samples.

Freezing point depression (ΔT) was measured in only 4 kinds of rocks,;A,B,C,D. ΔT of A and B were from 1.10 to 1.15°C. ΔT of A and B which had concentration values of all ions, were larger than the other rocks which were low.
That there were two type of Sodium in the reaction product. One was as sodium hydroxide, and the other was as sodium silicate.
The number of the sodium silanoxide group was variegated by degree of polymerization. (Fig-3)
If the amount of [Na] corresponding to this number was as Silicate, and the remainder was a NaOH, the component of the product could be calculated, and the values were showed in Table-4.
The degree of freezing point depression could be calucurated. These calculated values were also shown in Table-4. There was little difference to each other.
The authers have one explanation about A and B. It is the adsorption of sodium to the oxygen of silaxane bond. (Fig-4)
This consideration explain that [NaOH] in the reaction solution decreased compared with the values of Table-4, and the measurement of the decrease in values of ΔT.
But, this explanation cannot explain such rocks like C or D, because the silicon content of the

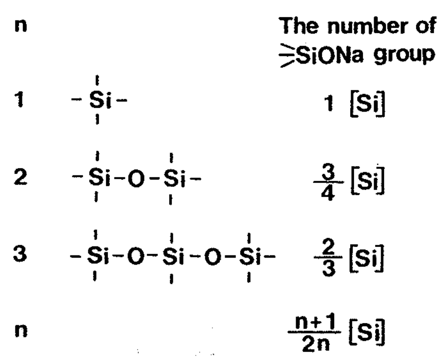

Fig-3 The number of -SiONa group when degree of polymerization is n

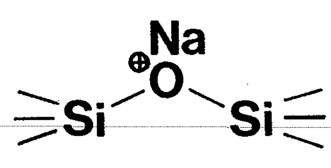

Fig-4 Adsorption of sodium cation to the silaxane bond

Table-4 Calculation of freezing point depression of the reaction solution

Rock	[Na]/M	[Si]/M	ΔT/℃	n	Calcurated [Na] of Silicate/M	Calcurated [Na] of NaOH/M	Calucurated ΔT from Sodium Silicate/°c	Calucurated ΔT from NaOH/°c	Total ΔT/℃
					$\frac{n+1}{2n}[Si]$	$[Na]-\frac{n+1}{2n}[Si]$	$\frac{[Si]}{n}\times 1.86$	$3.23[Na]-\frac{n+1}{2n}[Si]$	Calucurated ΔT from Sodium Silicated & NaOH
A	0.826	0.897	1.10	1	0.897	0	1.668	0	1.668
				2	0.673	0.153	0.834	0.495	1.329
				10	0.493	0.333	0.167	1.074	1.241
				∞	0.449	0.337	0	1.219	1.219
B	0.818	0.826	1.15	1	0.826	-0	1.536	0	1.536
				2	0.620	0.198	0.768	0.640	1.408
				10	0.454	0.364	0.154	1.176	1.330
				∞	0.413	0.405	0	1.308	1.308
C	0.913	0.053	3.20	1	0.053	0.860	0.099	2.778	2.877
				2	0.040	0.873	0.049	2.820	2.869
				10	0.029	0.884	0.010	2.855	2.865
				∞	0.026	0.887	0	2.865	2.865
D	0.922	0.114	3.10	1	0.114	0.808	0.202	2.610	2.822
				2	0.086	0.836	0.106	2.700	2.806
				10	0.063	0.859	0.021	2.775	2.796
				∞	0.057	0.865	0	2.794	2.794

reaction products of these rocks is not so much, and the influence of silicate to the freezing point depression is not so strong.

4. CONCLUSION

From the experiments of reactions between rocks and alkalies and the influence of alkali cation to the reaction, it was recognized that sodium cation influences the promotion of the reaction and potassium cation also influenced the promotion of the reaction a little. And the influence of lithium cation restrained influenced the reaction.

From the reaction product experiment, the reaction produced mainly a mixture of sodium silicate and sodium hydroxide, and it was recognized that sodium cation adsorbed into silicate.

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