

THE DISSOLUTION RATE OF QUARTZ AND THE RATE OF DESILICATION IN THE BAYER LIQUOR

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Abstract

The dissolution rate of quartz which occurred in the digestion of Australian monohydrate bauxite was determined at temperatures from 180 to 240°C. The rate of desilication was also measured in the temperature range from 100 to 180°C in the plant sodium aluminate solution where Southeast Asian trihydrate bauxite was dissolved. As the results of the measurements, Eqs. (1) and (2) were derived for the desilication and Eq. (3) for the dissolution of quartz.

$$-\frac{ds}{dt} = \exp. (26.376 - 14.44 \times 10^{-3}A - 10960/T) \cdot (S - S_{\infty})^2 \quad (1)$$

$$S_{\infty} = 2.7 \times 10^{-5} \cdot N \cdot A \quad (2)$$

where: S = SiO₂ concentration (g/l)
 A = Al₂O₃ concentration (g/l)
 N = caustic Na₂O concentration (g/l)
 t = time (min.)
 T = temperature (°K)

$$-\frac{dQ}{dt} = \exp. (12.09 - \frac{9900}{T}) \cdot (F - Na_2O) \cdot Q \quad (3)$$

where: Q = quantity of quartz in solution (g/l)
 F-Na₂O = free Na₂O concentration (g/l)

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1. Introduction

Bauxites are classified into two types, the alumina monohydrate and the alumina trihydrate type ore. In general, the former is digested at high temperature and the latter at low temperature. At low temperature the desilication rate is low, and the dissolution rate of reactive silica in bauxite is high. In order to reduce the scaling trouble and the silica contamination in the product Al₂O₃, the SiO₂ concentration in the pregnant liquor from the digester must be kept near the equilibrium. In this respect, the digestion time of an alumina trihydrate ore is controlled by the desilication rate of the pregnant liquor. In order to minimize the size of the digester, the desilication rate must be known. The quartz in bauxite dissolves scarcely in the Bayer liquor at low temperature, but at high temperature it dissolves considerably and causes the loss of soda and alumina. The dissolution rate of quartz must be clarified in order to reduce the loss of soda and alumina. Many works have been reported on desilication products. But a limited number of kinetics data for the quartz dissolution and desilication rate have been reported (1),(2),(3),(4). The present study reports on the dissolution rate of quartz which occurred in the digestion of Australian monohydrate bauxite in the temperature range from 180 to 240°C and the rate of desilication in the case of Southeast Asian trihydrate bauxite at temperatures from 110 to 180°C in the plant sodium aluminate solution. The rate equations were derived for the dissolution rate of quartz and desilication, respectively. Furthermore, the values calculated from the rate equations are compared with those observed in the plant digesters.

2. Experimental2-1. Materials

Sodium Aluminate Solution: The plant liquor was used for the digestion of bauxite. Tab. I shows the impurities in the plant liquor.

Table I. Impurities in the Plant Liquor
 (Based on caustic Na₂O conc. = 100g/l)

Impurities	Concentration (g/l)
SO ₄ ²⁻	0.3
Cl ⁻	2.0
CO ₃ ²⁻	6.0
F ⁻	1.0
Organic carbon	3.5

Bauxite: No. 1 bauxite (Australian) in Table II was used for the measurements of the quartz dissolution rate and No. 2 (Southeast Asian) for the desilication rate.

Table II. Constitution of the Bauxites (wt.%)

Components Bauxite	L.O.I	Al ₂ O ₃	T-SiO ₂	F-SiO ₂	Fe ₂ O ₃	TiO ₂
No. 1	26.06	57.99	5.95	2.31	7.10	2.52
No. 2	28.63	52.71	4.48	4.03	12.86	1.08

The particle size of No. 1 bauxite was under 42 mesh and No. 2 under 35 mesh.

2-2. Apparatus and Procedures

A 5 liter stainless steel autoclave used for the bauxite digestion is shown in Fig. 1. The solution was introduced into the autoclave so that the liquid level reaches just under the bottom of the sample container 5. The bauxite sample is placed on the container 5, so that the solution and bauxite were heated separately to a given temperature. The autoclave was rotated at the given temperature and the solution and bauxite were mixed. After a given reaction time, the slurry was taken out through the valve 3. The red mud was separated from the solution by filtration and the solution and red mud were both analysed.

2-3. Analysis

The chemical analyses of bauxite and red mud were performed by the JIS method. The NaOH concentration (K-Na₂O) of the sodium aluminate solution was determined by the volumetric analysis with HCl solution and phenolphthaleine as an indicator. The Al₂O₃ concentration was analysed by the chelating titration method with EDTA. The SiO₂ concentration in the solution was determined by the gravimetric analysis.

3. Results and Discussion

3-1. Desilication Rate

Fig. 2 and 3 show the change of the SiO₂ concentration with the reaction time at the temperature range from 100 to 180°C. The desilication rate equations as given by Eqs. (1), (2) were derived from the experimental results.

$$-\frac{ds}{dt} = \exp. (26.376 - 14.44 \times 10^{-3}A - 10960/T) \cdot (S - S_{\infty})^2 \quad (1)$$

$$S_{\infty} = 2.7 \times 10^{-5} N \quad (2)$$

where: S = SiO₂ concentration (g/l)
 A = Al₂O₃ concentration (g/l)
 N = K-Na₂O concentration (g/l)

t = time (min.)
 T = temperature (°K)
 S = SiO₂ equilibrium concentration (g/l)

As shown in Eq. (1), the desilication is a second order reaction with respect to SiO₂ supersaturated concentration. The constant in the right hand side of Eq. (1), 26.376, should change depending on the kind of bauxite. The activation energy for desilication is calculated as 21.8 kcal/mole from Eq. (1). This value is very high in comparison with the values of ΔE* = 4 kcal/mole which are usually observed in diffusion controlled reactions. Therefore, the desilication reaction is considered to be chemically controlled. Eq. (2) shows that the SiO₂ equilibrium concentration is determined by the NaOH and Al₂O₃ concentration and is independent of temperature. If a temperature is higher than 180°C, the SiO₂ equilibrium concentration becomes higher than the calculated value of Eq. (2). The constant in Eq. (2), 2.7 x 10⁻⁵, varies with the kind and quantity of the impurities in the solution. In the case of pure sodium aluminate solution the constant is higher than 2.7 x 10⁻⁵. Fig. 4 shows the effect of red mud quantity on the desilication rate and the desilication rate is approximately proportional to the red mud quantity. As to the reaction order of the desilication, Adamson⁽¹⁾ proposes the first order and Sugiyama⁽²⁾ suggests the second order as our results. On the other hand, Adamson⁽¹⁾ reports almost the same equation as Eq. (2) for the equilibrium concentration of SiO₂.

3-2. Dissolution Rate of Quartz

Fig. 5 - 7 show the dissolution rate of quartz in the temperature range from 110 to 240°C. From these results Eq. (3) is derived as the dissolution rate equation of quartz in the Bayer liquor.

$$-\frac{dQ}{dt} = \exp. (12.09 - \frac{9900}{T}) \cdot (F-Na_2O) \cdot Q \quad (3)$$

where: Q = quantity of quartz in solution (g/l)
 t = time (min.)
 F-Na₂O = free Na₂O concentration (g/l)
 T = temperature (°K)

The dissolution rate of quartz is proportional to the quantity of quartz present in the solution as is shown in Eq. (3). When the dissolution rate of quartz is measured on the flat surface of quartz, the reaction is obviously turned out to be of the first order with respect to the surface area as shown in Fig. 5. If the quartz in bauxite has a flat surface, the dissolution reaction must be of the two-thirds order with respect to the SiO₂ quantity. However, it was found that the reaction was of the first order. This suggests that the surface of the quartz in bauxite is not flat. Sugiyama⁽²⁾ reports that the dissolution rate of quartz in the Southeast Asian bauxite is proportional to the surface area of the quartz. The activation energy of 19.7 kcal/mole is calculated from Eq. (3). The fact that the dissolution rate of quartz increases with the increase

of OH⁻ concentration and of the surface area of the quartz and the fact that the activation energy is 19.7 kcal/mole indicate that the reaction of quartz with the Bayer liquor is controlled by the chemical reaction between OH⁻ and the surface of quartz.

3-3. Comparison of the Calculated Value with the Observed One

Desilication: Fig. 8 shows the observed SiO₂ concentration in the digestion plant. The SiO₂ concentration at the outlet of reactor is calculated in the following manner. When a reactor is of a piston flow type, the desilication proceeds according to Eq. (4), which is obtained by integration of Eq. (1).

$$\frac{S_o - S_t}{(S_t - S_{\infty})(S_t - S_o)} = kt \tag{4}$$

where: $k = \exp. (26.376 - 14.44 \times 10^{-3}A - 10960/T)$ (5)
 $S = \text{SiO}_2$ concentration at an inlet of reactor (g/l)
 $S_t = \text{SiO}_2$ concentration at an outlet of reactor (g/l)
 $t =$ residence time (min.)

When a reactor is of a perfect mixing type, the desilication rate is expressed as Eq. (6), which can be deduced from the fact that the SiO₂ concentration at the outlet equals to the one in the reactor.

$$\frac{S_o - S_t}{(S_t - S_{\infty})} = kt \tag{6}$$

We calculated the SiO₂ concentration in each reactor by using Eqs. (1), (2), (4), (5) and (6) and the SiO₂ concentration at the inlet of No. 1 reactor and the temperatures, K-Na₂O and Al₂O₃ concentrations and the residence time in each reactor. Table III shows the results of the calculation and the observed values.

Table III. Comparison of the Calculated Values with the Observed One

	No.1 reactor outlet	No.2 reactor outlet	No.3 reactor outlet
SiO ₂ concentration			
calculated	1.80	1.17	0.79
(g/l) observed	1.85	1.15	0.79

The agreement of the values calculated from the rate equation and those observed in the plant is satisfactory as shown in Tab. III.

Quartz Dissolution: The values observed in the plant digesters are shown in Fig. 9. The quantities of the dissolved quartz under the plant condition are calculated in the following manner. All digesters (No. 1 through No. 3) are of the perfect mixing type. The dissolution rate of quartz in a perfect mixing tank follows Eq. (7).

$$\frac{Q_o}{Q_t} = 1 - \frac{dQ_t}{dt} \cdot \frac{t}{Q_t} \tag{7}$$

Combining Eq. (3) and Eq. (7), we obtain

$$kt = \frac{Q_o - Q_t}{Q_t} \tag{8}$$

where: $k = (F-Na_2O) \cdot \exp. (12.09 - \frac{9900}{T})$ (9)
 $Q_o =$ quartz quantity at an inlet of digester (g/l)
 $Q_t =$ quartz quantity at an outlet of digester (g/l)
 $t =$ residence time (min.)

We calculated the percentage of the dissolved quartz in each digester by using Eqs. (8) and (9). The results of the calculation and the observed values are shown in Tab. IV.

Table IV. Quantity of Dissolved Quartz

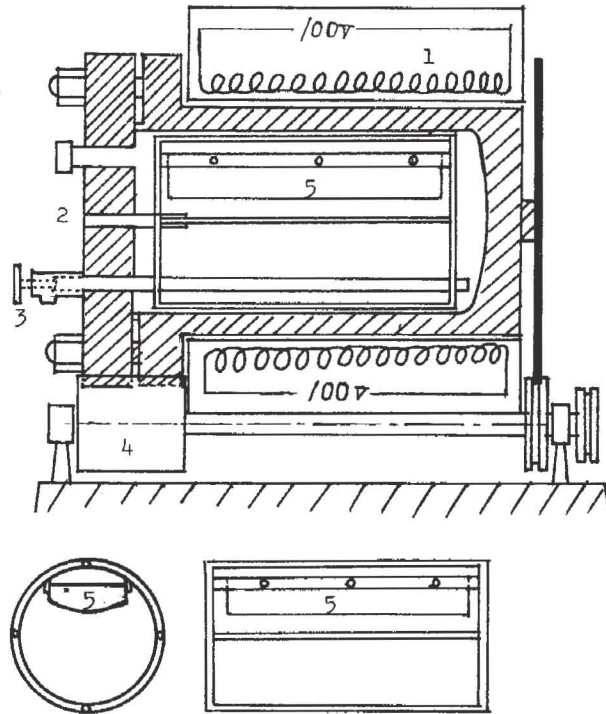
	No.1 digester	No.2 digester	No.3 digester
Dissolved quartz (%)	calculated 10	calculated 27	calculated 44
	observed —	observed —	observed 41

The calculated value in the No. 3 digester agrees with the observed one satisfactorily.

4. Conclusion

The rate equations of the desilication and the quartz dissolution in the Bayer liquor were proposed. The agreement of the values calculated from the rate equations and those observed in the plant digesters is satisfactory.

Fig. 1. 52 Autoclave for Bauxite Digestion



- 1 electric furnace
- 2 for thermometer
- 3 sampling valve
- 4 roller
- 5 sample container

Fig. 2. Desilication curve

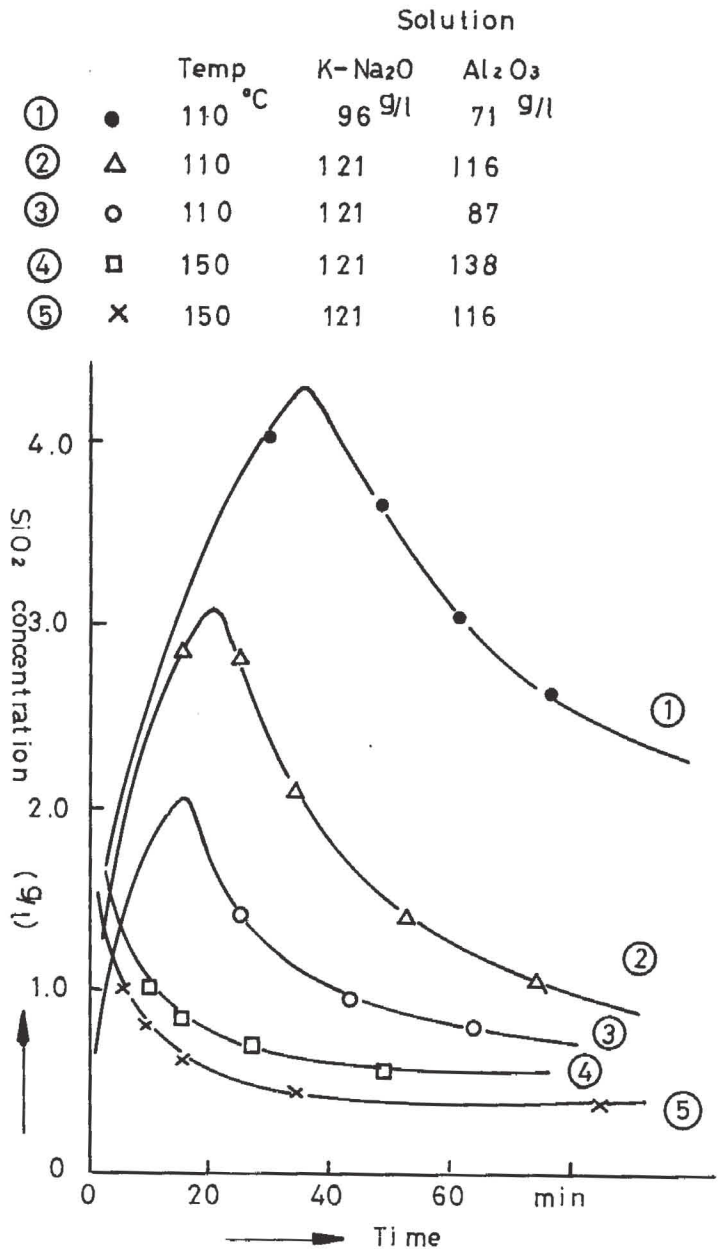


Fig. 3. Desilication curve

Solution				
		Temp	K - Na ₂ O	Al ₂ O ₃
⑥	×	130 °C	158 g/l	140 g/l
⑦	△	130	121	138
⑧	○	130	121	116
⑨	●	130	96	89
⑩	□	180	122	

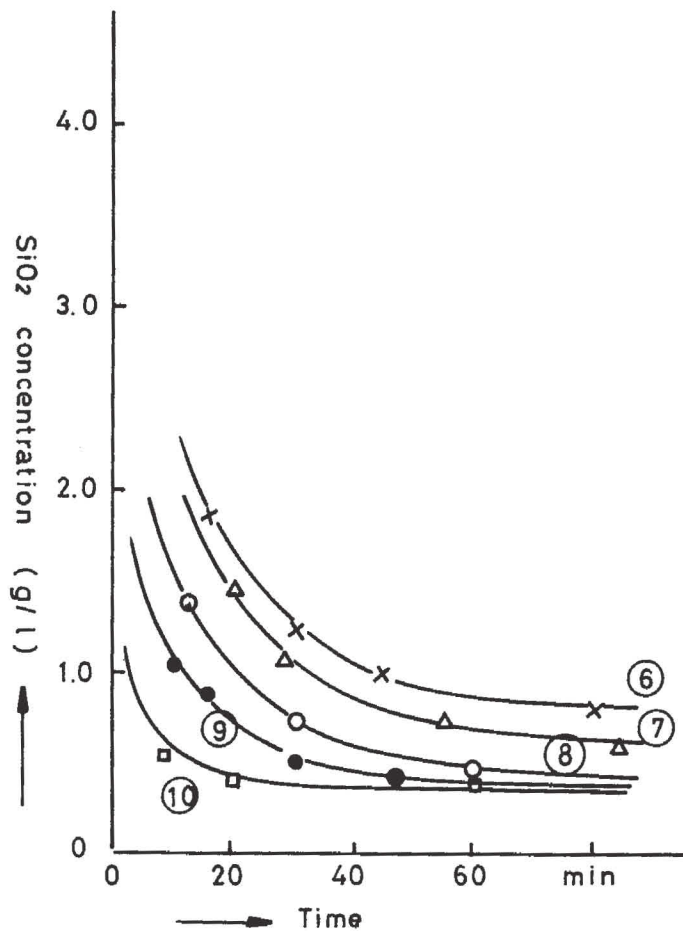


Fig. 4. Effect of amount of red mud on desilication rate

Solution					
		Temp	K - Na ₂ O	Al ₂ O ₃	red mud
⑪	○	130 °C	121 g/l	116 g/l	45 g/l
⑫	×	130	121	116	90

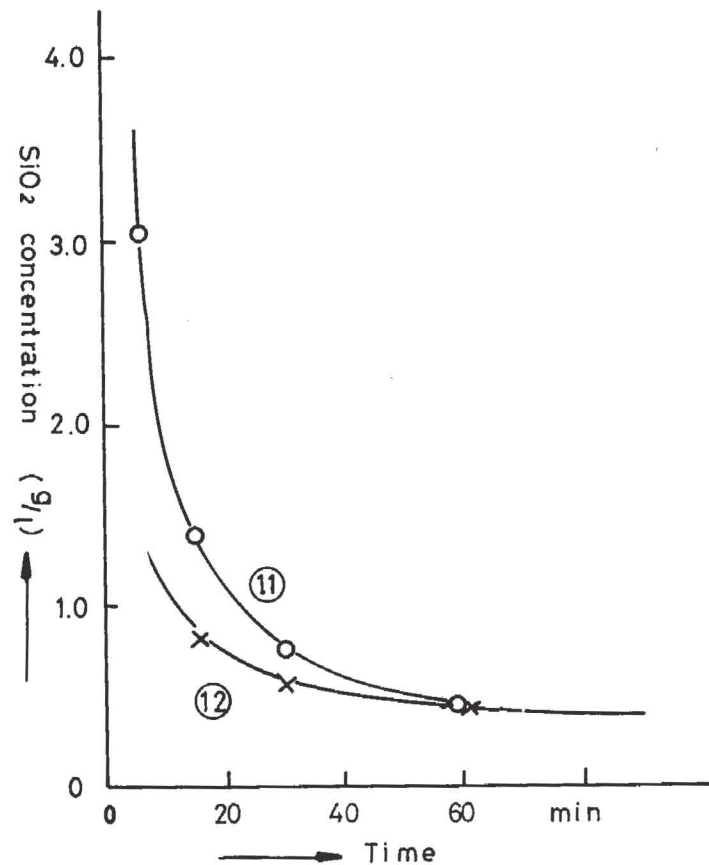


Fig. 5. Dissolution of quartz

		Solution			
	Temp	K-Na ₂ O	Al ₂ O ₃	F-Na ₂ O	
	°C	g/l	g/l	g/l	
①	▽	220	160	128	82
②	▲	240	135	154	42
③	△	220	125	130	46
④	○	220	220	92	38

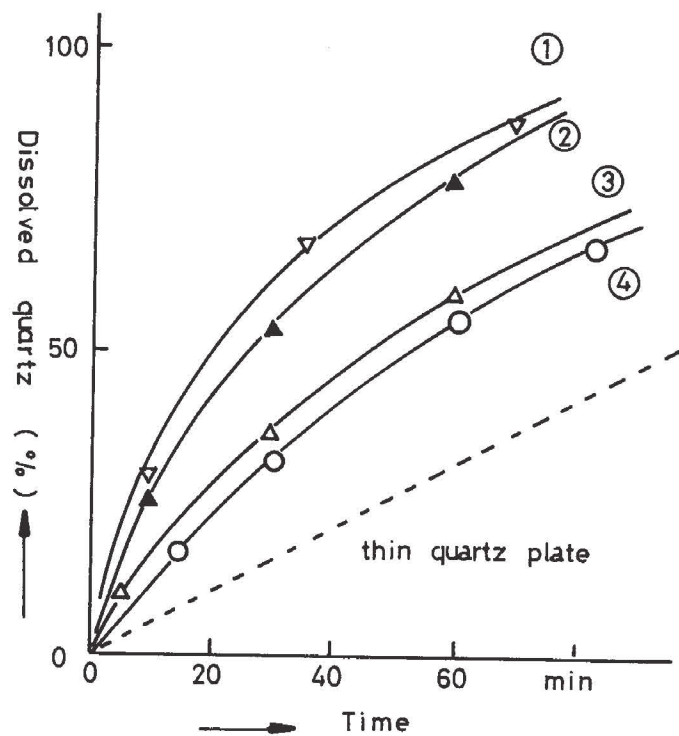


Fig. 6. Dissolution of quartz

		Solution			
	Temp	K-Na ₂ O	Al ₂ O ₃	F-Na ₂ O	
	°C	g/l	g/l	g/l	
⑤	△	230	127	137	44
⑥	□	220	91	84	40
⑦	●	190	144	130	65
⑧	×	180	158	125	81
⑨	○	180	127	100	66

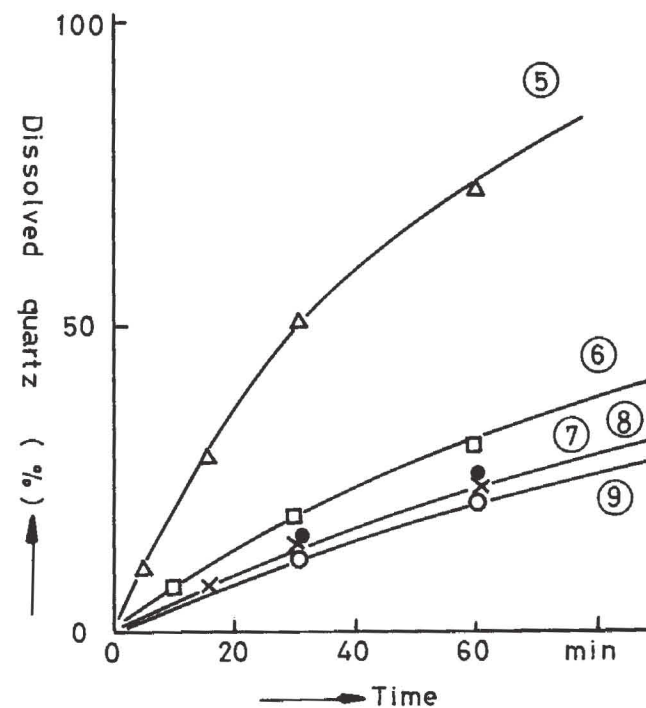


Fig. 7. Dissolution of quartz

		Solution			
		Temp °C	K-Na ₂ O g/l	Al ₂ O ₃ g/l	F-Na ₂ O g/l
⑩	▽	220	127	101	66
⑪	▲	220	126	115	56
⑫	△	220	156	165	56
⑬	X	200	128	102	66
⑭	○	200	125	115	55
⑮	●	200	96	92	40

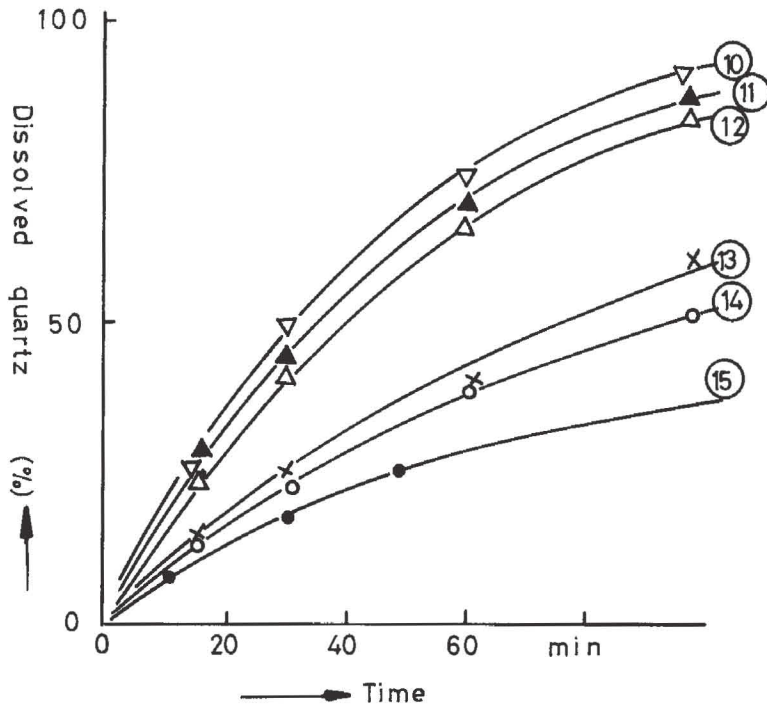


Fig. 8. Observed SiO₂ concentration in plant

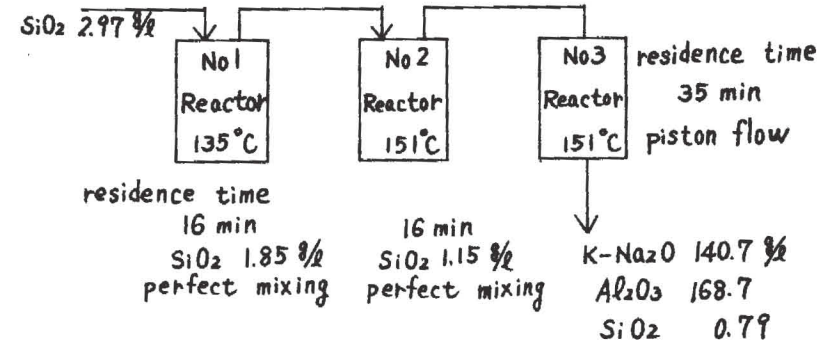
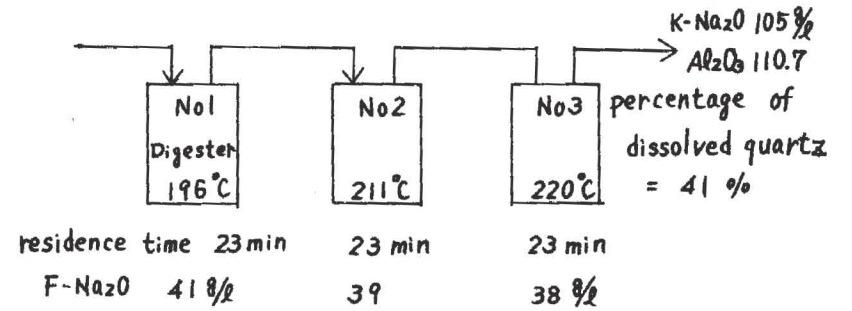


Fig. 9. Observed amount of dissolved quartz in plant



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