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A RELATIONSHIP BETWEEN LEACH RATE
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RESIDUAL AMOUNT OF SODIUM ON THE
GLASS SURFACE

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A Relationship between Leach Rate of Nuclear Waste Glass and Residual Amount of Sodium on the Glass Surface

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Leach tests of simulated high-level waste glass were carried out in order to examine the quantitative relationship between the amount of elements on the sample surface and that in the leachate. An experimental equation was obtained expressing the relationship between the amount of Na on the sample surface and that in the leachate. This shows that it is possible in some cases to estimate the amount of Na in the leachate by measuring the amount of Na on the sample surface. One example of such an estimation was observed with the simulated high-level waste glass leached at $100^{\circ}C$ in the presence of a backfill material.

ガラス固化体の浸出率とガラス表面に残ったNaとの関係

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　　模擬廃棄物入りガラス固化体の浸出後のガラス表面に残る元素の量と，浸出液中の元素の量との関係について検討した。その結果SEM－EDXで測定したガラス表面に残るNaの量と，浸出液中のNaの量との間の実験的関係が得られた。このことからSEM－EDXで測定したガラス表面に残ったNaの量は，浸出の程度を示す目安になると考えられた。また得られた実験式を用いて，ガラス表面に残ったNaの量から，浸出液中に放出されたNaの量を推定することを試みたところ，ベースガラスとベントナイトの混合粉末を埋戻し材として共存させると，浸出を約100倍抑制するという結果を得た。

Contents

I. Introduction

High-level liquid waste arising from a reprocessing plant of spent fuels will be incorporated into a solid matrix such as borosilicate glass. The resultant waste glass will be temporarily placed in a repository facility and finally in a geologic disposal site. The first step of migration of radionuclides from the disposal site to the biosphere is considered to be leaching of the radionuclides by groundwater, and so, much effort has been concentrated on the study of leaching phenomena. Solid-state analyses of leached samples[1-14] along with leachate analyses are generally conducted in laboratories and provide understanding of the mechanisms of waste glass leaching.

However, the authors recently encountered two cases in which leachate analyses are difficult. One is the case in which a backfill material coexists in leachates and disturbs the exact leachate analyses due to its adsorption and dissolution. The other is the case in which leach experiments are performed deep underground and the collection of leachate (groundwater) is virtually impossible. In these cases, it is necessary to get information about the extent of leaching by solid-state analyses of leached samples. The main purposes of the present paper are to examine the quantitative relationship of the amount of elements on the sample surface to that in the leachate and to show that it is possible in some cases to estimate the extent of leaching by measuring the amount of Na on the sample surface.

In order to measure the amount of elements on the sample surface, we used scanning electron microscopy with energy dipersive X-ray

analysis (SEM-EDX)[1-6] for two reasons; (i) this technique provides the quantitative composition of solid-state phases quickly, (ii) with this technique, it is possible to obtain information concerning the concentration of elements up to about 5 μm below the surface of the sample.[15]

II. Experimental Procedure

The simulated high-level waste glass used for the present study was a borosilicate glass containing 11.7 wt% simulated high-level waste,[16] which had the composition shown in Table I. All reagents for the simulated high-level waste were mixed with additives simultaneously, melted at 1150°C for 2 hours, poured into graphite molds, kept at 550°C for 1 hour and then slowly cooled to room temperature at a cooling rate of 20°C/hour. The resultant glass block was cut and polished into cubic specimens, which were 1 x 1 x 1 cm in size.

The cubic specimens were then subjected to two kinds of static leach test. Firstly, in order to examine the quantitative relationship of the amount of elements on the surface of the leached specimen to that in the leachate, the cubic specimen was leached at 100°C in about 20 ml of deionized water using a Teflon vessel. The duration of the leach test was varied from 1 hour to 12 days. The SEM-EDX technique was applied to analyze the contents of elements on the surface of the leached specimens. An area of about 20 x 20 μm was analyzed at the same time. This analysis was carried out six times for each specimen for the total area of about 2400 μm^2. In addition,

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the specimen leached for 5 days was cut and polished, and elemental depth profiles were examined by the point-to-point analysis. The accelerating voltage and the probe current of the electron beam were at a constant value of 20 keV and 10^{-10} A, respectively, throughout the SEM-EDX observations. All data by SEM-EDX were collected for the same amount of time (200 sec.). The concentrations of elements in leachates were measured by atomic absorption spectroscopy (AAS) and inductively coupled plasma atomic emission spectroscopy (ICP). The leachates were not concentrated before the AAS and ICP measurements.

Secondly, in order to show an example of the estimation of the extent of leaching by the SEM-EDX technique, leach tests of the simulated high-level waste glass were carried out in the presence of a backfill material.[17] The cubic specimen was placed in 5 g of the backfill material and then statically leached in about 15 ml of deionized water at 100°C for 5 days using the Teflon vessel. The backfill material was composed of base glass powder and bentonite powder, the composition of which is given in Table II. The mixing ratio (G/B) of the base glass powder (G) to the bentonite powder (B) in weight was varied from 0.2 to 2.

III. Results and Discussion

(1) SEM-EDX analysis of the surface of the leached specimens

Figure 1 shows the SEM-EDX spectra of the surface of the specimens before and after leaching at 100°C for 5 days without the backfill material. In the spectrum before leaching (Fig.1(a)), the peaks of ten elements, i.e. Na, Al, Si, Zr, Mo, Ca, Cs, Ce, Nd and Fe, are

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simulated high-level waste glass were carried out in the presence of a

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backfill material and then statically leached in about 15 ml of

deionized water at 100°C for 5 days using the Teflon vessel. The

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ten elements, i.e. Na, Al, Si, Zr, Mo, Ca, Cs, Ce, Nd and Fe, are

identified. In the spectrum after 5-day leaching (Fig.1(b)), the Na, Mo and Cs peaks have disappeared. The Na peak is clearly distinguishable from others in the SEM-EDX spectrum (Fig.1(a)). The Mo peak is located on the shoulder of the Zr peak, and the Mo and Cs peaks are relatively small in comparison with that of Na. These observations indicate that the amount of Na on the surface of the specimen can be used for the evaluation of the extent of leaching.

Figure 2 shows the variation of the amount of the nine elements displayed in Fig.1 (a) except Nd. When we tried to include Nd into the quantitative analysis of the other nine elements, the analysis stopped in the course of calculation due to the shortage of memory capacity. So, we did not measure the amount of Nd, but the change of the height of the Nd peak during leaching was qualitatively similar to that of Fe.

The amount of elements on the surface of the specimen leached for 12 days was not measured because the surface layer of the specimen partially flaked off after being dried for SEM-EDX observations.

The ordinates of Fig.2 represent the ratio (C/C_0) of the concentration of an element on the surface of leached specimens (C) to the initial concentration of the element before leaching (C_0). The relative amount of an element such as the C/C_0-value was used since this value is sufficient to express the extent of leaching and adequate for our purpose.

The C/C_0-values of Na, Mo and Cs decrease during leaching, and the C/C_0-values of Na and Mo change linearly on the figure of semi-logarithm. However, the amount of MoO_3 in the sample before leaching

was only 1.74 wt%, much smaller than that of Na_2O. The amount of Na_2O was greatly changed from the initial value of 11.3 wt% to nearly zero, indicating that the amount of Na can be measured more precisely in comparison with that of Mo. Thus, the following relation between the C/C_0-value of Na and the leach time in days (t) is notable here,

$$\ln C/C_0 = -0.80 \times t \tag{1}$$

The C/C_0-value of Si decreases initially and then reaches a constant value of about 0.56. This implies that a part of the Si remains on the surface of the specimen, resulting in the Si-rich surface layer.[1]

The C/C_0-values of Fe, Zr and Ce increase and reach about 2. This may be due to some type of precipitation during leaching or due to the shrinkage of the surface layer on the specimen during drying for SEM-EDX observations.[6]

The C/C_0-values of Ca and Al slightly decrease and then increase to a value of about 1.4. This means that the leaching process of Ca and Al is rather complex in comparison with the other elements.

The results described above show that the elements detected by the SEM-EDX technique may be classified into four groups as follows:

Group 1: Na, Mo, Cs

Group 2: Si

Group 3: Ca, Al

Group 4: Fe, Zr, Ce, (Nd)

As for the elements belonging to groups 2, 3 and 4, experimental equations between C/C_0-values and t could be obtained, but they can be expected to be more complex than the equation (1).

(2) SEM-EDX analysis of the section of a leached specimen

The polished section of the specimen leached for 5 days without the backfill material was observed in order to provide supplementary explanations for the C/C_0-values. Figure 3 shows the SEM-photograph of the specimen. This shows that the thickness of the surface layer is about 5 μm, which is determined by the contrast between the surface layer and the bulk glass. Figure 4 shows the elemental depth profiles for Na, Si, Ca and Fe measured by the SEM-EDX technique. The ordinate of Fig.4 represents the ratio (D/D_0) of the concentration of an element at a point on the section (D) to that at the center of the same specimen (D_0). The value of D_0 was measured for the area of 20 x 20 μm, and D was measured by the point analysis. As for the unleached specimen (Fig.4(a)), the amount of elements at a depth of about 1.7 μm from the surface does not decline in comparison with that at a depth of more than about 3 μm. From this observation, it is speculated that the sampling volume is less than about 2 μm along the principal axis of the electron beam and that the point-to-point analysis at the distance of about 2 μm is meaningful.

The D/D_0-values of Na less than 4 μm below the surface are not shown in Fig.4(b) because its concentrations were very small and not able to be measured quantitatively. This indicates that the amount of Na changes markedly at the boundary between the surface layer and the bulk glass.[6] In addition, it is considered that Na more than 5 μm below the surface is not detectable by the SEM-EDX technique since the C/C_0-value of Na of the specimen leached for 5 days was nearly zero

(Fig.1(b)).

The D/D_0-value of Si gradually increases in the surface layer, changing from 0.45 at a depth of 1.7 μm to 0.65 at a depth of 5 μm below the surface (Fig.4(b)). The C/C_0-value of Si of this specimen was 0.56 (Fig.2), which is approximately equal to an average of the D/D_0-values of Si in the surface layer.

The D/D_0-values of Ca and Fe are more than 1.0 at several points in the surface layer (Fig.4(b)). This is consistent with the fact that the C/C_0-values of these elements are more than 1.0 at the leach time of 5 days (Fig.2).

Although experimental evidence about the relation between C/C_0-values and D/D_0-values for the surface layer of less than 5 μm in thickness were not obtained, it is speculated that C/C_0-values of elements include the information from both surface layer and bulk glass when the thickness of the surface layer is smaller than 5 μm.

(3) Leachate analysis

Figure 5 shows the amount of the elements in the leachates as a function of leach time. The ordinate of Fig.5 represents the normalized elemental mass loss[2] for the element i (NL_i), which is defined as,

$$NL_i = m_i/(f_i \times SA) \qquad (2)$$

where m_i (g) is the mass of the element i in the leachate, f_i (unitless) is the mass fraction of the element i in the unleached solid, and SA (cm^2) is the geometric surface area of the specimen.

As shown in Fig.5, the normalized elemental mass losses for Na

(NL_{Na}), Mo (NL_{Mo}) and Cs (NL_{Cs}) increase with the leach time in days
(t). The relation between NL_{Na} and t was expressed as,

$$NL_{Na} = 4.48 \times 10^{-4} \times t^{0.80} \tag{3}$$

and NL_{Mo} and NL_{Cs} are almost the same as NL_{Na} at a fixed leach time
(t).

The normalized elemental mass loss for Si (NL_{Si}) also increases
with t, following the experimental equation,

$$NL_{Si} = 3.48 \times 10^{-4} \times t^{0.69} \tag{4}$$

On the whole, NL_{Si} is approximately equal to or slightly smaller than
NL_{Na} at a fixed leach time.

The normalized elemental mass losses for Ca (NL_{Ca}) and Al (NL_{Al})
increase initially, then decrease for leach times of more than 1 day.
This is probably because these elements are apt to be removed from the
leachates due to the precipitation of solid phases.[18] The relations
of NL_{Ca} and NL_{Al} to t were not expressed by a simple equation such as
the equation (3) and (4).

The amount of Fe in the leachates was measurable by the ICP method
for leach times of more than 0.33 days, and the normalized elemental
mass loss for Fe was smaller than NL_{Na} by about two orders of
magnitude. The amounts of Zr and Ce in the leachates were under the
detection limit of the ICP method.

(4) Relation between the C/C_0-value of Na and NL_{Na}

On using the C/C_0-value measured on the surface of specimens for a
index of the extent of leaching, it is reasonable to pay attention to
such soluble elements as Na, Mo and Cs, because the amounts of these

elements increased in the leachates and decreased on the surface of the specimens during the leach tests. The results of the previous sections show that Na is thought to be most suitable for our purpose since the amount of Na can be measured easily and precisely by the SEM-EDX technique in comparison with Mo and Cs. Moreover, with regard to Na, we determined two experimental relations, the equation (1) and the equation (3), which show the relationship between the C/C_0-value of Na and t or between NL_{Na} and t. By combining the equation (1) with the equation (3), we obtain the following equation,

$$-\ln C/C_0 = a \times NL_{Na}^b \tag{5}$$

The constants of a and b in the equation (5) are determined to be 2.37 $\times$ 10^4 and 1.32, respectively, by the least-squares method (Fig.6). The constants in the equation (5) can also be derived from the mathematical combination of the equations (1) and (3), and the resultant relationship is presented in Fig.6 as a broken line. As seen in this figure, the relationship obtained by the mathematical combination of the equations (1) and (3) is not consistent with that obtained by the least-squares method, but the difference between them is small. It should be mentioned that the relation that we want is the experimental relationship between the values of C/C_0 and NL_{Na}. Therefore, we think that the constants in the equation (5) should be derived by the least-squares method directly from the original data of C/C_0 and NL_{Na}. Thus, the following equation is obtained expressing the relationship between the C/C_0-value of Na and NL_{Na}.

$$-\ln C/C_0 = 2.37 \times 10^4 \times NL_{Na}^{1.32} \tag{6}$$

If experimental conditions such as the composition of the glass and

the leaching temperature are markedly different from those of the present work, the values of 2.37×10^4 and 1.32 in the equation (6) may change to a certain extent.

(5) Application

Based on the results described above, we examined the effects of a backfill material[17] on the leaching of simulated high-level waste glass. The C/C_0-value of Na of the cubic specimen leached at $100^{\circ}C$ for 5 days in the presence of the backfill material (with the G/B-ratio of 2.0) was 0.99. Putting this value into the equation (6), we obtained the estimated value of NL_{Na} of 1×10^{-5} g/cm^2, which was about 100 times smaller than the value of NL_{Na} of 1.4×10^{-3} g/cm^2 without this backfill material (Fig.5). It should be mentioned that the base glass powder in the backfill material does release Na and therefore raise the solution pH, and this could give a higher C/C_0-value by dissolving more of the surface layer away. However, the observations of sample size and weight before and after the leach test showed that there was little change in them. Moreover, other experiments showed that there was no noticeable difference between the concentrations of Na in leachates in sample and backfill runs and those in just backfill material runs.[19] Therefore, we think that the backfill material used in the present work actually prohibits the leaching of simulated high-level waste glass.

Some other experiments were carried out using the backfill material with different G/B-ratios. The C/C_0-values of Na of the leached specimens changed from 0.87 to 0.99 (Table III). Table III

shows that the higher the G/B-ratio becomes the lower the estimated NL_{Na} tends to be. This may indicate that Si which is dissolved in the leachate from the base glass powder has the suppressive effect on leaching of the simulated high-level waste glass.[17]

Finally, we note that there are some limitations for the usage of the technique presented here. Firstly, it is clear from the results obtained that the technique is limited to the surface layer less than 5 μm in thickness. The values of NL_{Na} within the above limitation are those less than about 6×10^{-4} g/cm^2 (Fig.6). So the technique is considered to be useful for analyses of a relatively early stage of leaching. Secondly, when partial leaching, which causes the formation of grooves on the surface of leached specimens, occurs markedly,[20] it is difficult to estimate the value of NL_{Na} directly from a measured C/C_0-value. However, such grooves resulting from uneven leaching can be observed by SEM, and so in this case, mistakes arising from the use of this technique can be avoided.[20]

IV. Conclusions

The results are summarized as follows:

(1) The amount of Na on the surface of simulated high-level waste glass leached in deionized water at 100°C decreased with the duration of leach tests in days (t), following the experimental equation, ln C/C_0 = -0.80 x t, where C_0 is the concentration of Na at t=0 and C is the value at t.

(2) On the other hand, the normalized elemental mass loss for Na (NL_{Na}) into leachates was changed with t as the following equation,

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(2) On the other hand, the normalized elemental mass loss for Na (NL_{Na}) into leachates was changed with t as the following equation,

$$NL_{Na} = 4.48 \times 10^{-4} \times t^{0.80}.$$

(3) The results (1) and (2) described above gave us the following relationship between the C/C_0-value of Na and NL_{Na},
$-\ln C/C_0 = a \times NL_{Na}{}^b$, and a and b were determined to be 2.37×10^4 and 1.32, respectively.

(4) Using this equation, we examined the effects of a backfill material on leaching, and showed that the coexistence of the backfill material during leaching could suppress NL_{Na} by a factor of about 100.

(5) The usage of the technique presented in this work is limited to the surface layer less than 5 μm in thickness, so this technique is considered to be useful for analyses of a relatively early stage of leaching.

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Table I Composition of Simulated High-Level Waste Glass

Component	(wt%)	Component	(wt%)
Additives			
SiO_2	48.49	Na_2O	11.30
B_2O_3	18.58	CaO	1.87
Al_2O_3	2.00	Fe_2O_3	2.96
Li_2O	1.87	ZrO_2	1.22
Simulated high-level waste (JW-D)[*]			
Pb_2O	0.12	BaO	0.63
SrO	0.34	La_2O_3	0.51
Y_2O_3	0.20	CeO_2	1.42
ZrO_2	1.65	Pr_6O_{11}	0.50
MoO_3	1.74	Nd_2O_3	1.65
$MnO2$	0.26	Sm_2O_3	0.33
Fe_2O_3	0.59	Ag_2O	0.03
CoO	0.12	CdO	0.03
NiO	0.33	SnO_2	0.02
TeO_2	0.23	Sb_2O_3	0.004
Cs_2O	0.98	Gd_2O_3	0.04

[*] This simulated high-level waste is called JW-D in our notation.

Table II Composition of Base Glass and Bentonite

Component	Base glass (wt%)[*]	Bentonite (wt%)[**]
SiO_2	62.38	70.5
B_2O_3	23.60	–
Al_2O_3	0.23	14.1
Li_2O	2.36	–
Na_2O	8.82	2.39
CaO	2.44	1.65
Fe_2O_3	–	2.48
MgO	–	2.16
K_2O	–	0.18
Ig.loss	–	4.70

* The particle size was in the range of 0.25 to 0.50 mm.

** This was produced in Ohe-machi, Yamagata-ken, Japan. The particle
size was under 200 mesh.

Table III Effect of the Backfill Material with Different G/B-
Ratios on Leaching

G/B-ratio	C/C_0-value of Na[*]	Estimated NL_{Na}[**]
2.0	0.99±0.03	1×10^{-5} g/cm^2
1.0	0.95±0.03	5×10^{-5}
0.5	0.96±0.02	4×10^{-5}
0.2	0.87±0.02	1×10^{-4}

* The C/C_0-value was shown with its standard deviation.

** The first one figure is considered to be significant for each
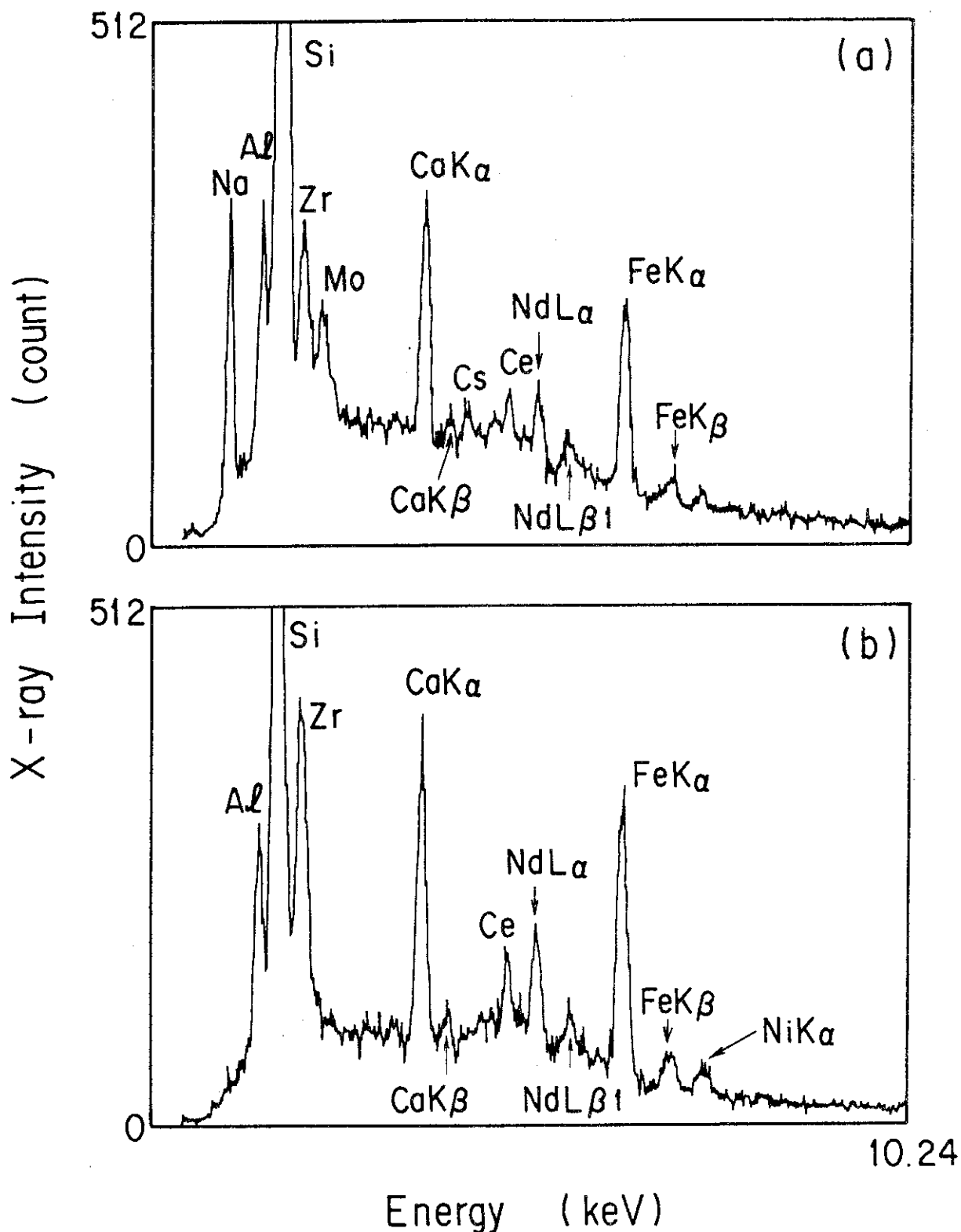estimated NL_{Na} value.

Fig.1 SEM-EDX spectra of the surface of the specimen before (a) and after (b) leaching for 5 days. These data were collected for the same amount of time (200 sec.)
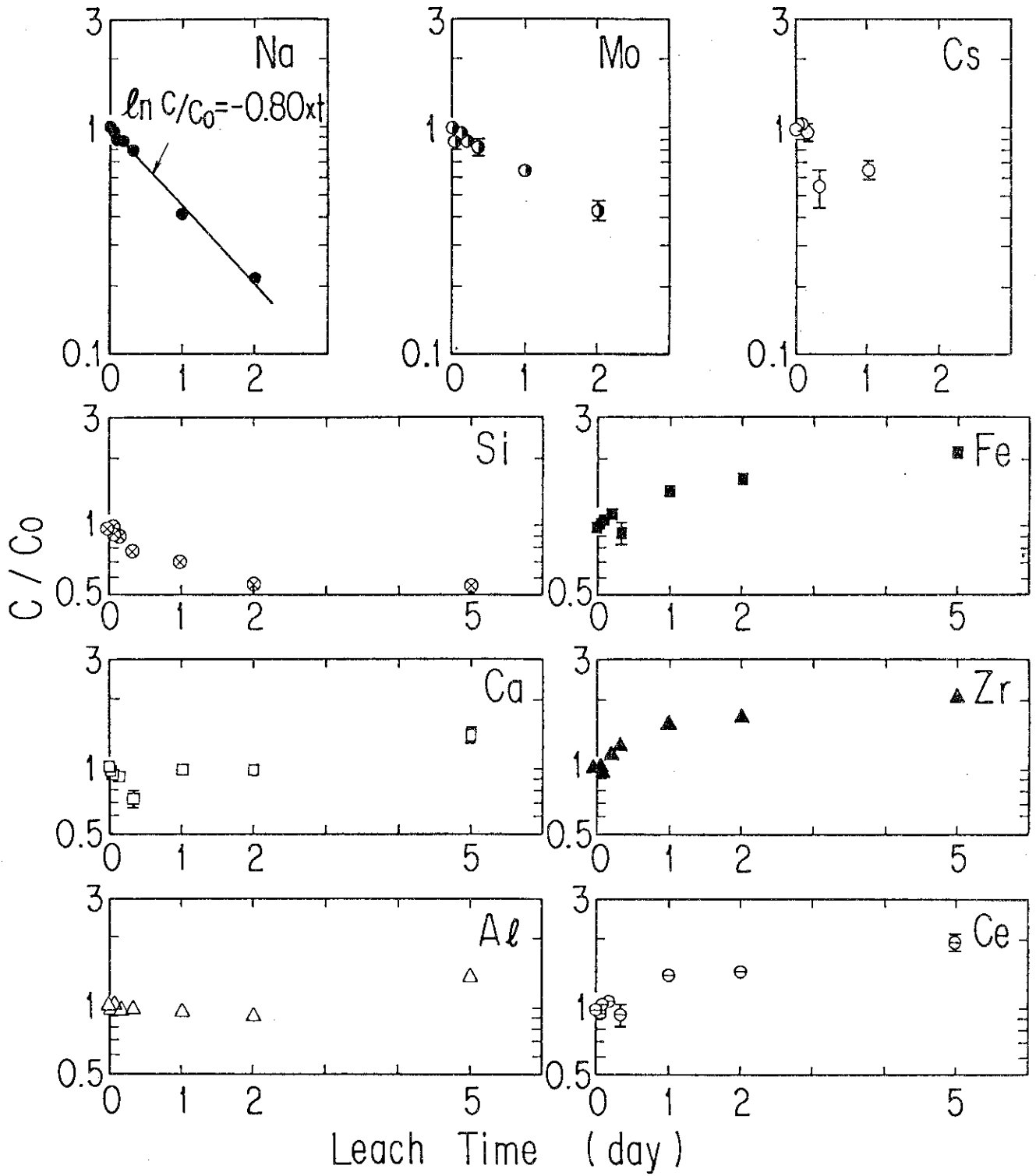
Fig.2 Amount of the elements on the surface of the specimens. In most cases, the standard deviation of each plot is within each plot's size
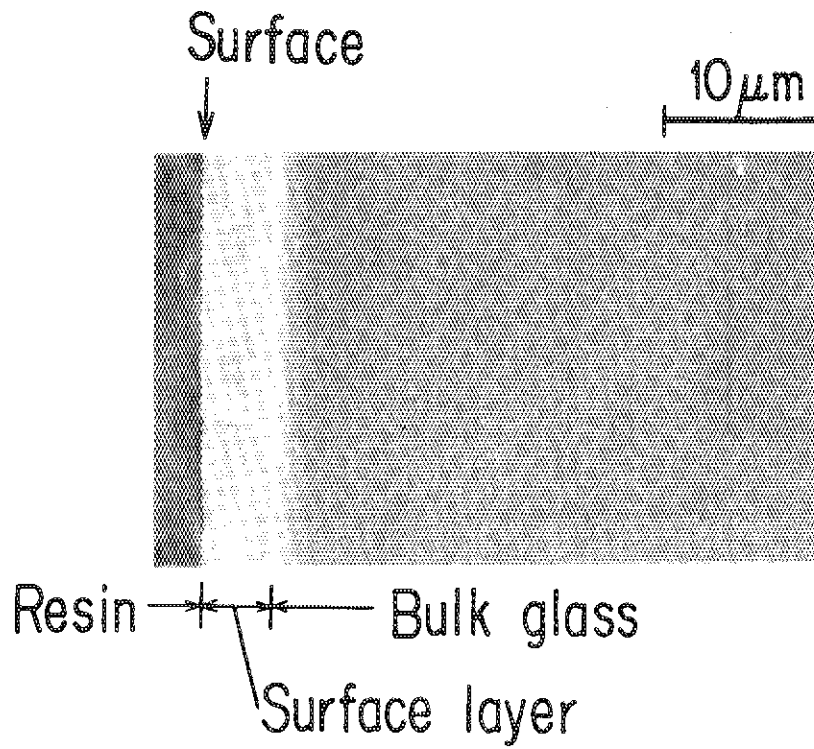
Surface

10 μm

Resin Bulk glass

Surface layer

Fig.3 Scanning electron microphotograph of the polished section of the specimen leached for 5 days
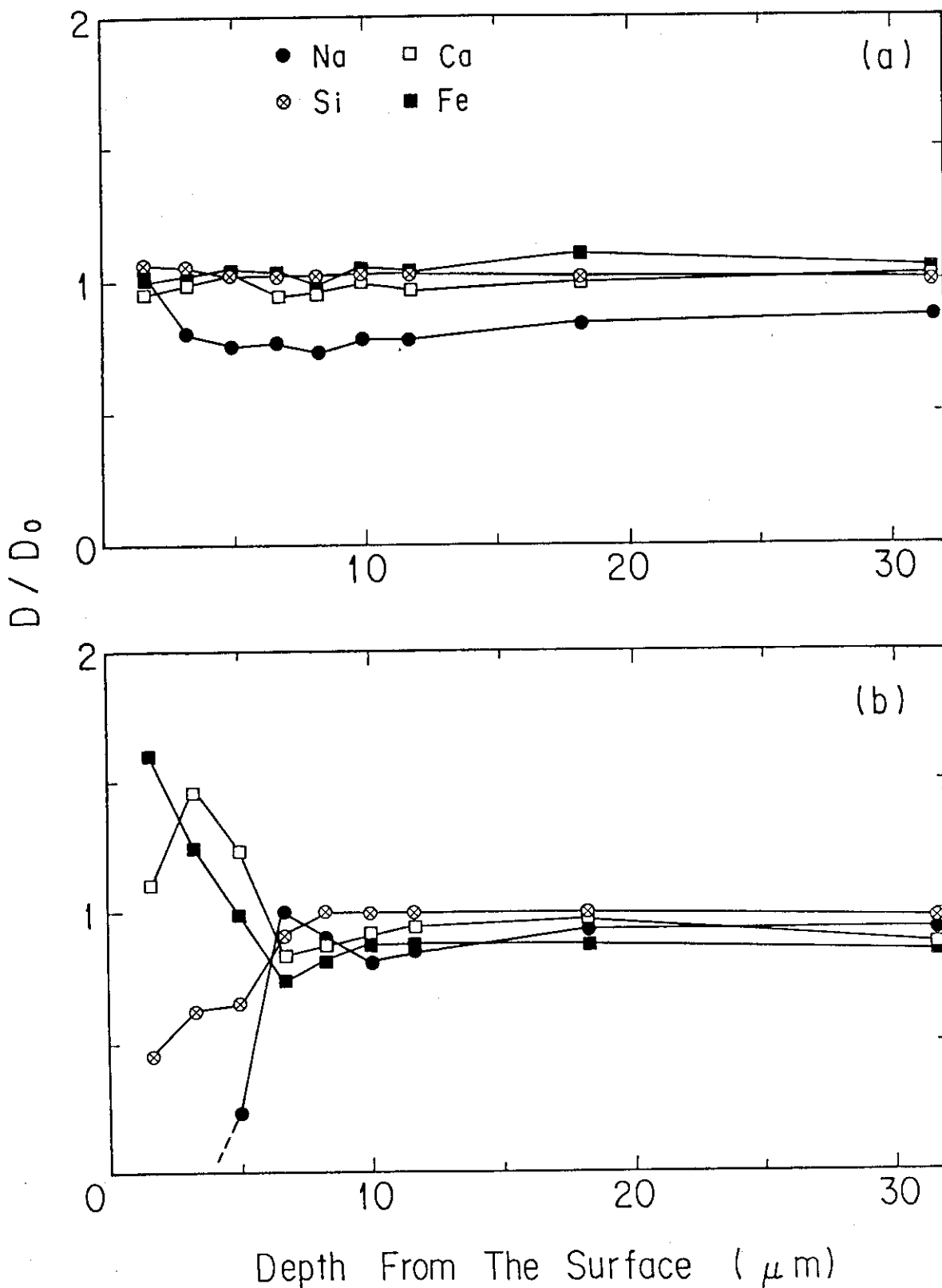
Fig.4 Amount of the elements on the polished section of the unleached specimen (a) and the specimen leached for 5 days (b)
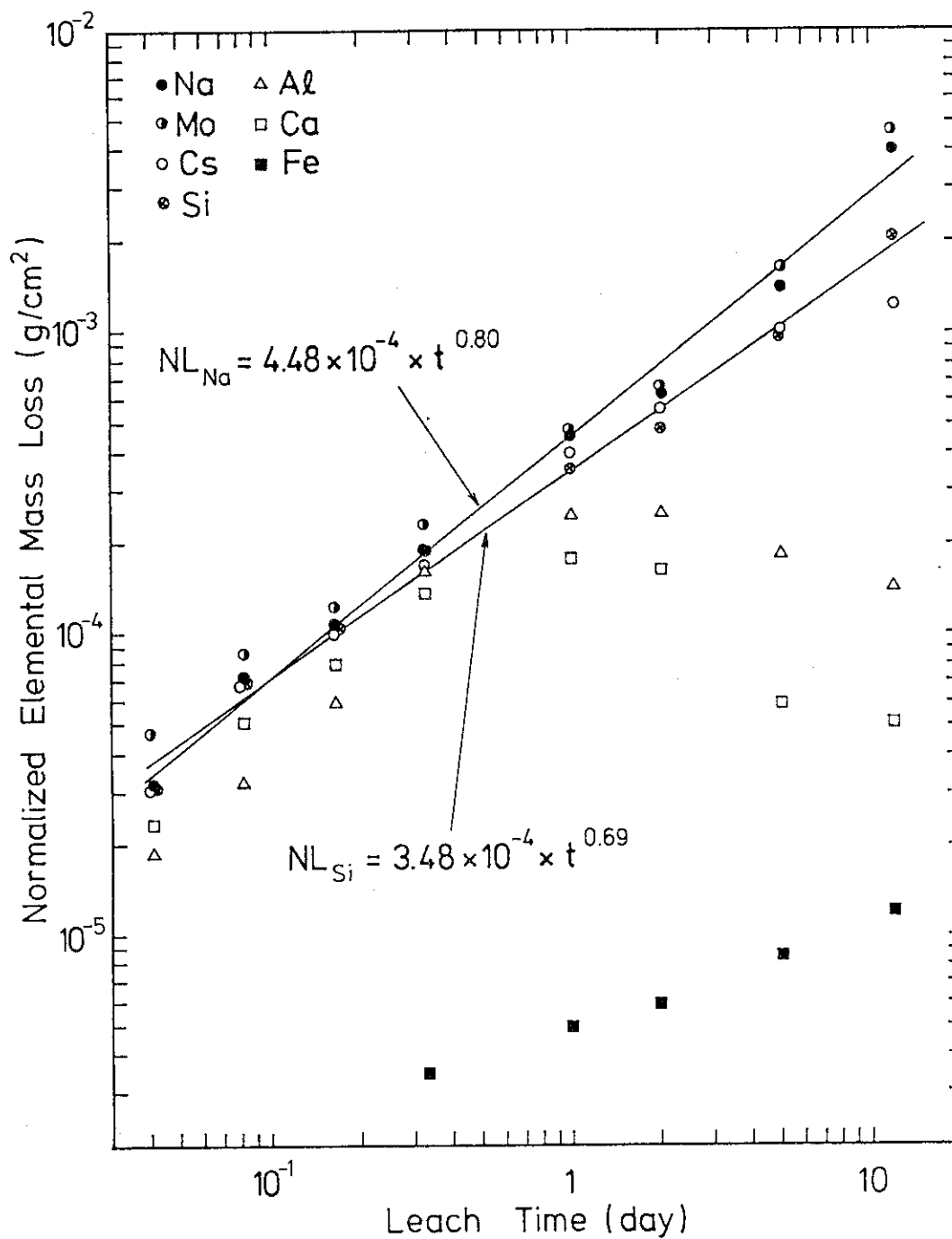
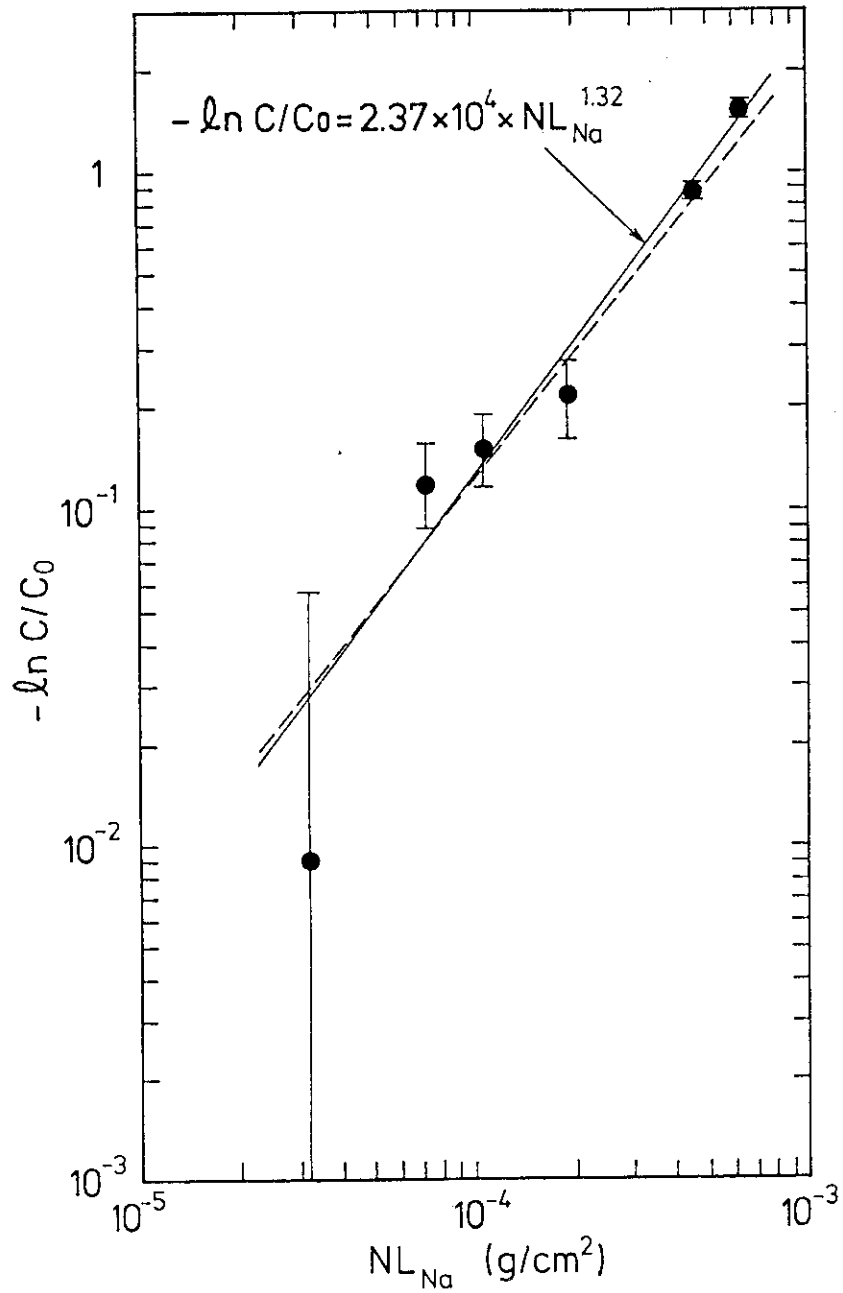Fig.5 Normalized elemental mass losses as a function of leach time

Fig.6 Relation between the C/C_0-value of Na and NL_{Na}. The solid line and the broken line represent the relationships obtained by the least-squares method and by the mathematical combination of the equations (1) and (3), respectively. Error bars show the standard deviation of $-\ln C/C_0$