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Growth of Surface Layer during the Leaching of the Simulated Waste Glass and Its Barrier Effects on the Leaching

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ABSTRACT

Growth behavior of surface layers on simulated waste glass during two different types of leaching has been studied associated with their corrosion kinetics. Static and Soxhlet leach tests were performed in distilled water at a temperature of 100°C. Auger and ESCA analyses of solid samples after leaching showed that the layers consisted of two or three sublayers which were distinguished by their different components. The transition elements Fe and Ni, the rare-earths Nd and La, and Zn were concentrated in the layers, while Si, B and alkali were depleted in most of the layers. Growth kinetics of the layers followed approximately linear relations for the two types of leaching. Growth rates and elemental profiles of the layers depended upon the leaching conditions. Comparison between the leaching rate and the thickness of the layer showed that layers did not work as effective diffusion barriers until the threshold thickness, which depended on the layer structures.

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INTRODUCTION

Leaching is a primary factor in evaluating long-term stability of nuclear waste forms and a number of tests have been performed. To predict the long-term leaching behavior it is particularly necessary to understand the reaction mechanism. As a knowledge of the leaching layer is a significant information to clarify the leaching mechanism, it is a first step to analyse the leached layers precisely. More recently surface analytical techniques have been used to study the layers, which enabled us to know elemental distribution through the layers [1], [2], [3], chemical bonding states of concentrated elements [4] and the surface fine morphology [5]. Some structural models of leached layers have been presented by several authors [1], [2] based on the data of surface analyses. As these layer structures are expected to depend upon various factors which affect the leachability, information about them would be a clue to know their leaching mechanism.

In the present study, leached layers prepared by two different leaching methods, static leaching and the Soxhlet leaching, have been analyzed with Auger and ESCA. Influence of leachant volume to surface area ratio (V/SA) on layer structures has also been studied in the static leaching. These analyses were aimed to understand effects of dissolved species on the leaching. Time dependences of elemental depth profiles were examined and influence of layer formation on the dissolution kinetics were discussed.

MATERIAL AND METHODS

Samples

The composition of the simulated waste glass used in the present study is given in Table 1. Glass samples for leach tests were cut from the cast bars into monolithic blocks (10 × 10 × 10 mm) and abraded with a micro

polisher . After cleaning with acetone in an ultrasonic degreaser, these samples were annealed at 500°C .

TABLE 1

Composition of PNC PO545 Glass (wt%)

SiO ₂	43.40	Cr ₂ O ₃	0.49	Nd ₂ O ₃	2.00
B ₂ O ₃	14.20	NiO	0.79	Sm ₂ O ₃	0.17
Li ₂ O	3.04	Rb ₂ O	0.15	ZrO ₂	2.00
Na ₂ O	8.43	Cs ₂ O	1.02	MoO ₃	1.99
K ₂ O	2.04	SrO	0.41	MnO ₂	0.29
CaO	2.04	BaO	0.68	TeO ₂	0.26
ZnO	2.04	La ₂ O ₃	1.12	CoO	0.12
Al ₂ O ₃	3.53	CeO ₂	1.23		
Fe ₂ O ₃	8.03	Pr ₆ O ₁₁	0.49		

Leaching Conditions

Teflon containers (with 100 ml capacity) were used in the static leach tests . One or two monolithic glasses were suspended in each container . Distilled water was used as a leachant, which was adjusted to provide the leachant volume to the geometric surface area ratio (V/SA) of 10 cm or 1.7 cm .

Flow leach tests were performed in the Soxhlet type apparatus with a syphon cell of 14ml . The frequency of leachant exchange was 15 times/hr . All parts of the apparatus were constructed of fused silica glass .

All leach runs in the both types of tests were performed at a temperature of 100°C from 10 hours up to 10 days . On completion of the test, the samples were rinsed with distilled water and then dried at 120°C for 2 hours .

Sample Analyses

Mass loss. Total mass loss was evaluated by weight loss measurements. Leachate solutions were analyzed by inductively coupled plasma spectroscopy (ICP) and atomic absorption method. Leachate concentrations in the Soxhlet tests were corrected by subtracting the corresponding concentrations found in the blank.

Surface Analysis. Sample glasses after leaching were analyzed using Auger coupled with ion sputtering, a commercial scanning micro-probe analyzer (PHI-590A). Primary electron beam with energy of 5kV and 5 μ A emission, yielded a beam of about 200 μ m in diameter. Sputter ion beam of about 3mm in diameter was used at a accelerating voltage of 2kV and at an argon pressure of 6×10^{-3} Pa. Sputter rate was estimated from the measurement of the sputtered crater depths using a multiple-beam interferometer. Some of the specimens were also analyzed with ESCA to obtain sodium profiles. All measurements were performed under the pressure of 10^{-7} Pa.

RESULTS AND DISCUSSION

Figure 1 shows total mass losses with time. Each kinetics curve was the same as expected from a previous work [6]. Decrease in the leaching rate was observed after two or three days for the static tests and after five days for the Soxhlet test. These results suggest that dissolved or readsorbed ions affect the leaching. Elemental mass losses for Si, B, Al and alkali evaluated from the leachate analyses, as shown in Table 2, were consistent with total weight loss from gravimetric data. Leachate concentrations for Fe, Zn, Ni and rare earths such as Nd, La and Ce were near or below the detection limits.

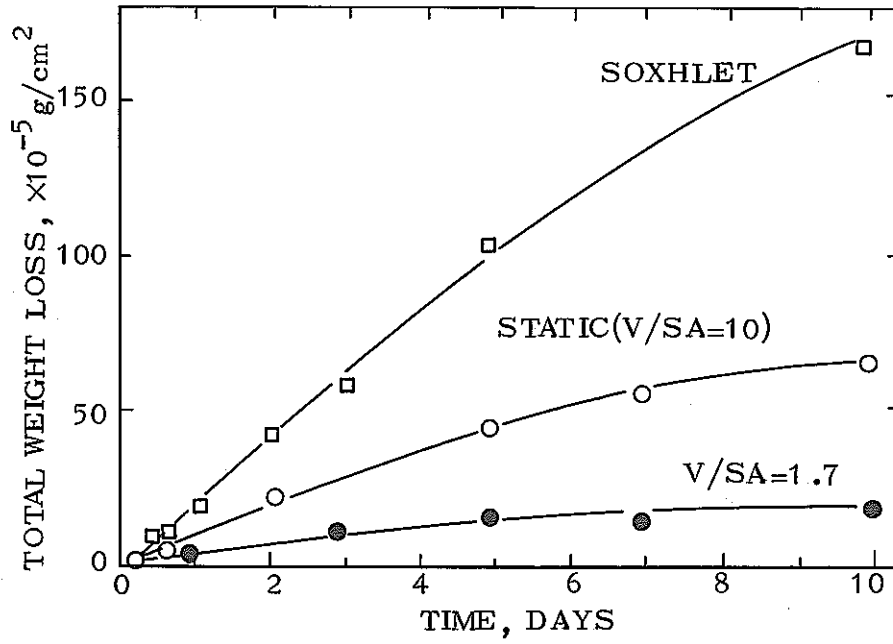


Fig. 1. Total weight losses as a function of leaching time for PO545 glass.

TABLE 2

Analysis of the leachate from 5-day leach test for PO545 glass
 ($\times 10^{-5} \text{ g/cm}^2$)

Oxide	Soxhlet	Static(V/SA=10cm)	Static(V/SA=1.7cm)
SiO ₂	119.74	32.92	9.84
B ₂ O ₃	32.73	12.28	3.96
Na ₂ O	14.61	9.53	3.98
Cs ₂ O	0.88	0.81	0.24
SrO	0.37	0.28	0.05
Al ₂ O ₃	4.15	0.05	-
Fe ₂ O ₃	< 0.23	< 0.03	< 0.005
ZnO	< 0.82	< 0.09	< 0.02
NiO	< 0.79	< 0.09	< 0.02
La ₂ O ₃	< 1.60	< 0.19	< 0.03
Nd ₂ O ₃	< 1.60	< 0.19	< 0.03
CeO ₂	< 1.60	< 0.19	< 0.03

Auger elemental depth profiles through the leached layers were illustrated in Figs. 2 and 3 for three different leach conditions. The surface elements except for oxygen were normalized to 100% in vertical scale. Enrichment of Fe, Zn, Ni and rare earths, and depletion of Si, B, alkali and alkaline earths through layers were common to all leached samples. Sodium depletion was also confirmed by ESCA analysis. These findings were supported by the data of leachate analyses as mentioned above.

For 1 day leached samples, similar concentration profiles were obtained (Fig. 2). Marked concentrations of iron in the outer layer and rare earths in the inner layer were observed. Thickness of these layers was about $1000 \sim 3000 \text{ \AA}$.

In 5 day leached samples, differences in the profiles became apparent between the static and the Soxhlet leached layers (Fig. 3). Although the elemental profiles were really complicated, two or three sublayers were distinguished by their different components for those leached layers. Three sublayers could be defined in the static leached samples. The outermost layers consisted of Zn, Al, Si and Ni, which were not found in 1 day leached samples. Iron was concentrated appreciably in the middle layers. Rare earths such as Nd and La were enriched in the inner layers. These situations did not change with V/SA except for their layer thickness, which was larger for the leached glass in higher V/SA. In the Soxhlet leached layers, two sublayers were defined. Iron, zinc and nickel were concentrated in the outer layer. Silicon was scarcely detected in this layer, while about one-half of its initial content remained in the static leached layers. The inner layer had similar profiles to those in the static leached layers.

Although those layers grew up with time, compositional structures did not change up to 10 days.

Schematic illustrations of those layer structures were shown in Fig.4. Structures for the static leached layers were analogous to those presented by Houser et al. [1] who used sputter induced optical emission technique. Layers in the static leaching conditions seem to be hydrated dealkalized layers with divalent and polyvalent cations. Trapping effects in dealkalized layers were discussed by Barkatt et al. [7] based on the order of charge density, Z/r . Formations of layer structures observed in the present study may be attributed to the trapping effect and the difference in diffusion rate of each element through the leached layers. Remarkable depletion of Si and formations of relatively thin layers in the Soxhlet leaching suggest that glass network dissolution was a predominant leach mechanism.

Secondary electron micrographs for the leached surfaces were shown in Fig. 5. Surface morphologies differed significantly between two distinct layers. The static leached layer appeared to be compact and have a fine structure.

Growth kinetics and changes in leaching rate were shown in Fig. 6. The layer thickness was evaluated by the sputter profiles. Approximately leached layers grew up linearly. Layers in the static leaching grew more rapidly than those in the Soxhlet leaching. Constant leaching rate at the early stage indicated that those layers were not protective enough to retard the ionic diffusion. However, they became to play a role as barriers with time. Thresholds of the layer thickness at which leaching rate decreased were about $3000 \sim 5000 \text{ \AA}$ for the static leaching ($V/SA=10 \text{ cm}$) and about 8000 \AA or over for the Soxhlet leaching. These results would be explained by the more compact structure of the static leached layers. Remaining Si framework with polyvalent metal elements such as Zn, Al, Ni and rare earths in the layers appeared to contribute their dense structures. Formation of the compact layers would be enhanced by decrease of V/SA

because of solution saturation effect. Saturation equilibria would also be a cause of the marked reduction in leaching rate for the static leached glasses. Especially, it may be a predominant process which controls the dissolution kinetics in V/SA of 1.7 cm.

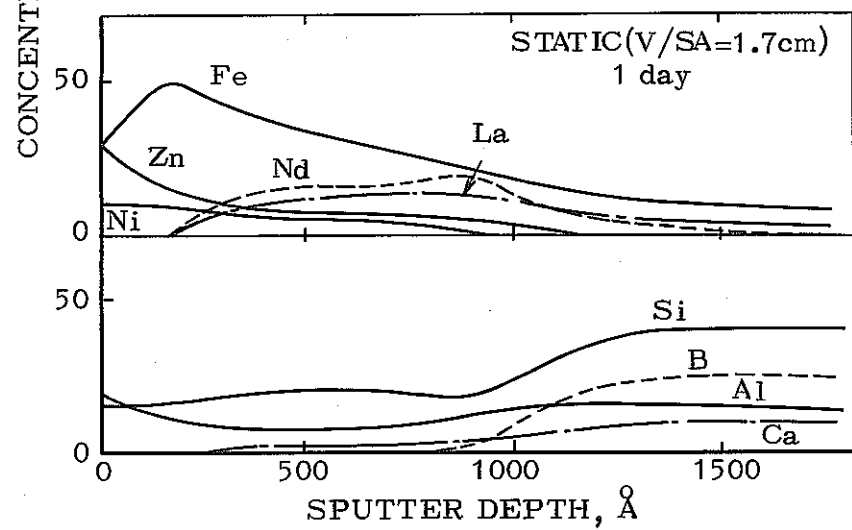
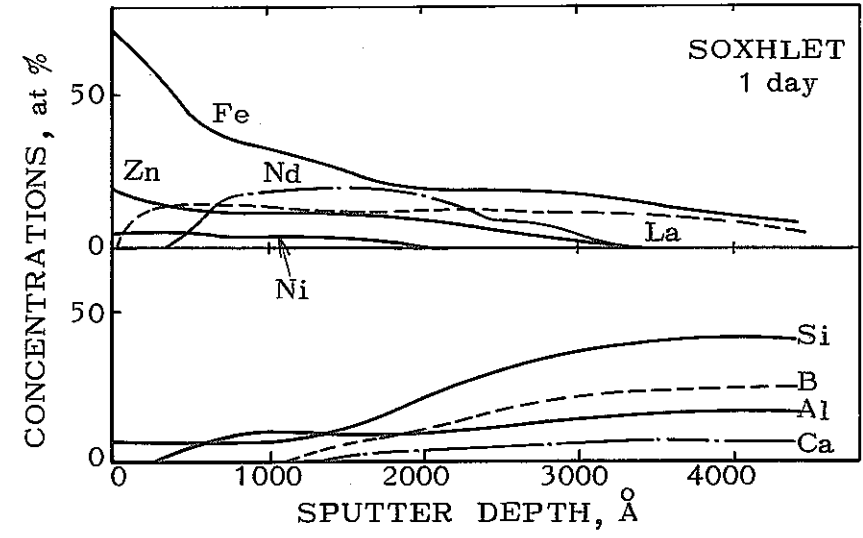
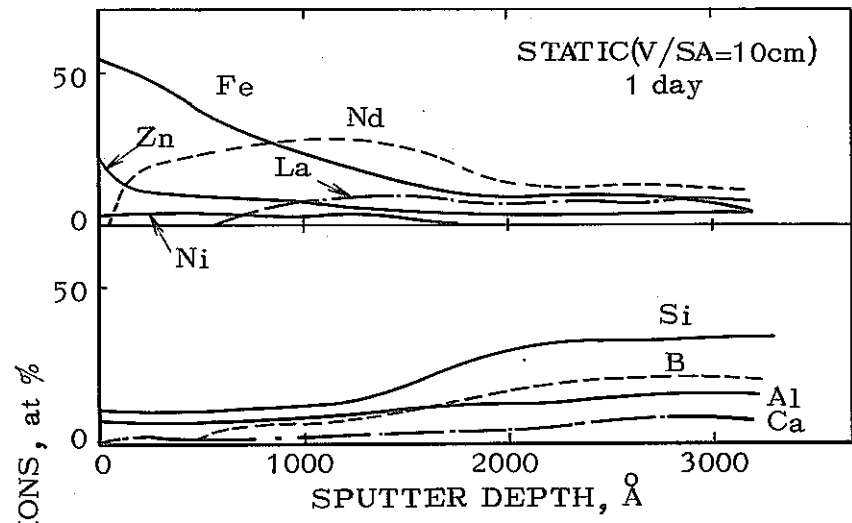


Fig. 2. Elemental concentration profiles through the leached layers. Glass samples were leached at a temperature of 100°C for 1 day.

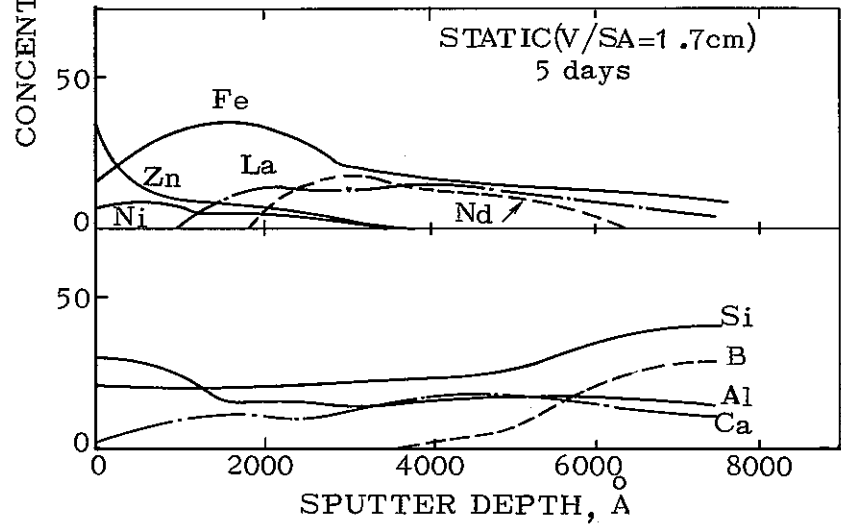
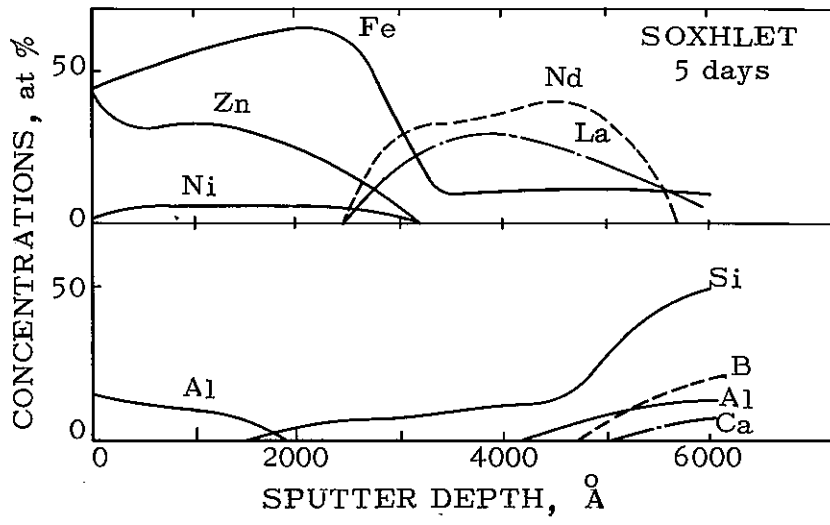
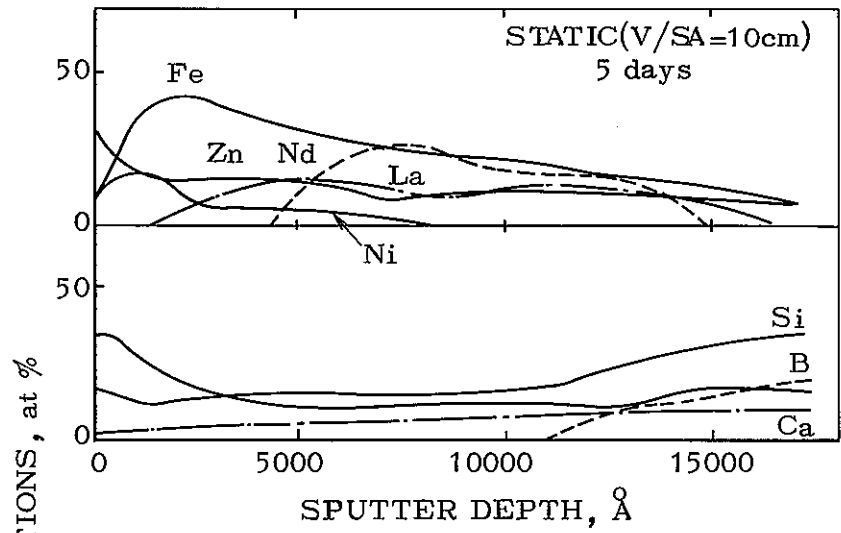


Fig. 3. Elemental concentration profiles through the leached layers. Glass samples were leached at a temperature of 100°C for 5 days.

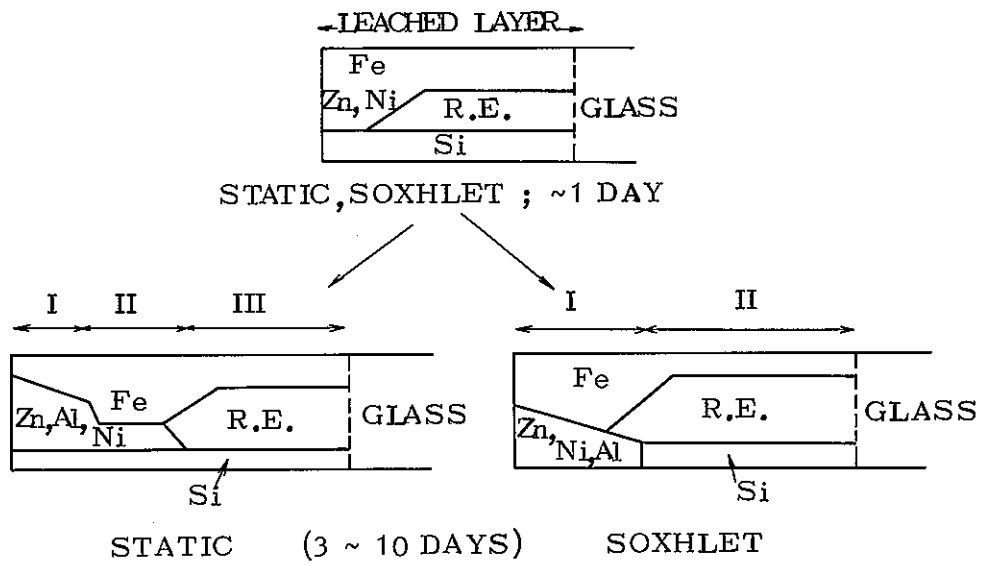


Fig. 4. Schematic drawing of structures of the leached layers. Elements indicated in the figure show major elements contained in the layers.

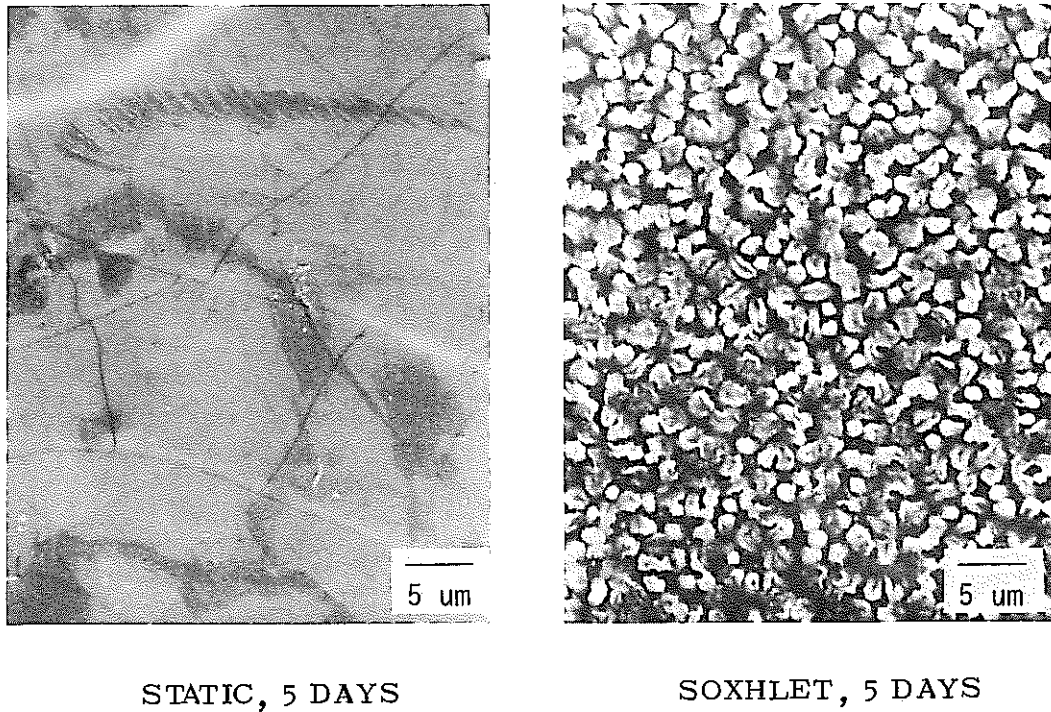


Fig. 5. Secondary electron micrographs for the leached surfaces of PO545.

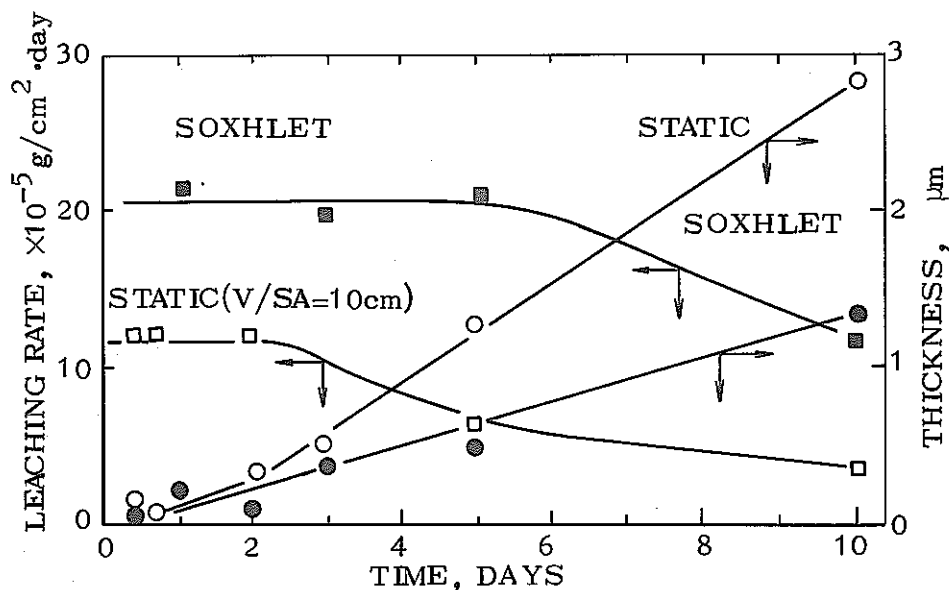


Fig. 6. Growth kinetics of the leached layers and changes in the leaching rate.

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