

# VITRIFICATION OF SIMULATED INTERMEDIATE-LEVEL WASTE FROM NUCLEAR POWER PLANTS

## I. MELTING BEHAVIOUR AND PROPERTIES OF SELECTED GLASSES

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*Glasses based on the system  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$  were prepared from natural aluminosilicate raw materials and their melting behaviour was explained by means of data obtained from DTA, GTA and heating microscope examinations. The viscosities established indicate ready meltability of the glasses in question ( $1000\text{--}1200^\circ\text{C}$ ). A short-term test of chemical resistance to water by the standard leaching method ranks the glasses at the best to the 4th hydrolytic class. The rate of quasicongruent dissolution in distilled water at  $95^\circ\text{C}$  during long-term exposure in the Soxhlett apparatus amounts to  $4.1 \times 10^{-6} \text{ g cm}^{-2} \text{ h}^{-1}$ , which corresponds to a boundary shift rate of  $4.7 \times 10^{-10} \text{ cm s}^{-1}$ . According to the results of long-term static tests at  $25^\circ\text{C}$ , the values are lower by more than one order of magnitude and comparable to the long-term corrosion of industrial glasses. The chemical durability of the glasses decreases in an acid medium.*

### INTRODUCTION

Operation of nuclear power station yields diverse types of radioactive waste, differing in their origin, composition as well as the degree of their activity. The present study is concerned with the so-called intermediate-level wastes (ILW) containing boric acid from the primary circuit, eluents from ion exchange stations, decontaminating solutions, etc. The composition of ILW depends on the actual conditions of operation and may show quite considerable quantitative differences in various power stations. As the main components, ILWs from Czechoslovak nuclear power stations contain alkali borates, nitrates, chlorides and carbonates, salts of oxalic and citric acids,  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$  in the form of sludge, and the like [1].

These primarily arising aqueous solutions are concentrated in order to reduce their volume for temporary storage in liquid state. For final storage, the solution must be converted to a solid product and in the next step immobilized, i.e. fixed in a suitable medium which renders the final product insoluble (or soluble to a limited degree) in water and natural aqueous solutions with which the product might come into contact. A leaching rate of  $1 \times 10^{-5} \text{ g cm}^{-2} \text{ h}^{-1}$  at  $25^\circ\text{C}$  is specified as an approximate maximum value for ILWs.

Bitumen and Portland cement are considered as suitable fixing media. As far as high content of  $\text{B}_2\text{O}_3$  and alkalis in the waste, fixation in the form of borosilicate glass, using a suitable silicate component, is regarded as being effective. The process, so-called vitrification, is the most suitable one for high-level activity wastes (burnt-out fuel cells) apart from fixation in a ceramic or mineral matrix [2]. In the case of ILW, vitrification appears to be likewise advisable, because the waste proper contains as the main components just the substances which are capable of

forming a well-meltable glass. This is why the respective glass system was investigated in the present study from the standpoint of technological properties, as well as from that of the hydrolytic durability of the product.

Papers [3–5] were devoted to studying the properties of model glasses in the system  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ , and proved that the system includes glasses suitable for fixation of ILWs. Study [3] earmarked as the most suitable ones glasses containing 48wt.%  $\text{SiO}_2$ , 18%  $\text{Al}_2\text{O}_3$  22–25%  $\text{Na}_2\text{O}$  and 8–11%  $\text{B}_2\text{O}_3$ . The study has linked up to the investigation of the system  $\text{Na}_2\text{O-ZnO-B}_2\text{O}_3\text{-SiO}_2$  [6]. Both systems produce glasses with low inclination to crystallization, that is glasses exhibiting stability in the course of processing.

The present study was aimed at preparing glasses similar to the model system  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ , but, at the suggestion by experts from the Institute of Nuclear Research (ÚJV) at Rež, the glasses were prepared with the use of natural aluminosilicate raw materials which could have earlier been used as sorbents, and of model substances corresponding to the active solutions from Czechoslovak nuclear power stations. The model waste was prepared from the respective pure substances; following their conversion to oxides, the representation of the main components considered for glass formation was as follows: 40.6 wt. %  $\text{B}_2\text{O}_3$ , 53.0%  $\text{Na}_2\text{O}$  and 5%  $\text{K}_2\text{O}$  (the rest being  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$ ). Kaolin and the zeolitic mineral clinoptilolite, extracted in Slovakia, were chosen as the natural aluminosilicates. The latter shows excellent sorbing properties with respect to Cr and Cs, and moreover has a high  $\text{SiO}_2$  content, which is favourable for preparing a chemically durable glass.

The vitreous products prepared by melting on a laboratory scale were subjected to measurements of

Table I

Theoretical composition of the melted glasses in wt.% (the actual composition of glasses designated by KL in the series with clinoptilolite is given in brackets)

Oxide	KL 30	KL 40	KL 50	KA 40	KA 50	P 40
SiO <sub>2</sub>	53.43 (54.0)	46.24 (45.7)	38.40 (38.4)	30.46	24.97	46.57
Al <sub>2</sub> O <sub>3</sub>	8.65 ( 9.2)	7.48 ( 8.1)	6.22 ( 6.7)	24.05	19.72	7.54
K <sub>2</sub> O	4.04 ( 4.0)	4.21 ( 4.1)	4.33 ( 4.2)	2.95	3.31	4.57
Na <sub>2</sub> O	17.41 (15.8)	21.78 (22.0)	27.05 (26.5)	23.44	28.76	21.38
Fe <sub>2</sub> O <sub>3</sub>	0.97 ( 1.2)	0.98 ( 1.1)	0.98 ( 1.1)	1.04	1.03	0.98
CaO	2.39 ( 2.3)	2.07 ( 2.0)	1.72 ( 1.7)	–	–	2.09
MgO	0.72 ( 0.8)	0.62 ( 0.6)	0.52 ( 0.5)	–	–	0.62
B <sub>2</sub> O <sub>3</sub>	12.19 (12.0)	16.40 (15.8)	20.48 (20.2)	17.83	21.93	16.10
MnO <sub>2</sub>	0.13 ( 0.1)	0.20 ( 0.1)	0.25 ( 0.1)	0.22	0.27	0.13

some technologically significant properties and chemical durability tests.

#### EXPERIMENTAL

As mentioned above, kaolin and clinoptilolite were used as the source of silica, and the model waste served as the source of B<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O. In addition to the main oxides, the product contained other components brought in by the two initial substances.

The kaolin contained 45.6 wt.% SiO<sub>2</sub>, 36.0% Al<sub>2</sub>O<sub>3</sub>, 1.38% of alkali oxides and 0.92% Fe<sub>2</sub>O<sub>3</sub>. Clinoptilolite from the Nižný Hrabovec deposit had the following composition: 67.0% SiO<sub>2</sub>, 10.85% Al<sub>2</sub>O<sub>3</sub>, 3.20% K<sub>2</sub>O, 0.52% Na<sub>2</sub>O, 0.85% Fe<sub>2</sub>O<sub>3</sub>, 3.0% CaO and 0.9% MgO. X-ray analysis indicated, apart from clinoptilolite, also the presence of quartz, cristobalite and mica.

The mixes for melting were prepared so as to contain 30%, 40% and 50wt.% of the model waste respectively, the rest being the aluminosilicate. The theoretical (calculated) and the actual analytically established compositions of the glassy product of melting are listed in Table I. Both series of samples were designated by the abbreviations of the aluminosilicate raw materials and by the percent content of the model waste in the mix. The KA 30 glass (i.e. kaolin + 30% of waste) could not be prepared owing to strong foaming of the mix. The glasses were melted in an electric furnace in porcelain crucibles by gradual heating up to 1050°C, and holding at this temperature for 1 hour. For the reason of strong foaming, the mix had to be added to the crucibles by parts. The samples were allowed to cool down in the furnace and adjusted for further purposes by melting in platinum crucibles, drawing into rods and fibres, etc. As indicated by Table I, the melting process did not result in any significant changes in composition due

to vaporization, in spite of the relatively high content of alkalis and B<sub>2</sub>O<sub>3</sub> which might be responsible for volatilization of sodium metaborate. In addition to laboratory melting, ÚJV Řež has also carried out a pilot-plant scale melting experiment in cooperation with the State Glass Research Institute in Hradec Králové. Its product, designated P 40, was likewise used in determining the properties. It is also listed in Table I and its composition is very close to that of KL 40.

#### Technological properties

The behaviour on melting was studied in more detail on the mixture of clinoptilolite with 40wt% of the model waste, by heating it in crucibles for 1 hour at various temperatures over the range of 100 to 900°C for one hour and then inspecting the samples visually. No visually discernible changes took place up to about 700°C. The samples began to fuse perceptibly between 700 and 750°C, producing a strongly porous frothy material. The level in the crucible fell at 800°C, and non-melted particles were still present in the bubbly glass. At 900°C, the samples were well melted and free of visible inhomogeneities.

To elucidate the processes involved in the course of melting, DT and GT analyses were carried out of the components and of their mixtures (Figs. 1 and 2).

Clinoptilolite does not exhibit any significant thermal effects on heating up, except for an indication of dehydration at about 70°C, and a mild exothermal effect at 540°C. According to the GTA curve, the loss of water is continuous and proceeds up to about 750°C. The DTA curve for the waste shows two low-temperature endothermal effects which can be attributed to dehydration of borax [7]. The other effects on the curve correspond to the other components of the waste or to their new compounds. The

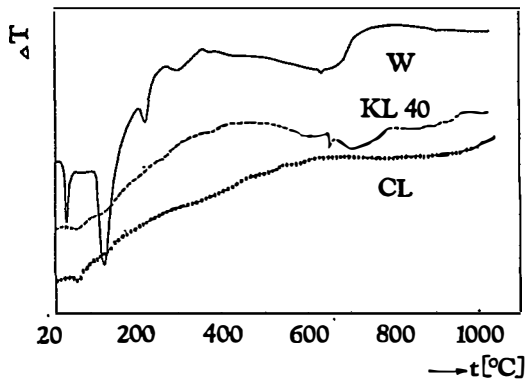


Fig. 1. DTA curves of clinoptilolite (CL), model waste (W) and the mixture of the substances for KL 40.

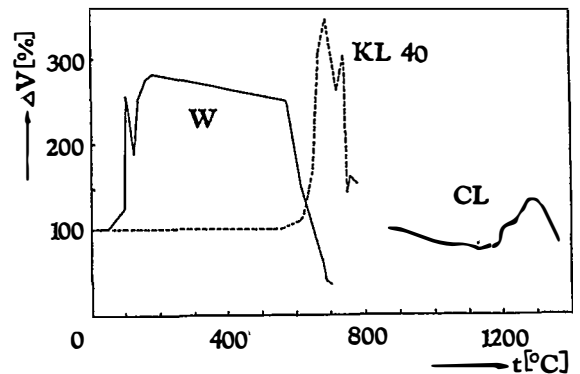


Fig. 3. Changes in volume on heating clinoptilolite (CL), model waste (W) and the mixture for KL 40.

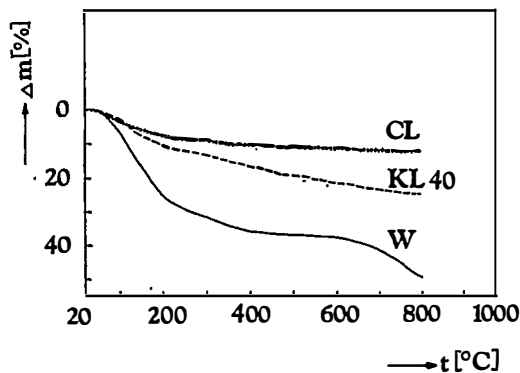


Fig. 2. GTA curves of clinoptilolite (CL), model waste (W) and the mixture of the substances for KL 40.

loss in weight on the GTA curve represents continuing dehydration or vaporization of alkali borates. The total loss in weight up to 800°C amounts to approx. 25% for the mixture, to 48.5% for the waste and to 11.5% for clinoptilolite (the GTA curves were obtained with different preset sensitivities). During the critical stage of foaming, the DTA curve exhibits effects which can be attributed to reactions between alkali oxides and the aluminosilicate.

The changes in volume of the mix were studied under the Leitz heating microscope. Fig. 3 shows the results, again for the individual components and their mix (KL 40).

Clinoptilolite alone expands its volume above 1200°C, whereas the model waste already expands to triple its original volume at 100°C and shrinks rapidly at about 600°C. Borax behaves in a similar way, indicating its gradual formation following the mixing of  $H_3BO_3$ , NaOH and  $Na_2CO_3$  during the compounding of the model waste; this fact was also proved by the DTA effects found for the mixtures [7]. The mixture of clinoptilolite and the model waste starts to expand

rapidly at about 650°C, increasing its volume up to 3.5 times; at about 750°C the volume regains its original value. The behaviour of the mix is quite different from that of the two components, as also demonstrated by the DTA curves. The foaming reactions can therefore be taken as being associated with reactions between the model waste and the aluminosilicate, probably involving formation of alkali silicates and liberation of  $CO_2$  and possibly also  $H_2O$  from the model waste. Unlike the normal types of glass, whose melting also includes similar interactions, the system in question already contains considerable amounts of melt at low temperature, and this makes the escape of gases difficult.

Viscosity is one of the most important properties with respect to melting and forming. It was measured by the standard methods [8], by determining the sink point, Littleton's softening point and  $T_f$  from the expansion curve. The results are plotted in Fig. 4.

Extrapolation of the regressive equation used in evaluating the sink point, yielded the following va-

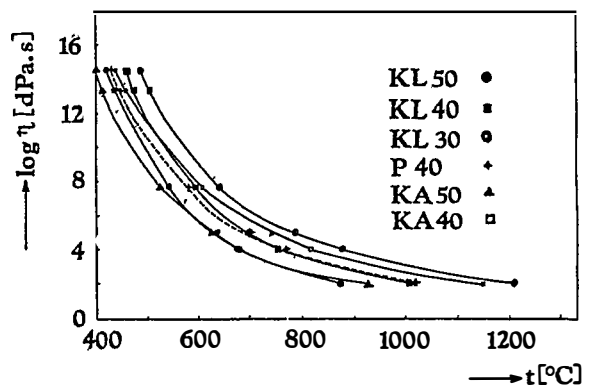


Fig. 4. Viscosity curves of the experimental glasses.

lues calculated for the standard melting temperature ( $\eta=10^{2.0} \text{dPa s}$ ):

Glass:	KL30	KL40	KL50	KA40	KA50	P40
Melting temperature [°C]	1213	1001	872	1148	927	1030

In comparison with standard glasses, the melting temperatures of the model glasses are very low, when assessed according to the viscosity values.

### Chemical durability

The chemical durability of the experimental glasses was assessed by the standard method to ISO 719 (durability with respect to water at 98°C on 2g of ground glass 0.315–0.5mm, leaching for 1 hour, determining the amount of leached alkalis by titrating with 0.01mol l<sup>-1</sup> HCl). The results are given in Table II. The best value of chemical durability was found for the glass with the highest content of silica (i.e. with the lowest content of the model waste incorporated).

However, it is the long-term chemical stability which is of basic significance for assessing the quality of the vitrification products. This property was tested on glass P 40, using the standard Soxhlett extractor. An amount of 1g of standard glass grit in a linen bag was placed in the leaching cell of 70 ml capacity. The boiling flask contained 200 ml of the leaching solution. The extractor was insulated with glass wool so that the inner temperature was 95±2°C. Water in the leaching cell was automatically replaced at intervals of about 10 minutes. The quantity of SiO<sub>2</sub> and Na<sub>2</sub>O in solution was determined colorimetrically and with a flame photometer. The values obtained were calculated per 1 cm<sup>2</sup> or 1 m<sup>2</sup> of glass surface area, using that of 110 cm<sup>2</sup>g<sup>-1</sup> given for standard glass grit [11]. The results are given in Fig. 5. The initially parabolic

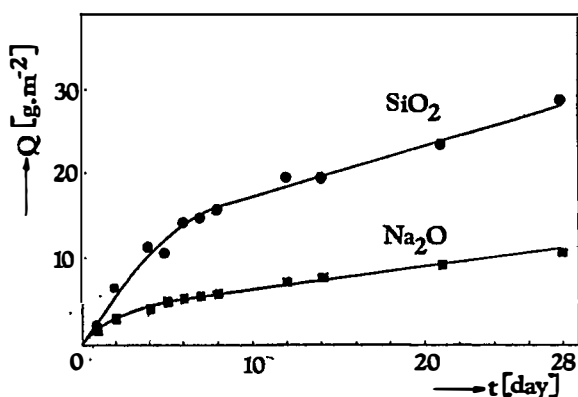


Fig. 5. Cumulated amount of SiO<sub>2</sub> and Na<sub>2</sub>O in solution after exposure of glass P 40 in Soxhlett's apparatus.

course becomes linear for both Na<sub>2</sub>O and SiO<sub>2</sub> after 200 to 300 hours of leaching.

The appearance of the leached surface of glass P 40 after 28 days in the extractor is shown on the scanning electron micrograph in Fig. 6. On the surface, there is a thick dealcalized layer exhibiting a tendency to cracking and perhaps also to exfoliation.

Long-term chemical durability at lower temperatures was established by static tests of leaching 1 g of standard grit in 70 ml of distilled water. In addition to analytical determination of SiO<sub>2</sub> and Na<sub>2</sub>O, also the pH of the extract was measured and found to vary considerably, attaining values of up to 8.7 at 25°C, 9.2 at 40°C, 10.4 at 70°C and 11.1 at 95°C. The results are plotted in Figs. 7 and 8. The substantial dispersion of values is characteristic of static tests, being due to poorly defined hydrodynamic conditions and local saturation of the solutions.

Resistance of the P 40 glass to an acid medium was assessed by leaching 1 g of the standard grit in 50 ml of 0.1 mol l<sup>-1</sup> mineral acid for 1 hour at 98°C. The

Table II

Chemical durability of the experimental glasses with respect to water, standard method to ISO 719

Glass designation	Consumption of 0.01mol l <sup>-1</sup> HCl [ml g <sup>-1</sup> ]	Durability class
KL 30	1.2	4
KL 40	6.0	lower than 5
KL 50	38.3	"
P 40	6.2	"
KA 40	10.0	"
KA 50	15.0	"

Table III

Comparison of chemical durability of glass P 40 with respect to water and solutions of acids

Eluting medium	Amount eluted [g m <sup>-2</sup> ]		Weight ratio SiO <sub>2</sub> /Na <sub>2</sub> O
	Na <sub>2</sub> O	SiO <sub>2</sub>	
H <sub>2</sub> O	0.24	0.13	0.54
0.1mol l <sup>-1</sup> HCl	2.43	0.79	0.33
0.1mol l <sup>-1</sup> HNO <sub>3</sub>	2.17	0.66	0.31

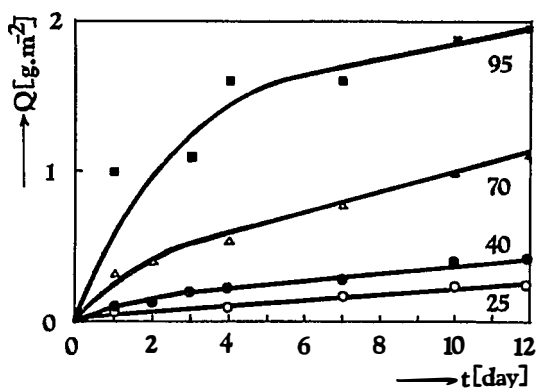


Fig. 7. Cumulated amount of  $\text{SiO}_2$  after static leaching of glass P 40 at various temperatures ( $^{\circ}\text{C}$ ).

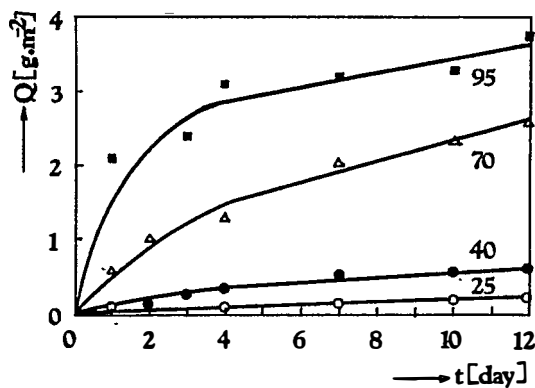


Fig. 8. Cumulated amount of  $\text{Na}_2\text{O}$  after static leaching of glass P 40 at various temperatures ( $^{\circ}\text{C}$ ).

results are listed in Table III. Compared to the effects of water, the durability in a strongly acidic medium is several times lower, as regards both the leaching of  $\text{Na}_2\text{O}$  and dissolution of  $\text{SiO}_2$ .

#### DISCUSSION

The ready fusibility of the glasses in question, due to their high content of alkali oxides and  $\text{B}_2\text{O}_3$ , is combined with a relatively satisfactory chemical durability on a long-term basis, although the short-term tests rank the glasses apart from the hydrolytical durability classes at an  $\text{SiO}_2$  content lower than about 50 wt.%.

The long-term test of leaching the P 40 glass in the Soxhlett apparatus (Fig.5) indicates that quasicongruent dissolution takes place after 200 to 300 hours, whereas on short-term basis, diffusion of alkalis through the leached layer, having the character close to that of silica gel, is the controlling process. Surface dissolution and exchange diffusion in the leached layer ( $\text{Na}^+ \rightleftharpoons \text{H}_3\text{O}^+$ ) are generally regarded as the basic processes involved in the corrosion of silicate glasses by aqueous solutions [10]. This concept has provided the basis for various kinetic models, and one of them [11] was used to calculate the kinetic parameters from the data given in Fig. 5. The value of  $4.7 \times 10^{-10} \text{ cm s}^{-1}$  was obtained for quantity  $a$ , characterizing the rate of dissolution of the surface layer, and the interdiffusion coefficient in the diffusion layer was found to be  $9.3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ . In study [12], the rate of dissolution of industrial sheet glass at  $90^{\circ}\text{C}$  in water on long-term exposure amounts to  $8.9 \times 10^{-4}$ , and that of Pyrex glass to  $2.3 \times 10^{-10} \text{ cm s}^{-1}$ . While the value of  $a$  corresponds to well durable glasses, the diffusion coefficient is relatively high (varying between  $10^{-11}$  and  $10^{-16} \text{ cm}^2 \text{ s}^{-1}$  for the various glasses). The non-linear increase in the amount of extracted  $\text{SiO}_2$  in Fig. 5 is probably due

to an elevated pH value of the solution, enriched by major amounts of alkalis during the initial stage.

According to the model mentioned, the thickness of the impaired surface layer is given by the equation  $x = D/a$ ; the ratio of the calculated values of both quantities gives a layer thickness of approx.  $20 \mu\text{m}$ . The thickness estimated from the micrograph in Fig. 6 corresponds well to this calculated value. From the value of parameter  $a$  for steady-state transfer of glass into solution it is possible to determine the rate of dissolution by multiplying with density ( $2.41 \text{ g cm}^{-3}$ ); it amounts to  $4.1 \times 10^{-6} \text{ g cm}^{-2} \text{ h}^{-1}$ . The sum of the amount of leached  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  gives the respective rate of dissolution of  $3.4 \times 10^{-6}$  and  $4.9 \times 10^{-6} \text{ g cm}^{-2} \text{ h}^{-1}$ , having used the correction factor of 0.68 for the proportion of the two components in the glass. These values hold for the temperature of  $95^{\circ}\text{C}$  and the test conditions in the Soxhlett apparatus. A value lower roughly by one order of magnitude may be expected for room temperature.

The long-term static tests carried out at various temperatures (Figs. 7 and 8) do not allow the kinetic parameters to be calculated owing to a considerable dispersion of results, and to the relatively short time of exposure. An approximate calculation made use of the total extracted amounts of  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  at  $25^{\circ}\text{C}$ , which amounted to  $58 \times 10^{-6} \text{ g cm}^{-2}$  after 336 hours, so that for the mean rate of dissolution (including the initial faster stage) one obtains the value of  $2.5 \times 10^{-7} \text{ g cm}^{-2} \text{ h}^{-1}$  or, expressed as the rate of the interface shift,  $2.9 \times 10^{-11} \text{ cm s}^{-1}$ .

A comparison of the static tests with the Soxhlett extraction ones can be made for the temperature of  $95^{\circ}\text{C}$ . The amount of statically extracted  $\text{SiO}_2$  after 336 hours was  $1.97 \times 10^{-4} \text{ g cm}^{-2}$  and that of  $\text{Na}_2\text{O}$  was  $3.76 \times 10^{-4} \text{ g cm}^{-2}$ , whereas with the Soxhlett test, the values for the same time of exposure were approximately  $19 \times 10^{-4}$  and  $7.5 \times 10^{-4} \text{ g cm}^{-2}$ , respectively (Fig. 5). Soxhlett's test thus yields sub-

Table IV  
Weight ratio SiO<sub>2</sub>/Na<sub>2</sub>O in solution  
after 24 hrs. of leaching

Type of test	Static				Soxhlett
Temperature [°C]	25	40	70	95	95
SiO <sub>2</sub> /Na <sub>2</sub> O	0.73	0.78	0.57	0.45	1.2

stantially higher results, particularly for SiO<sub>2</sub>, obviously as a result of saturation of the solution in the static arrangement. The periodical replacement of the liquid restricts the saturation effects, and the leaching also takes place under somewhat different conditions of pH resulting from the contact of glass with the replaced clean water. With all this in mind, the results of the static and the Soxhlett tests can be regarded as being consistent.

The distinct effect of alkalinity of the leaching solution can also be seen on the changes in the SiO<sub>2</sub>/Na<sub>2</sub>O ratio in the extract. The values of this ratio after 24 hours of leaching are given in Table IV. All the values are substantially lower than the weight ratio in the original glass [2,12] which indicates preferential leaching (extraction) of alkali oxides during the initial stage, in agreement with the concept of the mechanism of interaction between silicate glasses and water. In the case of Soxhlett's test, the SiO<sub>2</sub>/Na<sub>2</sub>O ratio is closer to that in the glass, as a result of periodical replacement of the leaching liquid, so that the saturation effect, particularly influencing the dissolution of SiO<sub>2</sub>, is suppressed. With static tests, the saturation of the solution suppresses the dissolution of SiO<sub>2</sub>, and there prevails the diffusion transfer of alkali oxides into solution, the more so the higher the leaching temperature (faster saturation of the solution with SiO<sub>2</sub>). A role may also be played by the effect of different temperature dependences (activation energy) for the dissolution and the diffusion process.

During short-term leaching for 1 hour (Table III), the SiO<sub>2</sub>/Na<sub>2</sub>O ratio is likewise shifted to the benefit of Na<sub>2</sub>O, more so in acidic solutions than in water. A more detailed study of the leaching of this type of glasses by acidic solutions is to follow. On taking a broader view of the relatively favourable corrosion behaviour of the type of glasses in question, one may take into account the peculiarities in the behaviour of Middle-Age glasses, which have been exposed to the effects of atmospheric humidity for centuries [13]. These glasses exhibit a sharp boundary between those with a satisfactory durability and those with a poor

one, whose surface was coated by a thick corrosion crust. The boundary is given by the SiO<sub>2</sub> content, and is at about 60 mol %. Our glasses with a relatively low SiO<sub>2</sub> content and a rather poor short-term durability achieve a comparatively good long-term durability at the expense of formation of a protective high-silica surface layer of great thickness, which is probably associated with the considerable permeability of the layer for the extraction of alkalis, and possibly other components having the character of network modifiers. It may be assumed that the higher permeability (a high interdiffusion coefficient) is basically due to the porosity of the layer, which has the character of a gel having its pores filled with water or a solution. Such a layer shows then a predisposition to cracking and exfoliation on drying, which is an unfavourable property when taking into account the possibility of alternating wetting and drying. It seems that the structure of the gel layers arising by topochemical reactions with water on the glass surface, are associated with the structure of the base (the original glass), i.e. with the polymeration degree of the glassy network, in which the siloxane bonds are impaired by entry of network modifiers, producing non-bridging oxygen bonds [14].

## CONCLUSION

- 1) In the system in question, melting of an aluminosilicate raw material with model waste at comparatively low temperatures yields glasses with a chemical durability that allows waste of medium activity to be immobilized.
- 2) In the course of melting, the glasses show major inclination to foaming due to the escape of gases and vapours (CO<sub>2</sub>, H<sub>2</sub>O) liberated by reactions between the waste components and the aluminosilicate component at the stage when the system already contains considerable amounts of melt.
- 3) A long-term leaching test of the P 40 representative glass in Soxhlett's extractor allows the rate of quasicongruent dissolution in the steady-state stage of corrosion in distilled water to be calculated; the rate amounts to  $4.1 \times 10^{-6} \text{ g cm}^{-2} \text{ h}^{-1}$  at 95°C.
- 4) The relatively high interdiffusion coefficient for the extraction of alkalis results in the formation of an impaired surface layer of considerable thickness, showing a tendency to cracking and exfoliation after drying; this phenomenon might lead to a suppression of the protective effect of the surface layer.
- 5) At 25°C, the rate of dissolution of glass P 40 in distilled water is lower than, or equal to,  $2.5 \times 10^{-7} \text{ g cm}^{-2} \text{ h}^{-1}$  by the static test; on replacing the leaching liquid, higher values of the same order of magnitude can be expected.
- 6) In acidic solutions, the corrosion of this type of glasses proceeds at a substantially higher rate than in

distilled water. The durability with respect to acidic solutions will be dealt with in part 2 of the present study.

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VITRIFIKACE SIMULOVANÝCH RADIOAKTIVNÍCH  
ODPADŮ STŘEDNÍ AKTIVITY Z JADERNÝCH  
ELEKTRÁREN

I. CHOVÁNÍ PŘI TAVENÍ A VLASTNOSTI VYBRANÝCH  
SKEL

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V základní soustavě  $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{Na}_2\text{O}$  byla utavena skla ze směsi přírodního hlinitokřemičitanu a modelového odpadu, který obsahuje zejména alkalické boritany a jiné alkalické soli. Složení skel je uvedeno v tab. 1 spolu s vybraným sklem P 40, jež bylo taveno při polo-  
provozním experimentu.

Chování směsí surovin při tavení bylo sledováno pomocí DTA, GTA a zahřívacího mikroskopu (obr. 1-3). Značný sklon k pění souvisí s reakcemi mezi alkalickými složkami modelového odpadu a hlinitokřemičitanem za vzniku alkalických křemičitanů; při reakci se u směsi uvolňuje

$\text{CO}_2$  a páry  $\text{H}_2\text{O}$  v etapě, kdy již je v systému značné množství nízkotající taveniny. Dobrou tavitelnost studovaných skel dokládají viskozitní křivky (obr. 4); z nich vyplývají standardní tavicí teploty ( $\eta = 10^2$  dPa s) mezi 1000 - 1200 °C.

Krátkodobé testy chemické odolnosti (tab.2) zařazují tato skla s výjimkou skla s nejvyšším obsahem  $\text{SiO}_2$ , mimo hydrolytické třídy ČSN 70 0531. Při dlouhodobém testu v Soxhletově aparatuře (obr. 5) však byla nalezena pro reprezentativní sklo P 40 poměrně nízká hodnota ustálené rychlosti kvazikongruentního rozpouštění  $4,1 \cdot 10^{-6}$  g  $\text{cm}^{-2}$   $\text{h}^{-1}$ , což odpovídá rychlosti posunu rozhraní  $4,7 \cdot 10^{-10}$  cm  $\text{s}^{-1}$ , tedy na úrovni běžných průmyslových skel. Na povrchu skla vzniká po dlouhodobém loužení narušená vrstva o značné tloušťce, jež má sklon k praskání a odlupování při vysoušení (obr.6). Dlouhodobé statické testy (obr.7 a 8) dávají, jak bylo možno předpokládat, nižší rychlosti loužení a rozpouštění; pro 25°C byla vypočtena hodnota ustálené rychlosti koroze  $2,5 \cdot 10^{-7}$  g  $\text{cm}^{-2}$   $\text{h}^{-1}$ . V kyselém prostředí byla nalezena podstatně vyšší rychlost loužení a rozpouštění. Podrobnější studium chování těchto skel v kyselých roztocích bude předmětem druhé části této práce.

Obr. 1. Křivky diferenční termické analýzy (DTA) klinoptilolitu (CL), modelového odpadu (W) a směsi těchto látek pro KL 40.

Obr. 2. Křivky vážkové termické analýzy (GTA) klinoptilolitu (CL), modelového odpadu (W) a směsi těchto látek pro KL 40.

Obr. 3. Objemové změny při zahřívání klinoptilolitu (CL), odpadu (W) a směsi pro KL 40.

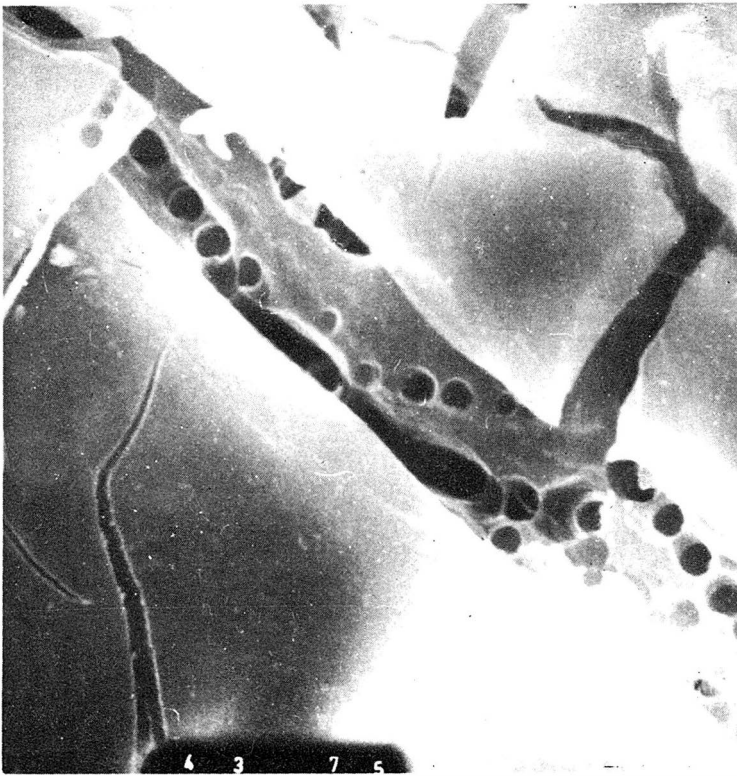
Obr. 4. Viskozitní křivky pokusných skel.

Obr. 5. Kumulované množství  $\text{SiO}_2$  a  $\text{Na}_2\text{O}$  v roztoku po expozici skla P 40 v Soxhletově aparatuře.

Obr. 6. Povrch drti skla P 40 exponované 28 dní v Soxhletově extraktoru (SEM, zvětš. 1000 ×).

Obr. 7. Kumulované množství  $\text{SiO}_2$  po statickém loužení skla P 40 při různých teplotách (°C).

Obr. 8. Kumulované množství  $\text{Na}_2\text{O}$  po statickém loužení skla P 40 při různých teplotách (°C).



*Fig. 6. The surface of glass P 40 grit after 28-day exposure in Soxhlett's apparatus (SEM, magn. 1000 ×)*