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THE FACTORS INFLUENCING THE RESULTS OF CHEMICAL DURABILITY TESTS

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Using two types of chemical durability tests (static and dynamic test in Soxhlet's extractor) at 95 °C, the resistance to water of two glasses (Float glass and a glass intended for the fixation of radioactive wastes) was determined while taking into account the following factors:

- a) the ratio of the sample surface area to the volume of the leaching solution (the so-called SA/V ratio);*
- b) the form of the sample, by comparing ground and compact ones;*
- c) various surface treatments of the samples (grinding and polishing).*

Their effect was established by determining the amount of alkalis and silica extracted into the solution.

The effect of the SA/V ratio on the amount of components eluted into solution was found to depend on the composition of glass. The form of the sample does not substantially influence the test results. The quality of surface finish affects the amount of components eluted into solution.

INTRODUCTION

Chemical durability of glass is a decisive property for its application in many fields. The determination of chemical durability has been standardized and the respective specifications stipulate precisely the respective test conditions. The tests are generally short-term in nature, taking at the most several hours. However, the short-term tests are not quite satisfactory for some special applications of glasses. For example, glassy materials for the fixation of radioactive wastes require much longer tests (of the order of months or years) in view of the long periods envisaged for their safe deposition. No tests for this type of special glasses have yet been standardized; there are only drafts which have not yet been approved in a binding way [1]. The working out of procedures and conditions for such tests requires perfect knowledge of the effects of factors influencing the chemical durability of glass.

The factors affecting the chemical durability of glass can be generally divided into three groups [2]:

1. System factors (the properties of the entire leaching system), i.e. temperature, ratio of the glass area to the volume of the leaching solution (SA/V), possibly the radiation level;

2. The properties of the leaching solution — its composition, pH, content of dissolved gases, rate of flow;

3. The properties of the glass, i.e. its composition, homogeneity (content of non-glassy phases), its form, surface characteristics, thermal history.

A number of data on the effects of these factors can be found in the literature. However, a critical study of their effect on the results of durability tests is still lacking.

The question of the effect of SA/V is one that is discussed very frequently [3–8]. Whereas the tests carried out on current simple glasses show that an increase in the SA/V ratio accelerates leaching, those on more complex glasses (usually those for the fixation of radioactive waste) brought the opposite results.

The comparison of powdered and compact samples is discussed as a theoretical problem of the suitability of a certain type of sample for the given test. The complications involved in the leaching of powdered samples are pointed out: the difficult determination of the specific surface area of powdered samples, formation of powder particle clusters, danger of sample compaction, change in the surface area of the sample during the test due to decreasing particle size and creation of so-called corrosion cells, i.e. areas in close proximity of the grain with a significantly higher concentration of the corrosion or leaching products in the solution [9, 10]. To reduce these effects to a minimum, the medium grain size of about 0.2 to 0.6 mm should be used.

Elution of specimens with various surface finishes was compared e.g. by Pederson et al. [3] who found that coarsely ground samples produce higher amounts of eluted Si, Na and B than the polished ones, even when calculated per area of eluted surface. A similar conclusion was reached by Sanders and Hench [11]. In the former case the measurements were carried out on a comparatively complex glass for the fixation of radioactive waste, in the latter a simple Li_2O —2 SiO_2 two-component glass was involved.

EXPERIMENTAL

The two glasses chosen have different compositions as well as practical applications. The current commercial glasses were represented by the FLOAT sheet glass, those for special applications by an experimental glass for the fixation of radioactive waste, designated G. The composition of the two glasses is listed in Table I.

The powdered glass tests were carried out with the grain size fraction of 0.315 to 0.5 mm prepared according to the Czechoslovak standard [12]. The compact

Table I
Composition of glasses FLOAT and G which were
used in the experiments (in wt. %)

Oxide	Elass	
	FLOAT	G
SiO_2	72.54	41.50
B_2O_3	—	10.70
Al_2O_3	0.75	1.35
Fe_2O_3	0.05	—
CaO	5.25	3.20
MgO	3.79	2.30
Na_2O	13.89	9.80
K_2O	0.41	8.50
Cr_2O_3	—	6.30
TiO_2	—	13.40
Li_2O	—	2.85

samples were prepared from the FLOAT glass only; the samples were cut into specimens of suitable sizes and then ground on disks with a diamond abrasive of various fineness (disks with 150 μm and 50 μm abrasive were used in the tests concerned with the comparison of compact and powdered samples). The individual specimens for the tests assessing the effect of surface finish were prepared as follows:

1. grinding on disk 150 μm
2. specimen ground as ad 1. additionally reground on disk 50 μm
3. specimen treated as ad 2. additionally ground on disk 20 μm
4. specimen treated as ad 3. additionally polished to optical gloss by means of CeO_2 .

The chemical durability tests employed

Two types of tests were used, namely a static and a dynamic one. Both tests proceeded at 95 °C, distilled water being employed as the eluent. A separate bottle with the sample was used for each experimental point and the volume of distilled water was always 70 ml. The dynamic tests were carried out in Soxhlet's extractor. The volume of distilled water in the boiling flask heated in a heating nest was 200 ml. The capacity of the extraction vessel up to the overflow amounted to 70 ml, so that the volume of the eluent changed during each cycle from the minimum value of the residual liquid following the draining of the vessel, up to the maximum value of 70 ml (cf. Table III). The eluting vessel was thermally insulated from outside, so that the solution change cycle was shortened to 5 minutes with a minimum temperature fluctuation (± 1 °C). The solution in the boiling flask was always replaced with distilled water and subjected to analysis after a certain period of time.

Analysis of the eluates

In all the tests, the eluate was analyzed for the change in the content of alkalis and SiO_2 and possibly for a change in pH. Silica was determined photometrically according to ČSN [13]. The total alkalinity was determined by titration according to ČSN [12]. The total amount of alkalis was recalculated to the Na_2O content in solution. In addition to this, the alkaline components in solution were also determined by flame photometry. It was found that with the FLOAT glass, the amount of eluted components, apart from Na, was negligible. In the case of glass G, the ratio of the eluted alkaline components $\text{Na}_2\text{O} : \text{K}_2\text{O}$ was about 1 : 0.8. The results of titration were also expressed as Na₂O content to allow the two glasses to be compared.

Evaluation of the experimental data

The values of the concentrations of the eluted components were calculated for the total volume of the eluate and related to the sample surface area according to the equation

$$Q_i = \frac{c_i V}{SA \cdot 100}$$

where Q_i is the amount of eluted oxide i in g m^{-2} , SA is the sample surface area in cm^2 , V is the volume of the eluting solution in ml , c_i is the concentration of component i in the eluate in $\mu\text{g ml}^{-1}$.

In the case of the time dependence for the Soxhlet extractor tests, the amounts were always added up from the beginning of the experiment. The surface area (SA) was estimated for the given powder fraction on the basis of data from the literature [10]. The value of 110 cm^2 per gram of powdered glass was used for the calculations.

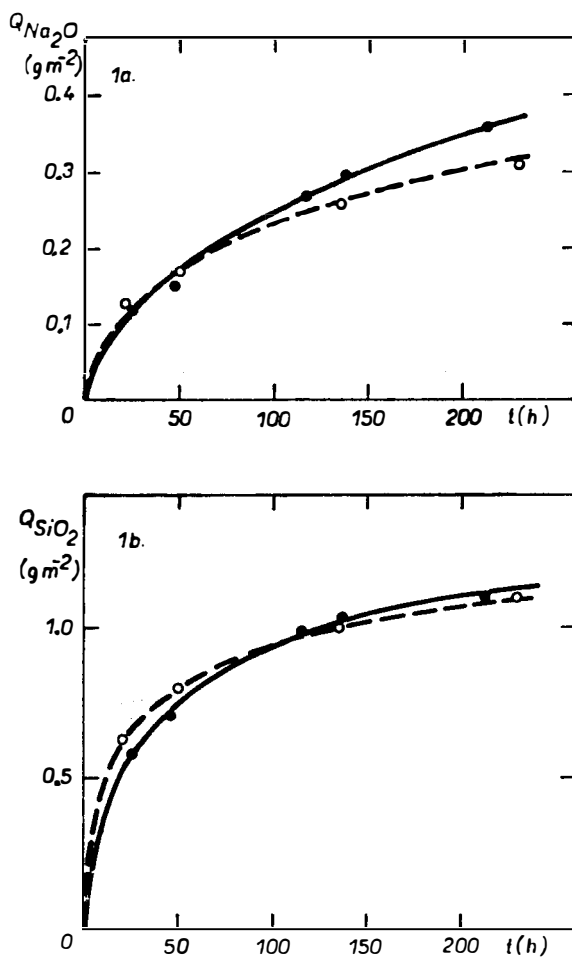


Fig. 1. Comparison of the time dependence for the elution of compact and powdered samples of FLOAT glass under static conditions; a — Na_2O , b — SiO_2 , $\circ$ — compact sample, $\bullet$ — powdered sample.

RESULTS

Tables II and III list the results of determining the effect of the SA/V factor on chemical durability of glasses as established by the static and the dynamic tests.

The time dependence of elution of compact and powdered samples of the FLOAT glass measured by both tests is plotted in Figs. 1 and 2. The weight of the powdered samples and the dimensions of the compact ones were chosen so as to achieve a comparable surface area and thus also the SA/V ratio.

The results of chemical durability of FLOAT glass specimens with various surface finishes, obtained by both methods, are given in Table IV.

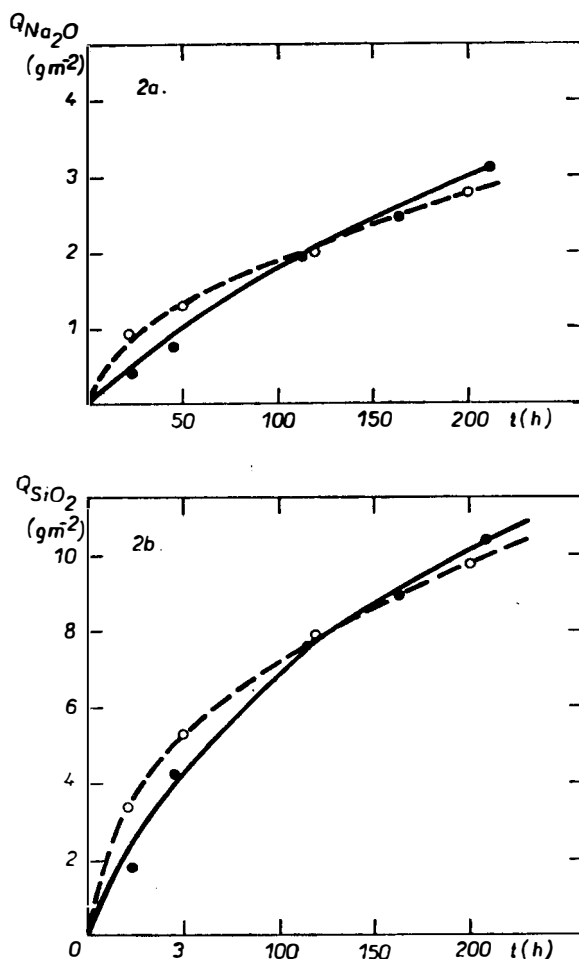


Fig. 2. Comparison of the time dependence for the elution of compact and powdered samples of FLOAT glass in Soxhlet's extractor; a — Na₂O, b — SiO₂, ○ — compact sample, ● — powdered sample.

Table II

Effect of the SA/V ratio on the amount of components eluted under static conditions (powdered samples, 95 °C, duration of test 90 hours)

Sample weight g	Volume of solution ml	FLOAT			G		
		pH	$\frac{\text{Na}_2\text{O}}{\text{g m}^{-2}}$	$\frac{\text{SiO}_2}{\text{g m}^{-2}}$	pH	$\frac{\text{Na}_2\text{O}}{\text{g m}^{-2}}$	$\frac{\text{SiO}_2}{\text{g m}^{-2}}$
0.10	70	8.1	0.15	0.36	9.0	1.02	3.04
1.00	70	9.0	0.24	0.80	9.3	0.64	2.22
2.00	70	9.2	0.30	0.93	9.4	0.45	1.08
5.00	70	9.2	0.45	1.21	9.7	0.30	0.84
10.00	70	9.4	0.65	2.51	—	—	—

Table III

Effect of the SA/V ratio on the amount of eluted components for the Soxhlet extractor test (powdered samples, 95 °C, test duration 90 hours)

Weight of sample g	Volume of solution ml	FLOAT		G	
		$\frac{\text{Na}_2\text{O}}{\text{g m}^{-2}}$	$\frac{\text{SiO}_2}{\text{g m}^{-2}}$	$\frac{\text{Na}_2\text{O}}{\text{g m}^{-2}}$	$\frac{\text{SiO}_2}{\text{g m}^{-2}}$
0.10	max. 70	0.38	1.46	9.18	34.16
1.00	max. 70	1.49	5.81	8.08	27.19
2.00	max. 70	1.82	7.09	5.95	12.15

Table IV

Effect of various surface finishes of compact samples on the amount of eluted components (FLOAT glass, 95 °C, test duration 50 hours, sample surface area 30 cm²)

Surface finish (abrasive grade)	Soxhlet extractor		Static test	
	$\frac{\text{Na}_2\text{O}}{\text{g m}^{-2}}$	$\frac{\text{SiO}_2}{\text{g m}^{-2}}$	$\frac{\text{Na}_2\text{O}}{\text{g m}^{-2}}$	$\frac{\text{SiO}_2}{\text{g m}^{-2}}$
150 μm	2.2	9.45	0.45	1.58
50 μm	1.28	5.28	0.29	0.88
20 μm	1.23	5.10	0.28	0.79
CeO ₂	1.10	4.82	0.22	0.66

DISCUSSION

The effects of the following three factors on the results of chemical durability tests on glass were investigated: the ratio of the sample surface area to the volume of the eluting solution (SA/V), the form of the sample (powdered and compact), the state of surface of the compact samples (degree of polishing).

The SA/V ratio

The effect of SA/V was established under static and dynamic conditions (Soxhlet's extractor) for two different glasses. Both tests showed that the direction of the effect depends on glass composition. With the comparatively simple FLOAT glass, an increase in the SA/V ratio brings about an increase in the amount of the components (Na_2O , SiO_2) passing into solution. The more complex G glass shows the opposite effect of the factor, as the amount of dissolved components decreases with increasing SA/V. However, the dependence is not linear in either of the cases. In interpreting the results, one has to take into account all phenomena that can affect the process. The amount of corrosion products found in the solution at a certain time is affected by time-dependent quantities which are moreover mutually dependent. For example, the pH value at the given conditions of elution (at a given value of SA/V and temperature) will rise to a certain value during a certain time and then remain essentially unchanged even when the test proceeds for a very long time (14–17). The value is specific for a given glass and the results obtained so far indicate that it is always lower than 10.5 even with glasses of low chemical durability (with the exception of two-component ones). There are also the significant effects of the concentration of corrosion products in the solution, particularly SiO_2 , PbO , Al_2O_3 and other components which are responsible for various reaction mechanisms.

SiO_2 can cause the solubility to be reduced: if the solution is saturated with dissolved SiO_2 (the value of saturated concentration depending of course on pH), the corrosion is significantly slowed down or stopped completely. Polyvalent ions in solution may precipitate the other corrosion products (including SiO_2). The precipitates can deposit directly on the corroded surface of the original sample in the form of a secondary layer which may suppress further leaching. On the other hand, a decrease of the concentration of components dissolved in the solution (resulting from their precipitation on the glass surface) may speed up the corrosion process. An explanation of the opposite effect of the SA/V factor on glasses of different composition should obviously be sought in the diverse effects of such factors as pH, the presence of leaching products in the solution, formation of secondary layers on the surface of glass, possible spalling of the partially corroded layers, etc. It is therefore apparent that the effects of the individual factors should not be assessed separately and that their interactions should be considered. The more complex the glass, the more complex conditions arise in the glass-solution system and the more difficult their interpretation.

The effect of the sample form

The time dependences for FLOAT glass in Figs. 1 and 2 indicate that under both static and dynamic conditions the corrosion proceeds at a somewhat higher rate with compact samples during shorter periods of time, the opposite applying for powdered samples and longer time periods (both cases expressed per unit surface area). However, the differences are not significant, so that it can be concluded that the form of the samples is not decisive with respect to corrosion tests. In view of the difficulties involved in the use of the powdered samples (precise surface area determination the presence of fine particles, possible formation of co-called corrosion cells), compact samples are often recommended for long-term tests. In the study of the effects of some factors, however, powdered samples are

preferred as they allow a wide range of SA/V ratios to be obtained. The advantage of powdered samples lies in their simple preparation which does not require any special technical equipment. They have the additional advantage of providing a fresh fracture surface for the tests.

The effect of glass surface finish

The comparison of four types of FLOAT glass specimens with surfaces treated in different ways showed the chemical durability to depend on the type of surface finish. The optically polished specimen yields, after 50 hours of leaching under both static and dynamic conditions at 95 °C, just one half of the leaching losses compared to that polished on the 150 µm disk only. The differences between the specimens ground on 20 µm and 50 µm disks are no longer so distinct. As the creation of the optical gloss is a quite demanding operation, final finishing with the 50 µm or 20 µm abrasive should be satisfactory for routine testing.

CONCLUSION

The following conclusions can be formulated on the basis of the results obtained.

The effect of the ratio of the sample surface area to the volume of the leaching solution on the amount of glass component passed into the eluate depends on the particular type of glass. With the complex G glass, an increase in this ratio leads to lowering the amount of the amount of components passed into the solution, and the opposite applies to the simple FLOAT glass.

The form of the samples does not substantially affect the results of the durability tests, so that the choice between a powdered or a compact sample is given rather by the nature and purpose of the test.

The quality of the glass surface is important for chemical durability testing; however, for routine tests it is not necessary to polish the specimens to optical gloss as grinding with fine abrasives (20 to 50 µm) should be satisfactory. In this case, the difference in the amount of eluted components compared to optically polished surface is not significant.

The FLOAT glass has proved suitable for the study of the factors given above. The glass can be readily made into both powdered and compact specimens and the concentrations of the eluted components can be easily determined by the analytical methods employed.

In testing the chemical durability of special glasses (such as those for the fixation of radioactive waste) it is convenient to measure a standard glass in a parallel test to allow the results to be compared. If such a glass has not been directly specified, it is possible to use a standard commercial glass with a composition that is virtually identical in many parts of the world, such as the FLOAT glass.

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FAKTORY OVLIVŇUJÍCÍ VÝSLEDKY TESTŮ CHEMICKÉ ODOLNOSTI

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Na dvou sklech (tabulové sklo FLOAT a experimentální sklo pro fixaci radioaktivních odpadů označené „G“) byl sledován vliv tří faktorů, které mohou ovlivnit výsledky testů chemické odolnosti proti vodě. Byly použity dva typy testů — statický a dynamický test na Soxhletově extraktoru; v obou případech probíhalo loužení při teplotě 95 °C. Byla stanovována celková alkalita výluhů (která byla přepočtena na obsah Na₂O) a koncentrace SiO₂, u statických testů hodnota pH výluhů.

Byl sledován vliv:

- a) poměru velikosti povrchu vzorku k objemu loužičního roztoku — SA/V, na drťových vzorcích;
- b) formy skla — porovnání drťových a celistvých vzorků;
- c) různé povrchové úpravy vzorků na množství složek vyloužených do roztoku.

Bylo zjištěno, že vliv poměru SA/V na množství korozních produktů přešlých do roztoku závisí na složení skla. U složitějšího skla „G“ vztůst tohoto poměru snižuje množství složek přešlých do roztoku u jednoduchého skla FLOAT je tomu naopak (tab. II. a III).

Forma vzorku výsledky testů podstatně neovlivňuje (obr. 1 a 2).

Kvalita povrchu vzorku ovlivňuje množství korozních produktů přešlých do roztoku, čím jemnějším brusivem je povrch opracován, tím menší množství látek přechází do roztoku (tabulka IV). Při použití celistvých vzorků je tedy důležité, aby všechny vzorky měly stejnou povrchovou úpravu.

Při studiu chemické odolnosti speciálních materiálů (např. skel pro fixaci radioaktivních odpadů) je účelné použít pro porovnání výsledků standardní sklo. Pokud není takové sklo speciálně určeno, je možné použít i vhodné komerční sklo s celosvětově ustáleným složením např. sklo typu FLOAT.

Obr. 1. Porovnání časové závislosti vyluhování celistvého a drťového vzorku skla FLOAT za statických podmínek; a) Na₂O, b) SiO₂ ○ — celistvý vzorek, ● — drťový vzorek.

Obr. 2. Porovnání časové závislosti vyluhování celistvého a drťového vzorku skla FLOAT na Soxhletově extraktoru; a) Na₂O, b) SiO₂. ○ — celistvý vzorek, ● — drťový vzorek.

ФАКТОРЫ ОКАЗЫВАЮЩИЕ ВЛИЯНИЕ НА РЕЗУЛЬТАТЫ ТЕСТОВ ХИМИЧЕСКОЙ СТОЙКОСТИ

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На двух видах стекла (листовое стекло FLOAT и экспериментальное стекло, предназначенное для фиксации радиоактивных отходов, обозначенное через „G“) исследовали влияние трех факторов, которые могут оказывать влияние на результаты тестов химической водостойкости. Применялись два типа тестов — статический и динамический тест на экстракторе Сокслета, в обоих случаях выщелачивание протекало при температуре 95 °C. Устанавливалась общая щелочность экстрактов (пересчитанная на содержание Na₂O) и концентрация SiO₂, у статических тестов величина pH экстрактов. Исследовали влияние: а) отношения размера поверхности образца к объему выщелачивающего раствора — SA/V на дробленых образцах, б) формы стекла — сопоставление дробленых и компактных образцов, в) разной поверхностной обработки на количество компонентов, выщелачиваемых в раствор.

Было установлено, что влияние отношения SA/V на количество коррозионных продуктов, перешедших в раствор, зависит от состава стекла. У сложного стекла „G“ рост отношения понижает количество компонентов, перешедших в раствор, у простого стекла FLOAT этому наоборот (табл. II и III).

Форма образца на результаты тестов не оказывает существенное влияние (рис. 1 и 2). Качество поверхности образца оказывает влияние на количество коррозионных продуктов, перешедших в раствор: чем более тонким абразивом обрабатывается поверхность, тем меньшее количество веществ переходит в раствор (табл. IV). Следовательно, при применении компактных образцов важно, чтобы все образцы выделялись одинаковой обработкой.

При исследовании химической стойкости специальных материалов (напр. стекло, предназначенных для фиксации радиоактивных отходов) целесообразно применять для сопоставления результатов стандартное стекло. В крайнем случае можно применять даже пригодное продажное стекло с установленным составом во всем мире, напр. стекло мина FLOAT.

Рис. 1. Сопоставление временной зависимости выщелачивания компактного и дробленого образца стекла FLOAT при статических условиях: а) Na₂O, б) SiO₂, о — компактный образец, о — дробленый образец.

Рис. 2. Сопоставление временной зависимости компактного и дробленого образца стекла FLOAT на экстракторе Сокслета: а) Na₂O, б) SiO₂, о — компактный образец, • — дробленый образец.

Zajímavosti

NOVOU METODU VÝROBY KERAMICKÝCH KOMPOZITNÍCH MATERIÁLŮ vyvinula firma Lanxide Corp. Materiál používaný jako plnivo je vázán na keramickou matrix připravenou řízenou oxidací roztaveného kovu. Během tvoření matrix reaguje roztavený kov s plynným oxidantem. Výsledkem procesu je kompozitní materiál keramika—kov. Mikrostruktura a vlastnosti matrix závisí na dopující látce, teplotě a době trvání reakce. Připraveny již byly keramické materiály soustavy Al₂O₃—Al, AlN—Al, TiN—Ti a ZrN—Zr. Proces tvorby kompozitního materiálu je charakterizován jako řízený růst matrix kolem materiálu používaného jako plnivo, kterým mohou být vlákna, whiskery nebo jinak tvarovaný materiál. Jedinou podmínkou je kompatibilitnost plniva jak s oxidantem, tak s roztaveným kovem. Např. pro soustavu Al₂O₃—Al se jako plniva používá dopovaná slitina Al. Jako dopant může být použit Mg, Zn, Si apod. Růst matrix je pozorován při 700 až 1350 °C. Vlastnosti konečného materiálu je možné řídit na základě složení slitiny, teploty procesu, atmosféry a výběru plniva.

Fryntová