

NATURAL CORROSION OF OLD POTASH GLASS COLOURED WITH URANIUM COMPOUNDS

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Submitted January 21, 2002; accepted April 10, 2002

Keywords: Uranium glass, Glass corrosion, Uranium migration, Soil

The study is concerned with the corrosion of ultrapotash uranium glasses from the Rejštejn - Klášterský Mlýn locality in Šumava Mountains, Czech Republic. The glass samples were taken from the dump of a former glassworks. They stemmed from the year 1925 ± 5 years (the dating was done historically). The section also comprises soil, coal slag and alluvial sediments from the Otava river. Planar beta activity was measured in the section: the lowest one of 0.34 kBq/m² in soil and the highest of 3.25 kBq/m² in the horizon of the U-glasses. Four types of U-glasses were distinguished: yellow, green alabaster, green and green-blue. They contain 0.088 to 0.33 wt.% U and 8 to 14 wt.% K. The pH (aqueous extract) varies from 5.11 in coal slag to 7.70 in the glass layers. The total content of U in the < 2 mm grain size fraction in the section was in the range from 4.8 ppm in the alluvial deposit up to 56.5 ppm in the glass layer. The content of U leachable by 1M CH₃COONa ranges from 7 ppb in soil to 65 ppb in the glass horizon. Uranium migrates into the alluvium in the underlying bed of the dump (content of up to 58.9 ppb of leachable U). Under the given conditions in alluvium one can suppose the immobilisation of U, whereas As and Pb are transported further. The green alabaster U-glass at the surface and along cracks has become corroded to a depth of 10 to 400 mm. Contraction fissures in the corroded layer are coated with precipitated calcite. The corrosion involves leaching of alkalis (up to 14 wt.% of glass) from the glass, redistribution of uranium and sorption of lead on the surface. IR spectroscopy prove the hydration of the glass, which is the result of K⁺ ↔ H₃O⁺ exchange.

INTRODUCTION

The results of research of natural corrosion of glass by water can be utilized in assessing the stability of vitrified radioactive waste [5]. Uranium in glass may be regarded as a chemical equivalent of some actinides and transuranium elements that are contained in nuclear waste.

It is assumed that the manufacture of uranium glasses in the Šumava and Jizerské Mountains (the main glassmaking regions in Bohemia in the 19th century) was started in about 1830.

The uranium colouring pigments were made from Joachimstal pitchblende, which was at first taken from dumps left over from extraction of silver ores, and later on extracted for this purpose. The following uranium compounds were used:

uranium light yellow colour (most frequently employed)	Na ₂ U ₂ O ₇ .nH ₂ O
orange-yellow colour	Na ₂ U ₂ O ₇
uranium yellow-red colour	K ₂ U ₂ O ₇
ammonia yellow	(NH ₄) ₂ U ₂ O ₇
uranium oxide	U ₃ O ₈

The new colouring agents had become popular and by 1850 "uranium" was used by all glassworks manufacturing coloured glass. The production of U-glasses was terminated with the end of the Second World War.

The Klášterský Mlýn glassworks (the firm Loetz), whose dump and scrap glasses are the subject of this study, was operated from 1836 to 1947. Among other types, yellow and green glass coloured with uranium compounds was probably manufactured there during the entire period mentioned. After 1851 also turquoise glass, or green opaline glass coloured with uranium compounds was produced (cf. table 1).

The corrosion was studied on green alabaster glass (type 2 - cf. table 1) as this was found to be the most sensitive one with respect to corrosion.

MATERIALS AND METHODS

Field research

The Rejštejn - Klášterský Mlýn locality is situated at the bank of the Otava river. The glassworks dump has an area of approximately 3000 m². It lies on alluvial se-

diments at a distance of about 5 m from the river. The horizon containing glasses, at the point of study about 1.3 m thick, is covered with a layer of soil 30 cm thick. Vegetation has grown on the surface of the dump. The glasses are in a mixture of moist soil and coal slag, but in places the scrap glass constitutes almost 100% of the material. The mean share of uranium glasses was estimated at roughly 5% of all glasses.

The basic lithological components of the glassworks dump are the following: glass scrap, loamy soil, sandy soil, coal slag and alluvial sediments of the Otava river - cf. figure 2.

About 15 kg of samples of uranium glasses and 19 samples of the soil were taken from the vertical section through the dump (1.9 m in height).

Table 1. Uranium glass types found at Rejštejn - Klášterský Mlýn.

classical yellow fluorescent glass	(type 1A)
light yellow glass	(type 1B)
deep green mat alabaster glass	(type 2)
green glass	(type 3)
green-blue turquoise glass	(type 4)

The uranium glasses were identified by measuring planar beta activity of radiation and by fluorescence under long-wave UV radiation. The beta activity of radiation with an energy exceeding 300 keV was determined in the field measurements as the difference between gamma + beta and gamma activities. For this purpose a portable instrument was designed and calibrated for beta radiation by means of the $\text{UO}_{2.22}$ planar standard. The share of uranium glasses in the individual horizons was estimated visually. The results are shown in figure 2. Several types of uranium glasses were identified (table 1).

Dating of the glass

The age of the glass was determined historically on the basis of the history of manufacture and according to the decorative characteristics of the fragments. Decorative glass has always been strongly dependent on the fashion of its time. As the glass objects made by the firm Loetz have become a part of many historical collections, it was possible to establish their age by comparison with the preserved objects of art.

The glasses in question stem from the period of the so-called second art nouveau from around 1925 ± 5 years when the firm Loetz was copying its famous art nouveau products. The glass coloured with uranium was used among others also as the base glass for various coloured decorative techniques (flashed glass, glass with applied threads, mosaic glass, etc.).

In the given case this glass dating method is much more precise than the physical and radiometric methods.

Gamma spectrometric measurement of U, Ra, K in soil (grain size fraction of minus 2 mm) and in the glasses

The measurements were carried out at the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague.

The soil samples from the Klášterský Mlýn locality were analysed on the laboratory gamma spectrometer with NaI(Tl) scintillation crystal 75×75 mm in size (standard dimensions) using the Canberra Series 10 analyser. The preparation of soil samples for analysis consisted of screening through 2 mm sieve and drying in air. The measurement proper took place in Marinelli's beakers (3π geometry) of 500 ml capacity. Uranium in radioactive disequilibrium (U (ppm)) was measured in the region of interest of isotope ^{234}Th with an energy of 92.4 keV, uranium in radioactive equilibrium (Ra (ppm eU)) in the region of interest of isotope ^{214}Pb with an energy of 352 keV. The total contents of uranium in radioactive disequilibrium, radium (uranium in radioactive equilibrium) and potassium were determined (table 2). The content of uranium in the minus 2 mm mesh fraction is important, because if the uranium in radioactive disequilibrium was released from the glasses into the environment, it was exactly from this fraction (from the fine grains and microscopic rubbed-off particles) of the scrap glass.

The glasses from the Klášterský Mlýn locality were analysed by the same method as the soil samples. The total content of uranium in radioactive disequilibrium, radium and potassium was determined (table 3).

Determination of pH of soil extracts

The pH of the environment is a significant factor describing in a certain way the conditions to which the glasses were exposed. The pH of the soil was determined in laboratory on 19 soil samples from the Klášterský Mlýn locality (figure 2).

The pH of the soil was determined on extracts from the minus 2 mm mesh fraction with distilled water and 1 M KCl.

Analysis of U, Pb, As in soil extracts by the ICP-MS method

The measurements were carried out at the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University Prague.

The soil extracts were prepared from the minus 2 mm mesh fraction of the material contained in the glassworks dump. 1 M CH_3COONa of pH 5.0 was used as extraction agent. The amount of soil 5 g in weight was extracted in 40 ml of the acetate buffer. The mixture of soil and buffer was shaken for 2 hours, and then

the soil suspension in the buffer was equilibrated for 24 hours. The soil was separated by centrifugation, washed with 20 ml of distilled water and centrifugated again. The water was added to the original extract.

Uranium, lead and arsenic in the extract were determined by the ICP-MS method.

Optical and electron microscopy

For observation under the optical microscope as well as for the EM-EDS and WDS methods, polished sections of the glasses were prepared, altogether 29 specimens (figures 4 and 5). Some of the specimens were impregnated with resin.

The EM-EDS measurements were carried out at the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University Prague.

The method was employed for the purpose of studying the morphology and thickness of the corroded layer on green mat alabaster glass (type 2) and for preparing a distribution map of the main elements, cf. figures 6, 7, 8, 9.

Chemical analyses of the glass by the WDS electron microprobe method

The measurements were carried out at the Řež Nuclear Research Institute.

Quantitatively analysed were all elements present in amounts exceeding the detection limits of the method, namely Si, O, K, Na, Ca, Mg, Al, P, S, Cu, Fe, Ti and U.

The difference in concentrations between the corroded surface layer and the compact glass was determined by a line of point analyses from the surface towards the unaffected centre of the sample. Figure 10 shows the analysed points 1 through 4. Points 1, 2 and 3 were in the corroded layer, which in the given place was about 400 µm thick. Point 4 represents a quantitative analysis of the unaffected glass.

Determination of U concentration in the glass by the LA ICP-MS method

The measurements were carried out at the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University Prague.

The U content was determined in a sample of green alabaster glass of type 2. The line segment analysis by laser ablation (LA ICP-MS) was employed. Standard reference materials SRM NIST 610 and NIST 612 were used in the calibration.

The measurements were carried out on the PQ 3 apparatus made by VG Elemental, with the use of the ²³⁵U isotope.

X-ray diffraction study of the glasses

The measurements were carried out at the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University Prague.

The X-ray diffraction was used to distinguish the structural (and possibly chemical) changes occurring in the course of glass corrosion. The powdered specimens were separated from one of the most extensively corroded pieces of green alabaster glass of type 2.

The glasses were studied by the method of powder diffraction on the DRON 2.1 diffractograph. The data were obtained in the step-scanning mode at a step of 0.05° 2θ and a counting period of 5 seconds; the sample carrier was of diffraction-free Si.

IR spectroscopy

The measurements were carried out at the Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University Prague.

IR reflectance spectra of two phases, the non-corroded glass and the corroded one, were measured on the FT-IR spectrometer made by Nicolet Instrument Corporation. The powdered specimens were separated from one of the most extensively corroded pieces of green alabaster glass of type 2. The reflectance spectra were carried out from the powdered samples mixed with KBr. Background signal was collected on poor KBr powder.

RESULTS

The results of gamma spectrometric measurement of U, Ra and K in soil (minus 2 mm fraction) and in the glasses

The content of uranium in radioactive disequilibrium, established by the laboratory gamma spectrometer in the minus 2 mm fraction of the individual soil horizons is in a good agreement with the field measurement of planar beta activity, as well as with the content of glass (both uranium and non-uranium) in the material. The U concentration varies over the range from 4.8 ppm in the deepest part of the section up to 56.5 ppm measured in the horizon containing the glasses (figure 2, table 2).

As the glass colouring compound Na₂U₂O₇ does not contain any radium, the anthropogeneous uranium can only be revealed according to its radioactive disequilibrium. In the soil samples (< 2 mm) there is much less radium than would correspond to radioactive equilibrium. This can be described by the coefficient of radioactive equilibrium C_{re} :

$$C_{re} = \frac{Ra \text{ (ppm eU)}}{U \text{ (ppm)}} \cdot 100 \%$$

The values of the coefficient of radioactive equilibrium are given in table 2.

As a rule, natural environments exhibit high Cre (almost 100%). In the profile, the first sample and the last three ones were close to radioactive equilibrium. The first sample comprised humus soil, while the last three horizons were sandy alluvial sediments of the Otava river.

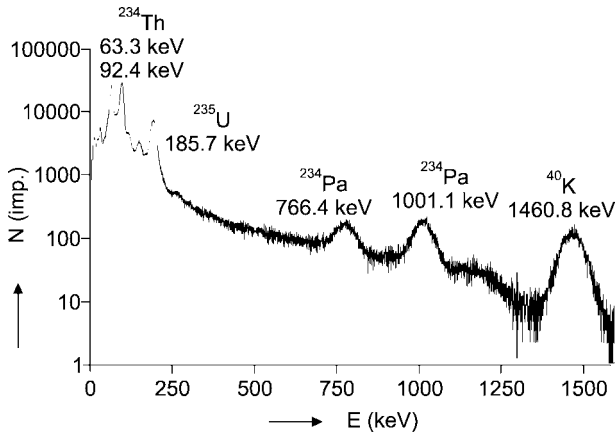


Figure 1. The gamma spectrum of type 2 green alabaster glass. Marked are peaks of ²³⁴Th and ²³⁴Pa, which are short-lived products of ²³⁸U transformation. The peak of ²¹⁴Pb, a conversion product of radium with an energy of 352 keV, is absent because the glass contains less than 0.5 (ppm eU) ²²⁶Ra.

The K content in the profile ranges from 0.9 wt.% in the surface humus layer to 3.9 wt.% in the glass scrap containing horizon. The content of K in the soil (minus 2 mm fraction) is correlated in the top part of the section with the content of uranium in radioactive disequilibrium and with the content of glass (the K content in glass varies around 8 wt.%). However, the expected increase in K concentration did not arise in the lower, thinner horizon of glasses, obviously as a result of the higher K content in the sand and in the alluvium (approx. 2.5 wt.%).

The type of glass designated 1B (light yellow) contained 0.29 wt.% of uranium in radioactive disequilibrium. The green alabaster glass (type 2) exhibited the highest concentration of U in radioactive disequilibrium, namely 0.33 wt.%. The green glass of type 3 was found to contain 0.088 wt.% of uranium in radioactive disequilibrium, that is significantly less than in types 1 and 2.

The uranium in radioactive disequilibrium is not in equilibrium with some of its decay products (radium) and its content gives evidence of the amount of the colouring compound, probably Na₂U₂O₇.nH₂O, that had been added to the glass. On the other hand, uranium in radioactive equilibrium, expressed as Ra (ppm eU), gives evidence of the uranium content in the primary components of the batch. The uranium added to the glass as colouring compound represents about 99.9% of total uranium content in the glass. The results are summarized in table 3 and figure 1.

Table 2. Laboratory gamma spectrometry of soil and content of U in soil extract. The theoretical share (wt.%) of U glasses in the minus 2 mm fraction was calculated from the content of uranium in radioactive disequilibrium for the mean U concentration in the glass (0.29 wt.%). The share of free U (%) in the 1M CH₃COONa extract was calculated from the U content in soil and in the soil extract.

depth (cm)	U glasses (wt.%)	K (wt.%)	soil, < 2 mm fraction			extract	extract/soil
			U (ppm)	Ra (ppm eU)	C _{re} (%)	U (ppb)	free U/U (%)
0-10	0.0	0.9	9.4	9.3	98.6	7.8	0.8
10-20	0.1	0.9	12.7	9.2	72.8	25.5	2.0
20-30	0.9	2.1	37.1	9.6	25.9	39.2	1.1
30-40	1.8	3.9	56.5	4.8	8.5	65.5	1.2
40-50	1.5	3.4	49.3	4.4	8.9	50.6	1.0
50-60	1.3	3.3	43.8	4.7	10.8	55.5	1.3
60-70	1.4	3.5	45.3	4.4	9.6	57.2	1.3
70-80	1.5	3.3	47.2	4.5	9.6	40.0	0.8
80-90	0.5	2.1	19.6	4.7	23.8	24.1	1.2
90-100	0.3	1.4	13.3	4.8	36.2	18.4	1.4
100-110	0.3	1.7	14.1	4.3	30.3	36.3	2.6
110-120	0.3	2.0	12.0	4.2	35.0	21.3	1.8
120-130	0.6	2.2	22.6	4.8	21.4	39.9	1.8
130-140	1.5	1.9	46.3	3.2	7.0	38.9	0.8
140-150	1.6	2.2	50.0	3.7	7.4	53.7	1.1
150-160	0.9	2.1	31.5	3.8	12.0	47.2	1.5
160-170	0.1	2.5	6.2	3.6	58.3	50.9	8.2
170-180	0.1	2.5	5.8	3.4	59.2	54.6	9.4
180-190	0.1	2.7	4.8	3.2	66.7	58.9	12.3

Measurements of the individual types of uranium glasses on the gamma spectrometer showed that the glasses in the locality have a mean potassium content of about 8 wt.%. The exception was the most extensively corroded green alabaster glass of type 2 which contained 14 wt.% K.

Table 3. Results of gamma spectrometric measurement of different types of glass.

	type 1B light yellow	type 2 green alabaster	type 3 green	type 4 blue
U (ppm)	2858	3300	885	974
Ra (ppm eU)	7.8	2.8	1.0	3.2
K (wt.%)	8.1	14.2	7.5	8.2

pH of soil extracts

The mean pH 6.69 for aqueous extract and pH 6.03 for 1M KCl extract (figure 2) does not deviate much from values usual for soils, but the changes in pH along the section are interesting. A comparison of the lithological section with pH in the individual horizons allows us to conclude that coal slag is the main lithological component responsible for acidification. In contrast to this, horizons containing a large share of glass or composed of sandy loam were more alkaline (figure 2).

The results of determination of U, Pb and As in soil extracts by the ICP-MS method

The concentration of U extractable with 1 M CH₃COONa in samples of dump material ranges from 7 ppb in the surface humus layer up to 65 ppb, which is

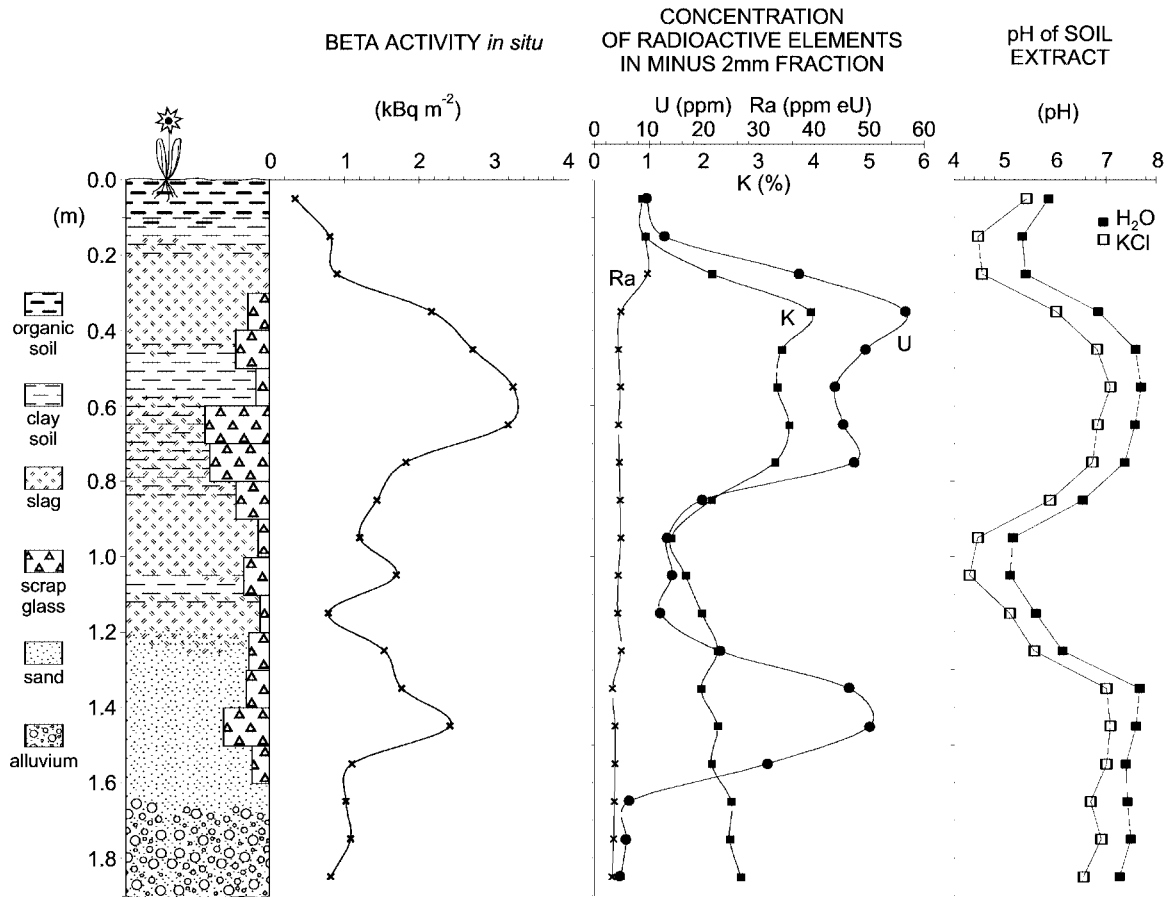


Figure 2. Lithological section of the glassworks dump at Klášterský Mlýn. The triangular hatch represents the share of glass (both uranium-free and uranium one) in the total lithology. The left-hand diagram: Field-measured beta activity in the section. Middle diagram: laboratory gamma spectrometry of the minus 2 mm fraction of the dump materials. The content of U, Ra and K was determined in the samples. When the sample from a certain depth is in radioactive equilibrium, the points on curves for U (ppm) and Ra (ppm eU) are identical. The higher the content of U (ppm) compared to Ra (ppm eU), the greater the radioactive disequilibrium (in the minus 2 mm fraction) at the given depth. Refer also to C_{re} , the coefficient of radioactive equilibrium, in the chapter Results of gamma spectroscopic measurement of U, Ra and K in the soil (minus 2 mm fraction) and in the glasses.

the maximum value in the glass scrap containing horizon (table 2). The second highest value (58 ppb) was measured in the last sample composed of alluvial sediments of the Otava river. In the first two thirds of the section through the dump the U content in soil extracts corresponds to the total uranium concentrations determined by gamma spectrometry in the same samples - cf. figures 3 and 2.

The situation is different in the bottom part of the section. The higher concentration of extractable uranium in the alluvium where the content of total uranium is low, is indicative of migration of U from the glass horizon into the sub-base. The extractable U comprised at least 0.8 ‰ of total uranium in the sample of surface humus soil, and at the most 12 ‰ in the last bottom sample of the alluvium (table 2, figure 3).

The concentrations of extractable Pb in the samples range from 0.2 ppm to 32 ppm. The concentration of extractable As in the samples was in the range of 0.1 ppm to 3.8 ppm. As the total concentration of Pb and As in the dump material is unknown (in contrast to that of U) it is impossible to assess what share of total Pb or As is extractable with 1 M CH₃COONa from the soil. However, the concentration curves of the two elements copy the total content of glasses in the individual horizons of the section. From this it may be considered that the free As and Pb also stem from the glasses. Arsenic used to be employed for refining glass and some highly refractive glasses contain up to 20 wt.% PbO. Unlike extractable uranium, however, neither As nor Pb show elevated concentrations in the bottom part of the section, that is in the Otava alluvium where the content of scrap glasses is extremely low. *Eh-pH* conditions in alluvium cause the immobilisation of U in this layer, whereas As and Pb are transported further (figure 3).

The results of study by optical and electron microscopy

Study of the individual glasses under the optical microscope revealed a corroded surface layer up to 400 µm in thickness on the green mat alabaster glass. The glass also contained larger amounts of seed than the other types of glass. According to the technological specifications of the time, the mat alabaster colour was achieved by cooling the glass and reheating it in a certain stage of manufacture. The corroded surface exhibited optical properties different from those of the intact glass. Under open nicols the corroded glass is accentuated by a mild defocusing of the microscope which reveals Becke's lines whose progression shows that the corroded layer has a lower refractive index than the intact glass.

Under the electron microscope the corroded layer shows a microporous morphology. The individual cavities are 5 to 40 µm in size. The corroded layer has such a character throughout its thickness. The active surface area of the glass has thus increased many times compared to that of the glossy intact surface - cf. figure 6.

Between the unaffected glass and the corroded layer there is a sharp transition within the framework of the resolution of EM, free of any distinguishable intermediate zone.

It has been found that the thickness of the corroded layer on the mat green glass varies from 10 to 400 µm, and that the corrosion progresses inside along the cracks, there attaining a thickness of 10 to 70 µm (cf. figure 4).

The image provided by reflected electrons showed that the corroded layer of glass type 2 has a lower mean atomic number than the original glass.

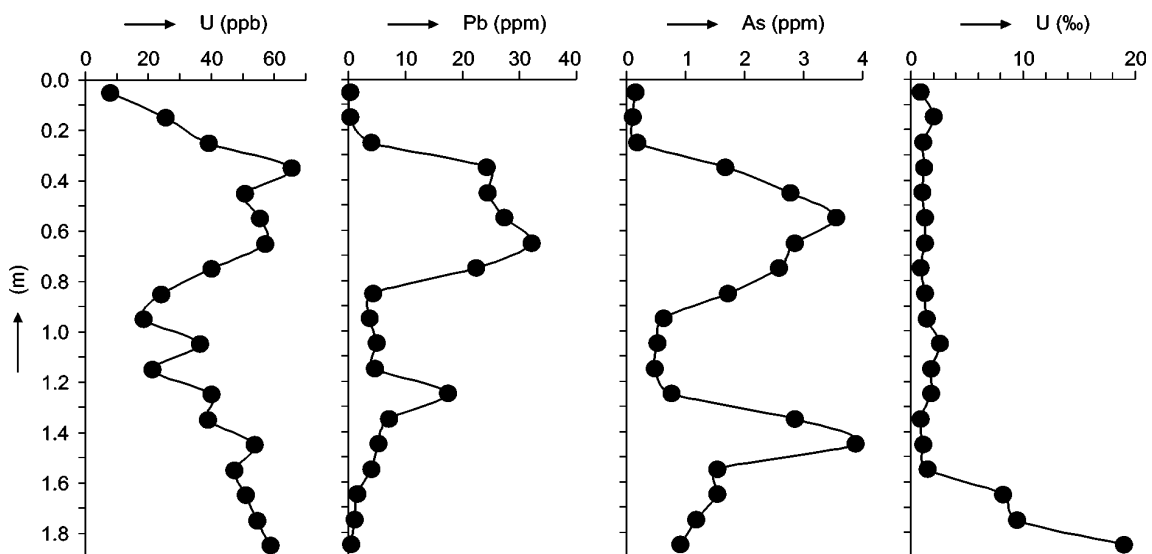


Figure 3. The concentration of leachable U, Pb and As in extracts from the moist soil. The increase in concentration of leachable U in the bottom parts of the dump is due to greater sorption of U compared to that of As and Pb under the given conditions.

The corroded parts of the glass contained contraction cracks. From the main cracks (axial seams) there grew smaller radial fissures. These microstructural phenomena are probably indicative of contraction of glass during corrosion (figure 4).

The distribution maps of elements showed that the corrosion of the mat green glass is mainly due to leaching of potassium (figure 8). Leaching of up to 90 % of K from the surface layer has been proved. A loss of sodium and a relative increase in the content of SiO₂ was also established compared to the original glass. The map of Ca distribution revealed that the calcium phase has precipitated at the cracks of the corroded glass (figure 9). X-ray diffraction (see below) showed that the precipitate was composed of calcite. This finding was in agreement with that of Cooper et al.[2].

The results of chemical analyses by WDS electron microanalysis

The main components of the glass were SiO₂, K₂O, CaO, Na₂O, P₂O₅, CuO, UO₂ (in the sequence of decreasing content). S, Mg, Al, Fe and Ti were represented in the order of tenths of wt.%. The results are summarized in table 4. All the elements including oxygen were determined directly by electron microanalysis (figure 10).

Table 4. WDS analysis of original and corroded glass. Corroded layer - points 1-3. Original glass - point 4. See figure 10.

(wt.%)	Analysis at point 1 ± 2σ		Analysis at point 2 ± 2σ		Analysis at point 3 ± 2σ		Analysis at point 4 ± 2σ	
Na ₂ O	nd	-	nd	-	0.02±0.02		0.75±0.05	
K ₂ O	0.09±0.04		0.31±0.06		0.72±0.08		12.58±0.41	
CaO	4.25±0.32		4.17±0.30		4.38±0.32		3.88±0.31	
MgO	0.03±0.01		0.05±0.01		0.04±0.01		0.04±0.02	
Al ₂ O ₃	0.04±0.02		0.07±0.02		0.05±0.02		0.05±0.02	
SiO ₂	95.13±1.54		93.49±1.51		94.35±1.54		80.99±1.36	
P ₂ O ₅	0.77±0.07		0.83±0.07		0.66±0.06		0.98±0.08	
SO ₃	0.23±0.04		0.31±0.04		0.26±0.04		0.35±0.05	
CuO	0.29±0.12		0.59±0.11		0.62±0.14		0.38±0.16	
FeO	0.05±0.05		nd	-	nd	-	nd	-
TiO ₂	nd	-	0.03±0.02		nd	-	nd	-
UO ₃	0.52±0.08		0.61±0.09		0.50±0.10		0.37±0.10	
	101.39		100.47		101.58		100.37	

nd = not detected

The results of line segment point chemical analyses of the glass by the LA ICP-MS method

Five analyses by the line segment method about 200 μm in length with a crater diameter of 35 μm were carried out (figure 10). The analyses were performed from the surface of the corroded sample towards its centre.

The accuracy of the method was within the limits usual for this type of analyses and the determination error did not exceed 10 %. The results are listed in table 5.

Table 5. Concentrations of heavy elements in fresh and corroded glass. Points 1-3 altered layer. Points 4, 5 fresh glass. See figure 10.

analysis at point #	1	2	3	4	5
U (ppm)	11500	7769	7260	8755	8887
Pb (ppm)	189	79	73	77	78
Th (ppm)	0.20	0.15	0.14	0.16	0.18

The results of X-ray diffraction

Glasses as amorphous substances have a structure arranged over the so-called close distance. This arrangement applies to the closest adjacent atoms, and no periodicity occurs over longer distances. For this reason glasses do not exhibit any sharp diffraction peaks as do crystalline substances. However, the close-distance arrangements appear on diffraction patterns as a strong increase in the background within the range of diffraction angle of 15 to 40 degrees of angle 2 Θ, similar in shape to a minor hump.

The non-corroded glass of type 2 has a symmetrical diffraction peak over the range of 2.3 Å to 5.6 Å with a maximum at 3.2 Å (figure 11).

The diffraction pattern of the corroded layer of type 2 glass is different. The diffraction peak is shifted towards the larger interplanar distances and becomes asymmetrical (figure 11). The diffraction peak lies within the range of 2.3 Å to 6.2 Å and has a maximum at 3.7 Å. A line of 3.018 Å calcite also appears in the pattern. This is in agreement with the findings of Cooper et al. [2].

According to the EDS Ca distribution maps the calcite is present in the form of irregular veinlets in the contraction seams of the corroded layer.

The results of IR spectroscopy

The main purpose of the measurements was to distinguish the changes between the corroded and the intact parts of the glass while detecting the possible presence of O-H groups in the corroded glass.

Three absorption bands of type 2 green alabaster glass, at 1100 to 1050 cm⁻¹, 800 cm⁻¹ and 450 cm⁻¹ respectively (figure 12), are identical with the absorbance peaks of silicate glasses published by Parke [7]. These features are typical of four-coordinated silica (Moenke [6]).

The O-H stretching is present in the region of 3700 to 3400 cm⁻¹, and the water bending vibration is close to 1630 cm⁻¹ [6]. The corroded glass showed two broad absorption bands in near 3600 and in the region of

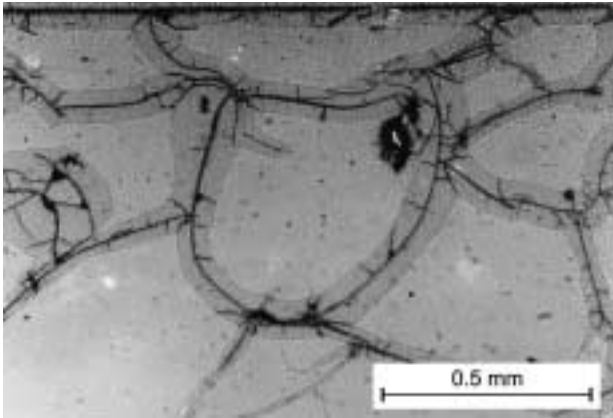


Figure 4. The image of green alabaster glass under the optical microscope, in reflected light. Open nicols, slightly out of focus. The corroded phase has a lower refractive index. The corroded edge and the progress of corrosion along the cracks are discernible.

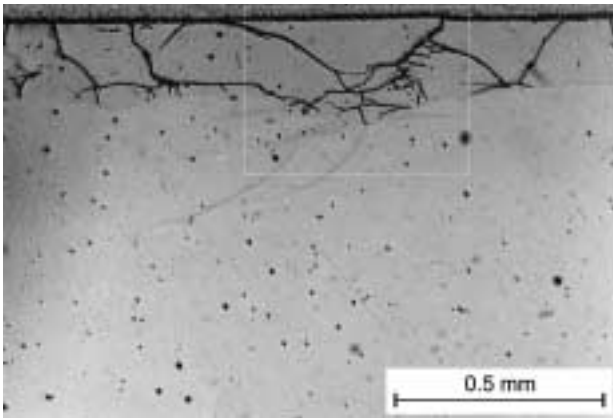


Figure 5. Image of green alabaster glass under the optical microscope, in reflected light. Open nicols. The corroded edge is discernible.

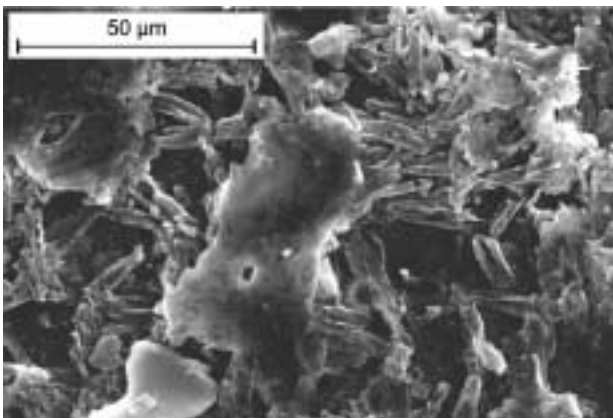


Figure 6. A micrograph of the corroded glass surface. Electron microscope, secondary electrons. The visible microporous morphology is responsible for the large surface area of the corroded glass.

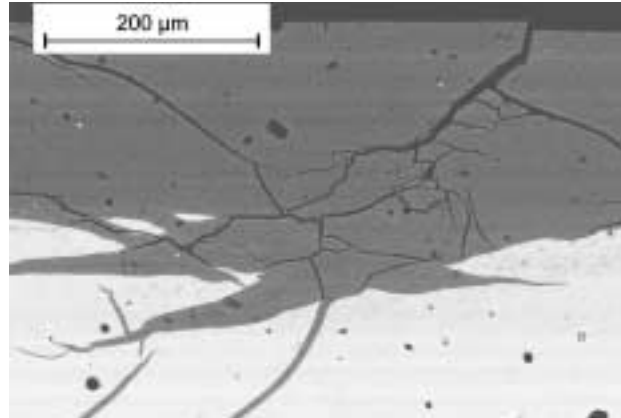


Figure 7. Image of the corroded edge under the electron microscope (reflected electrons) - enlargement of marked area from the figure 5. Resin shows black, the leached zone is darker, the intact glass is of light shade. The two phases with different atomic numbers can be well distinguished. The corroded edge has a lower mean atomic number.

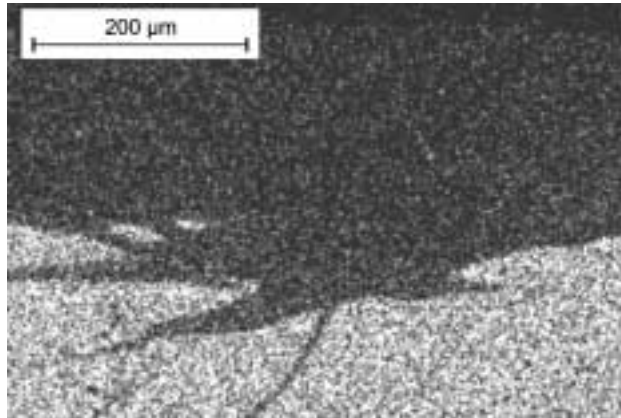


Figure 8. Planar distribution (map) of K concentration in the corroded glass - enlargement of marked area from the figure 5. Electron microscope with EDS analyser. The lighter colour indicates a higher content of K. The two phases of corroded and intact glass are well discernible. More than 90 wt.% of K has been leached.

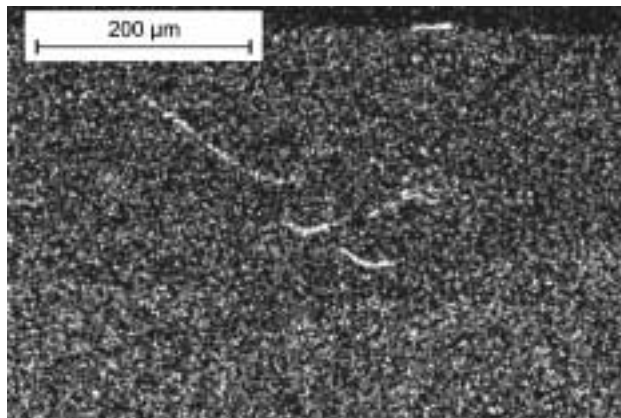


Figure 9. Planar distribution (map) of Ca concentration in the corroded glass - enlargement of marked area from the figure 5. The lighter colour indicates a higher content of Ca. The precipitated phase rich in Ca is visible at the cracks of the corroded zones (white threads). X-ray diffraction showed the precipitate to be calcite.

3500 cm^{-1} to 2700 (figure 12). These features are typical for O–H vibrations. The absorption band near 1630 cm^{-1} is also notable and indicates molecular water in the corroded glass (figure 12).

There is a medium intensity band at 970 cm^{-1} due to the Si–O stretching of $\equiv\text{Si-OH}$ groups [6]. $\delta \equiv\text{Si-OH}$ vibration is present in region 1500 to 1200 cm^{-1} . The absorption bands near 1440 cm^{-1} and 970 cm^{-1} typical for $\equiv\text{Si-OH}$ are present in the corroded glass as well (figure 12).

Uranium silicate vibration at 900 cm^{-1} is not present due to low uranium concentration in the glass.

The methods prove the presence of the $\equiv\text{Si-OH}$ group and molecular H_2O in the corroded phase. The presence of the O–H bond was detected in corroded glass by Cooper et al as well [1].

DISCUSSION

The present study showed that the corrosion brings about the following phenomena: The pieces of the originally unimpaired glass in the dump were only slightly mechanically damaged, probably during the dumping and later on by subsistence of the dump. Damage to the glass due to frost is improbable. Access of the corrosive media to the glass is facilitated by fissures already present in the glass which increase the active surface area. The elements are leached from the surface as well as from the surface of the cracks. The main chemical reactions take place at the progressing sharp corrosion front (cf. figure 5). An undisturbed direct transfer of fluids not involving any additional significant chemical changes then takes place through the corroded layer of the glass. The corrosion involves changes in volume. On the microscopic scale the corroded zone contains well discernible axial cracks, wider at the points of

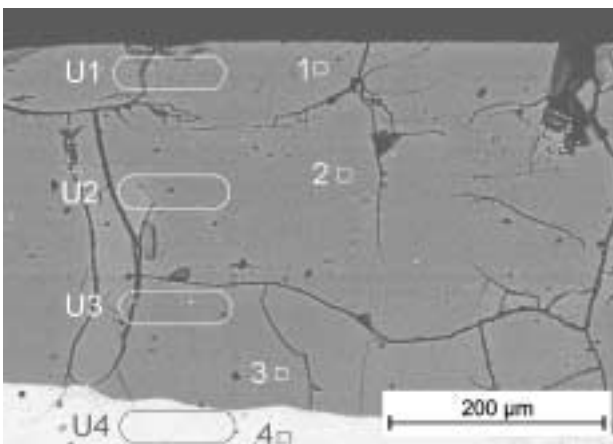


Figure 10. A sample of type 2 green alabaster glass with a very thick corroded surface layer (400 μm). The points analysed by the WDS and ICPMS-LA method are marked in the picture.

greater thickness of the corroded layer. Minor radial fissures have developed perpendicularly to the axial cracks and without exception are terminated at the corrosion front. The contraction phenomena are probably due to the leaching of large amounts of alkalis (up to 14 wt.% of glass) from the glass.

The main factors influencing corrosion were obviously the presence of water, that of soil humic acids [3] and radiation [10]. The additional factors may include bacterial activity [9] or the presence of clay minerals in the proximity of glass [4]. The factors affecting the corrosion rate are the glass composition, composition of the soil solution, pH and Eh of the aggressive solution.

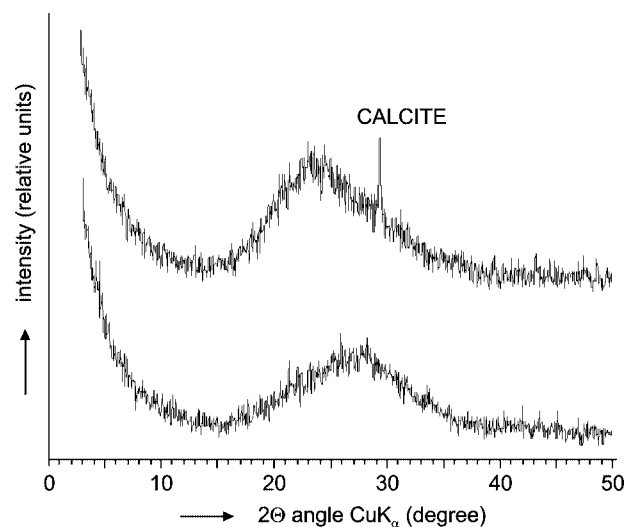


Figure 11. X-ray diffraction patterns of type 2 green alabaster glass. The patterns represent the corroded and the intact glass. Calcite as the only crystalline phase was identified in a sample of the corroded glass.

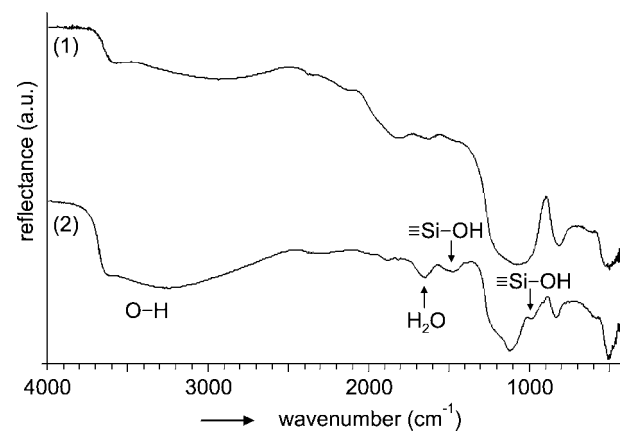
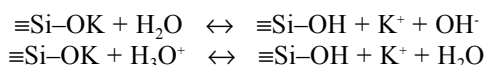


Figure 12. Reflectance spectrum of corroded phase (2) and intact phase (1) of the sample of green mat alabaster glass. The features typical of $\equiv\text{Si-OH}$ and water are present in the corroded glass.

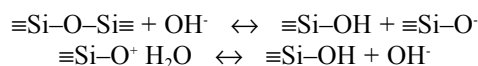
As the corrosive medium we may therefore consider the soil H₂O with a large amount of dissolved soil CO₂. The pH of the soil solution will significantly change due to the presence of coal slag as one of the main lithological components of some horizons of the dump. However, some glasses contain 10.5 wt.% K. The K⁺ ions liberated from the glass probably maintain a slightly basic pH in their proximity.

According to [8], corrosion of alkali-lime glasses proceeds in two stages:

1. Substitution of the alkali, such as e.g. K⁺, for H₃O⁺:



2. Dissolution of the glass structure - hydration of Si-O bonds:



The presence of $\equiv\text{Si}-\text{OH}$ in the corroded glass was proved by IR spectroscopy.

From the macrochemical point of view the corrosion manifests itself above all by almost complete leaching of alkalis (K, Na). On the element distribution maps (EM-EDS) also leaching of calcium is slightly discernible. The corroded layer contains only Si and a small amount of Ca combined with oxygen. Calcite precipitates in the corroded layer as a result of the alkaline microenvironment. The calcium may have stemmed from the glass, but more possibly from the soil solution. The study of the microchemical composition of the glass does not so far allow an explicit conclusion to be made. According to the results of WDS analyses, partial redistribution of copper and uranium is obviously taking place. Both copper and uranium show elevated contents inside the corroded layer. At the advancing corrosion front they become partially dissolved and subsequently absorbed in the surface of the corroded layer.

The mobility of uranium is also indicated by the results of LA ICP-MS. This method has revealed the highest uranium concentrations at the edge of the corroded layer. A similar trend can also be observed in the case of thorium. The results also indicate that lead is not extracted from the glass during its corrosion. In spite of this the surface of the corroded layer has an elevated lead content. This was probably due to absorption of lead from non-uranium high-lead glasses also present in the glassworks dump.

The uranium liberated from the corroded layer is only partially absorbed by the surface layer, and moreover is very readily leachable. The major part of uranium in the form of UO₂²⁺ (which is highly mobile) migrates in solutions through the soil section, until it is retained by the alluvial sediments in the dump base.

Even here all of the uranium leached from the glass will not obviously be retained, being subject to further leaching by subsurface water and a transfer to the river.

From the crystallochemical point of view the structure of corroded glass is composed only of macroelements Si, K, Ca and Na in oxide forms. WDS analyses showed that the corrosion resulted in almost complete leaching of sodium and potassium from the glass. Shortening of mean interatomic distances might be expected as a result of the loss of cation K⁺ as the largest component (with its effective ionic radius of 1.37 Å). However, the X-ray diffraction experiment is indicative of the opposite effect.

One of the possible explanations of the phenomenon may be based on a collapse of the bonding network of glass following removal of K⁺ from the structure. The lengthening of interatomic distances is that case would be due to an increase of entropy in the system. This, however, is contradicted by the microscopically observed contraction phenomena in the corroded layer.

The study of the material of the dump allowed the distribution of uranium in the minus 2 mm fraction to be quantified. The processes taking place in the glassworks dump represent an interesting experiment taking place under natural conditions and are suitable for studying the migration of uranium. The total content of U was precisely measured in the minus 2 mm fraction, and extracts were simultaneously prepared from the same samples. The extracts were analysed by the ICP-MS method. The U concentrations in the extracts correspond very well to the total content of U (figure 2, 3) in the individual horizons of the dump. In the bottom part of the section, the alluvium of the Otava river, there is a high content of extractable U that must have migrated from the dump into the alluvium.

CONCLUSION

The stability of a glass exposed for 75 years to leaching by soil solution under natural conditions was studied. Among all the glasses found, the green alabaster glass of type 2 (cf. table 1) was the most sensitive one with respect to corrosion. It has the highest content of K (12.6 wt.%) and U (0.4 wt.%) of all the glasses studied.

Access of the aggressive medium to the subsurface parts of the glass was facilitated by microcracks on the surface. The corrosion also involved changes in volume resulting in contraction cracks always terminating at the boundary with intact glass. The WDS analyses have proved that the corrosion has manifested itself by total leaching of alkalis from the glass.

Uranium in the glass was bound much more firmly compared to alkalis. WDS and LA ICP-MS analyses nevertheless revealed a redistribution of uranium in the corroded surface of the glass.

IR spectroscopy prove the presence of $\equiv\text{Si}-\text{OH}$ groups in the corroded glass. It is the result of substitution alkalis for H_3O^+ .

The field studies as well as the study of the soil samples allowed the conditions under which the samples were exposed to be described. The mean *pH* of the environment of the glassworks dump was 6.4. As a result of elution of alkalis into the aggressive solution the glasses were corroded in an alkaline microenvironment.

A radioactive disequilibrium determined by gamma spectrometry was caused by the presence of tiny and microscopic particles of uranium glasses. Analyses of soil extracts by the ICP-MS method revealed bonds of leachable U in the horizons containing U glasses, and also in the sub-base of the dump. Uranium has thus been migrating into the Otava river alluvium.

Explanation of abbreviations

EM-EDS - Electron Microscope and microanalyzer with Energy Dispersive analytical System.

WDS - electron microanalyzer with Wave Dispersion analytical System.

LA ICP-MS - Inductive Coupled Plasma Mass Spectrometry with Laser Ablation of the solid sample.

FT-IR - Fourier Transform Infra Red spectrometer.

Ra (ppm eU) - concentration of ^{226}Ra in units of ppm U equivalent. The content of 1 ppm eU of radium 226 is exhibited by a sample with established radioactive equilibrium between ^{238}U and ^{226}Ra , containing 1 ppm of uranium. $1 \text{ ppm eU } ^{226}\text{Ra} = 3.4 \times 10^{-13} \text{ grams of } ^{226}\text{Ra}$ in one gram of sample.

Acknowledgement

The authors wish to express their thanks to Jakub Haloda for measuring the IR spectra of the glasses, to Jiří Hovorka for preparing the pictures and the planar distribution maps of the main elements by the EM-EDS method, to Radim Rybka for carrying out the qualitative WDS analyses, Jiří Čejka for help with the IR spectra interpretation, for the financial support provided by GAUK (Grant No. 219/2001/B-GEO/PrF) and to the research program of the Ministry of Education No. 113100005.

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PŘÍRODNÍ ALTERACE HISTORICKÝCH DRASELNÝCH SKEL BARVENÝCH SLOUČENINAMI URANU

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Byla studována alterace ultradraselných uranových skel z lokality Rejštejn - Klášterský mlýn, Šumava, Česká republika. Vzorky skel byly odebrány na profilu odvalet sklárny. Pocházejí z roku 1925 ± 5 let (určeno historicky). V profilu se kromě skla vyskytuje půda, škvára a podložní aluviální sedimenty řeky Otavy. V profilu byla měřena plošná beta aktivita, nejnižší 0,34 kBq/m² v půdě, nejvyšší 3,26 kBq/m² v poloze s U-skly. Byly rozlišeny 4 typy U - skel: žluté, zelené - alabastrové, zelené a zelenomodré. Obsahují 0,088 - 0,33 hmot.% U a 8 - 14 hmot.% K. V profilu kolísá *pH* (výluh H₂O) od 5,11 ve škváře do 7,70 v horizontech se skly. Celkový obsah U v materiálu skládky, ve frakci < 2 mm, je od 4,8 ppm v aluvii do 56,5 ppm horizontu se skly. Obsah uranu loužitelného 1M CH₃COONa je od 7 ppb v půdě do 65 ppb v horizontu se skly. Uran migruje do aluvia v podloží odvalu (obsahy až 58,9 ppb loužitelného U). V podmínkách aluvia dochází k imobilizaci uranu, zatímco As a Pb nejsou v podloží zachyceny. Zelené - alabastrové U-sklo je při povrchu a po puklinách alterované v šířce od 10 do 400 mm. V alterovaném povrchu jsou kontrakční trhliny, na kterých se sráží kalcit. Při alteraci dochází k odnosu alkálií (až 14 hmot.% skla) ze skloviny, redistribuci uranu a sorpci olova na povrch. Infračervená reflektanční spektroskopie prokázala hydrataci skloviny, která je důsledkem výměny alkalických kationtů za H₃O⁺.