

Article

Long-Term Chemical Alteration of ^{238}Pu -Doped Borosilicate Glass in a Simulated Geological Environment with Bentonite Buffer

Bella Zubekhina ^{1,*}, Boris Burakov ² , Andrei Shiryayev ³ , Xiaodong Liu ⁴ and Yury Petrov ⁵¹ Japan Atomic Energy Agency, 2-4 Shirakata, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan² The Ioffe Institute, 26 Politekhnicheskaya St., St. Petersburg 194021, Russia³ Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr., 31 korp. 4, Moscow 119071, Russia⁴ State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, 418 Guanglan Ave, Nanchang 330013, China⁵ Khlopin Radium Institute, 28 2-nd Murinskiy Ave., St. Petersburg 194021, Russia

* Correspondence: zubekhina.bella@jaea.go.jp

Abstract: Chemical degradation of borosilicate glass doped with ^{238}Pu was modelled in conditions of a failed underground radwaste repository in granite host rock with bentonite buffer material after penetration of aqueous solutions at temperature of 90 °C. The total duration of the experiment exceeded two years. It is shown that wet bentonite preserved its barrier function and prevents migration of plutonium to the solution. The total amount of plutonium adsorbed on bentonite clay during the experiment did not exceed 0.02% of the initial amount of plutonium in the glass sample. Estimated accumulated dose of self-irradiation of the glass sample after the experiment varies from 3.16×10^{15} to 3.39×10^{15} α -decays per gram, which is equivalent to more than 1000 years storage of ^{239}Pu doped sample with the same Pu content. Beishan granite remained intact, with no evidence of Pu penetration into the granite matrix along mineral grain boundaries.

Keywords: plutonium; bentonite; leaching; alteration; granite; waste



Citation: Zubekhina, B.; Burakov, B.; Shiryayev, A.; Liu, X.; Petrov, Y. Long-Term Chemical Alteration of ^{238}Pu -Doped Borosilicate Glass in a Simulated Geological Environment with Bentonite Buffer. *Sustainability* **2023**, *15*, 6306. <https://doi.org/10.3390/su15076306>

Academic Editor: Barry D. Solomon

Received: 14 February 2023

Revised: 17 March 2023

Accepted: 4 April 2023

Published: 6 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Effective development of nuclear energy is strongly depending on implementation of safe and sustainable solutions on each stage of the nuclear fuel cycle, from uranium mining to waste treatment. Treatment of radioactive wastes containing long-lived actinides is an extremely important issue in terms of sustainability, since all the decisions made in this field will be affecting next generations for thousands of years. Final disposal of highly-radioactive waste is one of the most challenging issues in both open and closed nuclear fuel cycles. Two basic strategies are considered for high-level radioactive waste management in the closed nuclear fuel cycle. Nuclear waste streams after the fuel reprocessing can be treated by a solidification technology like vitrification or immobilization into crystalline ceramic matrix. Another approach suggests partitioning the waste to separate long-lived actinides and other relatively short-lived fission products followed by immobilization in more targeted ceramic or glass-ceramic matrix [1–3]. In both cases, deep geological disposal is considered for the final stage of the nuclear fuel cycle. A common well-known international approach to the immobilization of highly radioactive wastes (HLW) is based on their vitrification [1] followed by deep geological disposal. A suitable site for the long-term safe geological disposal has to meet set of requirements such as stable geological and hydrogeological settings (including their eventual changes in future), acceptable construction and engineering conditions, low human activities and land use, environmental protection, and good logistics. Among several types of geological formations suitable for the HLW repository, granite rock is one of the most promising candidates because of

its good mechanical properties and low permeability. A repository in granite rocks is considered in many countries operating underground research facilities (Finland, Sweden, Czech Republic, Switzerland, Republic of Korea) or constructing them (China, Russia). A deep geological repository relies on multi-barrier concept comprising several geological and engineering barriers to minimize the migration of radionuclides during the intended period of disposal, lasting up to 1 million years. A swelling clay, for example, a bentonite buffer, is an important engineering barrier suggested for placement around metal containers filled with the vitrified HLW [4]. This barrier, so-called “buffer” zone, has very low permeability and can protect the waste canister during the rock movements. Bentonite has a high capacity for physical sorption of radionuclides and pronounced swelling upon contact with water helps suppressing migration of underground fluids coming from cracks in the host rock. However, the protective properties of bentonite can weaken because of physical and chemical factors affecting it under hydrothermal conditions of a geological repository. The effect of the bentonite degradation is determined by the presence of water and temperature conditions.

Despite all the components in the multibarrier concept being considered simultaneously, every single barrier material has to meet the safety requirements and acceptance criteria. For each candidate repository site, the safety case studies should include numerical modeling, long-term geological and geochemical investigation, small-scale laboratory experiments, and large-scale experiments in underground research facilities. It is critically important to take into account complex radiation effects affecting a HLW matrix behavior in contact with steel, bentonite, host rock, and underground water. These effects include chemical degradation of the glass matrix, thermal and radiation damages in bentonite, and local change of reducing and oxidizing conditions due to water radiolysis. Since experiments with real vitrified HLW are expensive and complicated, information about the long-term behavior of highly radioactive glass under self-irradiation and contact with water is very limited [5–10]. However, it was reported earlier that the chemical alteration of a real highly radioactive glass doped with ^{238}Pu in water is much more intense in comparison with a simulated non-radioactive glass of similar chemical composition; pronounced glass degradation is observed [9,10].

Radiation effects in bentonite and other clay materials had been studied mainly in terms of the stability of clay materials under external gamma-irradiation [9–11]. It was shown that bentonite has high radiation stability and preserves crystallinity with no significant changes in its structure at accumulated doses as high as 3×10^{10} rad at room temperature and at 3.5×10^9 rad at 300 °C [12,13]. However, the radiation stability of bentonite under external and internal alpha-irradiation is still unclear. It is expected, that under radiation damage from α -particles the lattice of montmorillonite—a basic mineral of a bentonite clay—can be fully amorphised. As a consequence of this process, the sorption capacity of newly formed products of the montmorillonite destruction can decrease dramatically in comparison with the fresh bentonite. Radiolysis of water may chemically destroy montmorillonite as well. In addition, water radiolysis decreases the pH level in the system which leads to bentonite degradation and changes in montmorillonite chemical and physical properties such as structure, composition, morphology, and sorption capacity [14–16].

Alteration of a highly radioactive glass surrounded by water-saturated bentonite is a complex process and can be properly addressed only in dedicated experiments. The presence of granite parent rock in the vitrified HLW repository adds additional uncertainty to the modeling of the long-term behavior of all components [17]. For simplification, we consider the interaction between granite, bentonite, metallic container, vitrified waste, and water as a static system. In this case, migration of radionuclides will be limited by ion diffusion along the grain boundaries in granite rock. However, in a long term (up to 100,000 years period), we should consider the formation of the cracks in the granite host rock and the convective transport of radionuclides along the cracks. In this case, the cracks

will play a main role in the transport of the long-lived actinides in ionic or colloidal forms and their migration into the biosphere [18].

Experiments with trace amounts of radionuclides were performed in several underground research facilities (URF) [19–21], however, experiments with real vitrified radioactive waste were not yet performed in URF. Up to now, laboratory scale leaching and alteration tests is the only possibility to study complex interactions between the solidified waste, buffer, and host rock in static and dynamic conditions. Long-term experiments are very important for prediction of features of the Pu sorption behavior such as reaching the sorption equilibrium and process of Pu(V) reduction on montmorillonite clay [22].

The main objective of this work is to study the long-term behavior of a borosilicate glass doped with ^{238}Pu in the system “water—bentonite buffer—granite host rock”. High specific α -activity of this isotope dramatically accelerates rate of radiation damage and, with certain caution, allows projection of the current results to relatively long periods. The results obtained may contribute to clarifying the model of radionuclide migration from corroded containers filled with vitrified HLW under conditions of a geological repository located in the granite massif.

2. Materials and Methods

The experiment is designed to simulate ageing of the Pu-bearing glass matrix in conditions of a failed container placed into a deep geological repository (DGR). In this experiment, we neglect the contribution of a metal container and model the situation when groundwater equilibrated with bentonite accessed the vitrified waste, e.g., via a crack or corrosion pit in the metal cask.

2.1. Pu-Doped Highly Radioactive Glass Synthesis

^{238}Pu -doped glass was used for the experiment as a simulated vitrified waste sample. ^{238}Pu isotope dramatically accelerates the radiation damage rate in comparison with ^{239}Pu because of its shorter half-life (88 years) and higher specific activity (6.32×10^{11} Bq/g for ^{238}Pu and 2.2×10^9 Bq/g for ^{239}Pu). Thus, using ^{238}Pu , more pronounced aging of the glass can be achieved in a shorter period of time; more extensive radiation damage of the surrounding bentonite can be expected as well. The Pu-doped borosilicate glass has been synthesized in 2016 [9,10] by melting the oxide mixture with a suitable frit at temperature of 1400 °C for 2 h in air atmosphere (Figure 1). The glass was doped with 0.42–0.45 wt. % of ^{238}Pu (recalculated to Pu metal) to accelerate radiation damage in the glass matrix; Eu_2O_3 was added to simulate the presence of trivalent lanthanides. The chemical composition of the glass is presented in Table 1. After the synthesis, the crucible with the glass sample was broken and one solid fragment of the glass (1216 mg) was used for the experiment (Figure 1).

Table 1. The chemical composition of ^{238}Pu -doped borosilicate glass used for experiment.

| Element/Oxide | Content, wt. % |
|-------------------------------|----------------|
| SiO_2 | 47.86 |
| Na_2O | 14.60 |
| B_2O_3 | 21.20 |
| Al_2O_3 | 6.84 |
| Eu_2O_3 | 3.02 |
| CaO | 5.87 |
| PuO_2 (all isotopes) | 0.58–0.65 |
| $^{238}\text{PuO}_2$ | 0.47–0.53 |
| ^{238}Pu (as metal) | 0.42–0.45 |

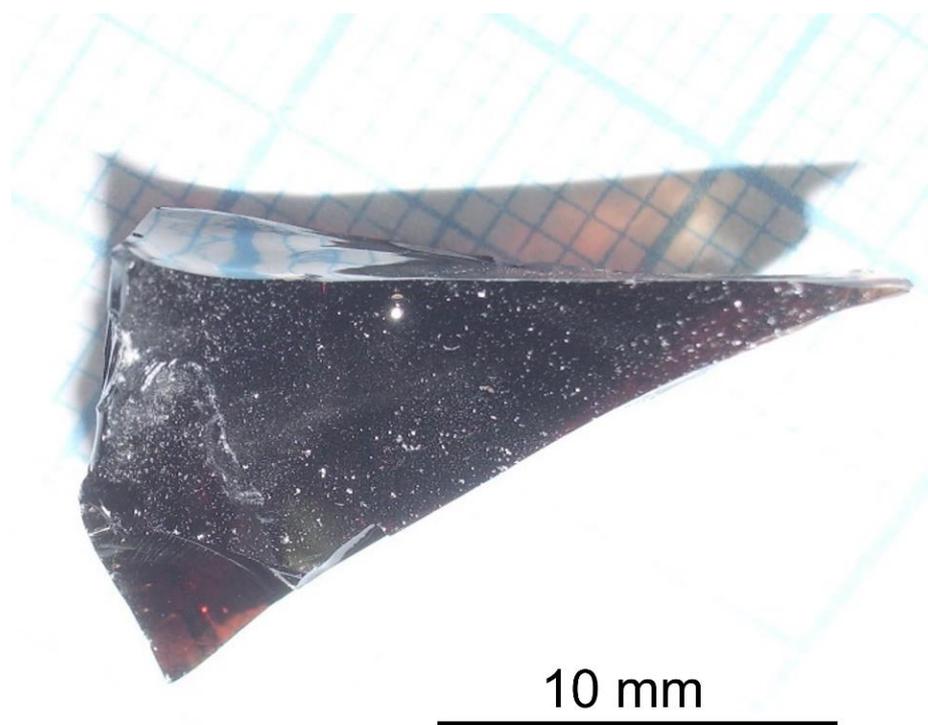


Figure 1. Sample of the borosilicate glass doped with ^{238}Pu prior to the experiment.

As the Pu-doped glass sample was synthesized two years before the experiment, it has already suffered radiation damage. For evaluation of number of alpha decays, we used Pu content of 0.42 wt. % as a minimum and 0.45 wt. % as a maximum content values. Then, for the initial glass sample (1216 mg) the Pu content varies from 5.11 to 5.47 mg of ^{238}Pu per whole sample. Using ^{238}Pu specific activity we can recalculate this content as $(3.23\text{--}3.46) \times 10^7$ Bq per sample. For the entire storage period (22 months) the of self-irradiation dose can be estimated in a range from 1.51×10^{14} to 1.62×10^{14} α -decays per gram of the sample.

After two years of the experiment, the total accumulated dose of self-irradiation naturally increased and can be estimated in a range from 3.16×10^{15} to 3.39×10^{15} α -decays per gram of the sample. Mass loss caused by Pu leaching during the experiment was neglected in this estimation. The dose of self-irradiation calculated above is equivalent to the one accumulated by the sample doped with 0.45 wt. % of ^{239}Pu after more than 1000 years of storage.

2.2. Granite Rock

A sample of granite rock from the Beishan area of Gansu Province, China was used for the experiment. This sample represents the actual host rock of emerging Beishan HLW geological repository in China. Magmatic granites of the Beishan area mainly possess granitic and porphyritic structures. The rock body is characterized by batholiths, stocks, dykes, etc. According to surface geological mapping and boreholes investigations, the main rock types of the planning DGR are biotite monzonitic granite and biotite granodiorite [23]. The mineralogical and chemical compositions of Beishan granite are presented in Tables 2 and 3, respectively.

Table 2. Mineralogical composition of Beishan granite rock and Gaomiaozi (GMZ) Na-bentonite used for experiment, wt. %.

| Mineral | Beishan Granite [24] | Bentonite GMZ [25] |
|-----------------|----------------------|--------------------|
| Microcline | 46.14 | - |
| Albite | 27.50 | - |
| Biotite | 15.65 | - |
| Quartz | 8.50 | 11.7 |
| Cordierite | 1.33 | - |
| Amesite | 0.89 | - |
| Montmorillonite | - | 75.4 |
| Cristobalite | - | 7.3 |
| Feldspar | - | 4.3 |
| Kaolinite | - | 0.8 |
| Calcite | - | 0.5 |

Table 3. Chemical composition of Beishan granite rock and Gaomiaozi (GMZ) Na-bentonite used for experiment, wt. %.

| Oxide | Beishan Granite [24] | Bentonite GMZ [25] |
|--------------------------------|----------------------|--------------------|
| SiO ₂ | 57.78 | 67.43 |
| Al ₂ O ₃ | 15.42 | 14.20 |
| Fe ₂ O ₃ | 4.07 | 2.40 |
| Na ₂ O | 2.54 | 1.75 |
| CaO | 3.25 | 1.13 |
| K ₂ O | 6.15 | 0.73 |
| FeO | - | 0.29 |
| TiO ₂ | 0.79 | 0.12 |
| MgO | 2.12 | 0.10 |
| MnO | - | 0.02 |
| P ₂ O ₅ | 0.96 | 0.02 |
| SrO | 0.13 | - |
| Loss of ignition | 6.45 | 11.38 |

2.3. Bentonite Clay

A sodium bentonite powder from the Gaomiaozi (GMZ) deposit was used for the experiment. The GMZ bentonite is a Na-montmorillonite clay that was formed in the late Jurassic period. The formation of bentonite clay was caused by mineralization due to interaction with groundwater and weathering of newly formed volcanic deposits. The experimental samples of bentonite were excavated from a large clay deposit located in Inner Mongolia Chinese autonomous region, around 300 km northwest of Beijing. The deposit may contain up to 160 million tons of clay materials [24]. The high content of montmorillonite leads to a high cation exchange capacity (CEC = 77.30 meq/100 g), a large plasticity index ($I_p = 275$), and large specific surface area ($S = 570 \text{ m}^2/\text{g}$). The major exchangeable cations are Na^+ , Ca^{2+} , Mg^{2+} and K^+ [25,26].

A sample of the initial bentonite was received in form of a homogeneous powder, with a soft texture and waxy appearance. The mineralogical and chemical composition of GMZ bentonite is presented in Tables 2 and 3, respectively.

2.4. Leaching Solution

The distilled water was used as a leaching solution to allow a comparison of the results of the Pu-doped glass alteration in a water-saturated bentonite with previously published results on Pu-bearing glass leaching and alteration mostly performed in distilled or deionized water. Taking into account relatively long duration (2 years) and high temperature (90 °C) of the experiment, it was supposed that the initial distilled water will be saturated with chemical elements from granite and bentonite during the granite-bentonite-water interaction.

The experimental design is presented in Figure 2. The experiment was performed according to the following scheme:

- A small amount (15–20 g) of water saturated (wet) bentonite clay was placed into granite block 70 × 70 × 125 mm in size.
- A chip of the ^{238}Pu -doped glass (weight 1216 mg) was placed into the wet bentonite mass inside the container. The thickness of the bentonite layer around the glass sample was about 15–20 mm (Figure 2).
- The granite container was filled with distilled water up to the 10–20 mm above the bentonite surface, sealed with Teflon™ lid, placed into a stainless steel clamp and tightened (Figure 3a).
- After that, the clamped container was immersed into a Teflon™ case filled with water (Figure 3b) and sealed with a screw cap. The sealed container was placed into a thermostatic oven maintaining a temperature of 90 °C for 2 years.

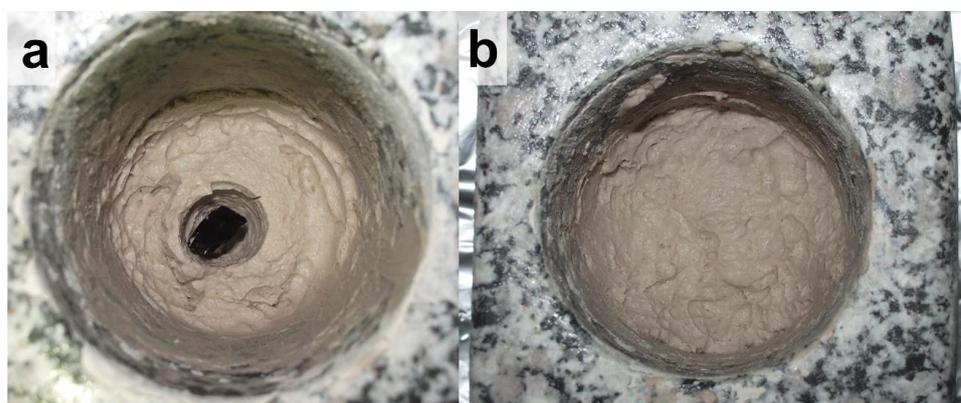


Figure 2. Preparation of the experiment: (a)—the Pu-doped borosilicate glass surrounded by wet bentonite inside the granite container; (b)—view after sealing filling with bentonite.

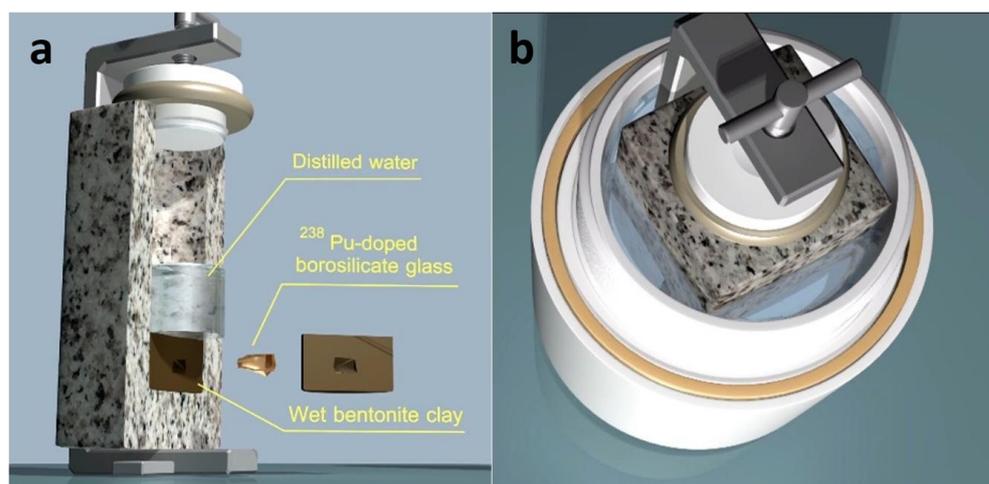


Figure 3. 3D model of the complete experimental setup. (a) virtual cross-section of the experimental assembly. (b) virtual top view of the clamped granite container in a protective Teflon™ vessel.

Every 6 months sampling of ~5 mL of the leachate solution from the granite container was performed and an equivalent amount of distilled water was added after the sampling. The aqueous solution between the granite container surface and the inner wall of Teflon™ cask was also sampled every 6 months to control eventual plutonium release through granite. The sampled solutions were centrifuged at 4500 rpm for 10 min and separated liquid phase was analysed by alpha- and gamma-spectrometry (Canberra-7401 and multichannel analyser DSA-1000 with Ge-detector, Canberra, respectively).

After completion of the experiment, the granite container was cut with a saw and a cross-section was put into direct contact with a Retina XBM film for 2 months. Wet bentonite was mechanically extracted from the container, intermixing of the bentonite layers was avoided as much as possible, see below. The extracted bentonite was examined with X-ray powder diffraction using Empyrean or Aeris diffractometers operated with Cu-K α radiation in reflection (Bragg-Brentano) geometry. The sample was placed on a zero-background Si holder or, in case of abundant initial (reference) material, was backloaded. Note that the initial bentonite sample was analysed in fully dry state, whereas the bentonite from the container was measured both in partly wet state and after overnight drying at ambient conditions; deep drying was not performed to minimise amounts of radioactive dusting. Comparison of the same sample measured in wet and “dry” conditions show similarity of the diffraction patterns with exception of position of the reflection corresponding to the basal plane of montmorillonite, which shifts considerably. Of course, the presented results are only qualitative, since no attempts to separate clay minerals was attempted.

3. Results

The Pu content in the leachates is presented in Table 4. The lack of data after the first 6 months is due to the full water consumption in the granite container by the bentonite (Figure 4a).

Table 4. Results of Pu α -spectrometry measurements of water solution inside and outside the granite container during the experiment.

| Sample | Pu Content, Bq/mL | | | |
|--|-------------------|-----------|-----------|-----------|
| | 6 Months | 12 Months | 18 Months | 24 Months |
| Water sample from the inner space of granite container | No data | 50–110 | <50 | <50 |
| Water sample from outside area of granite container | | <10 | | |

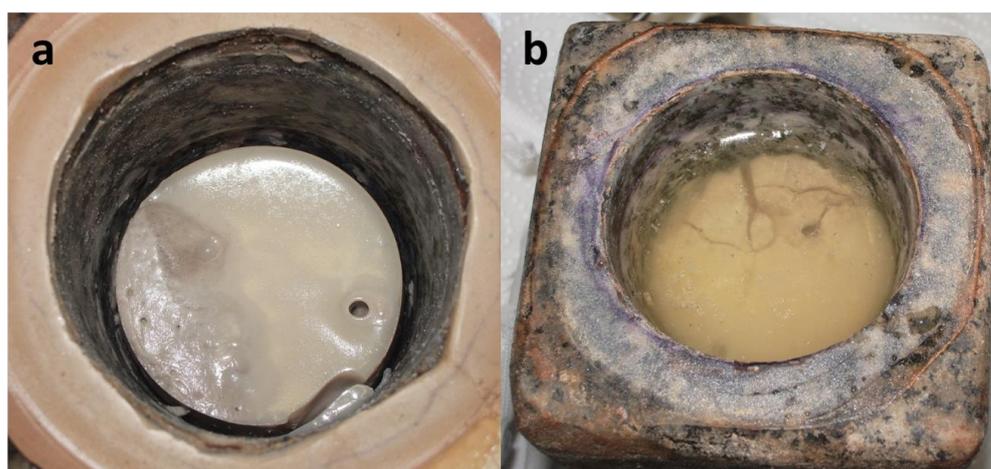


Figure 4. Photo of the wet bentonite inside granite container after 6 months (a) and 2 years (b) of the experiment at temperature 90 °C.

After two years of the experiment (Figure 4b) all water above the bentonite surface was removed and the bentonite was extracted layer by layer with a thickness of about 1 cm each (Figure 5). The glass sample was washed in distilled water and dried in air. Both inner and outer surfaces of the granite container were carefully washed, and the container was sawn across into several fragments using a low-speed saw. All surfaces of the granite samples used for further radiography tests were carefully ground and washed.

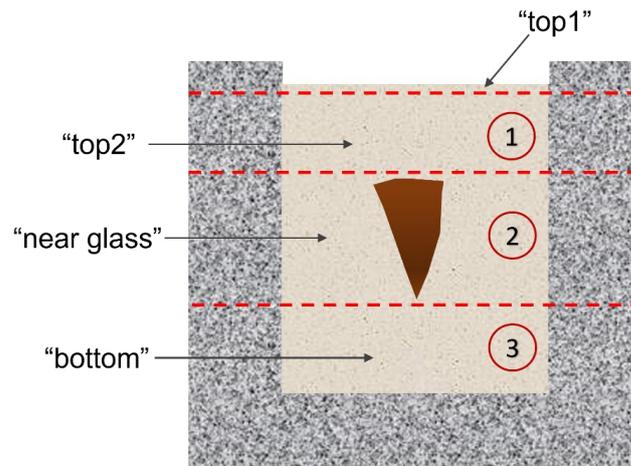


Figure 5. Scheme of the bentonite removal and sampling areas.

XRD patterns of initial dry bentonite (“start”) as well as partly dried bentonite with unknown content of water (see Section 2 for details) from different locations inside the granite container are shown in Figure 6.

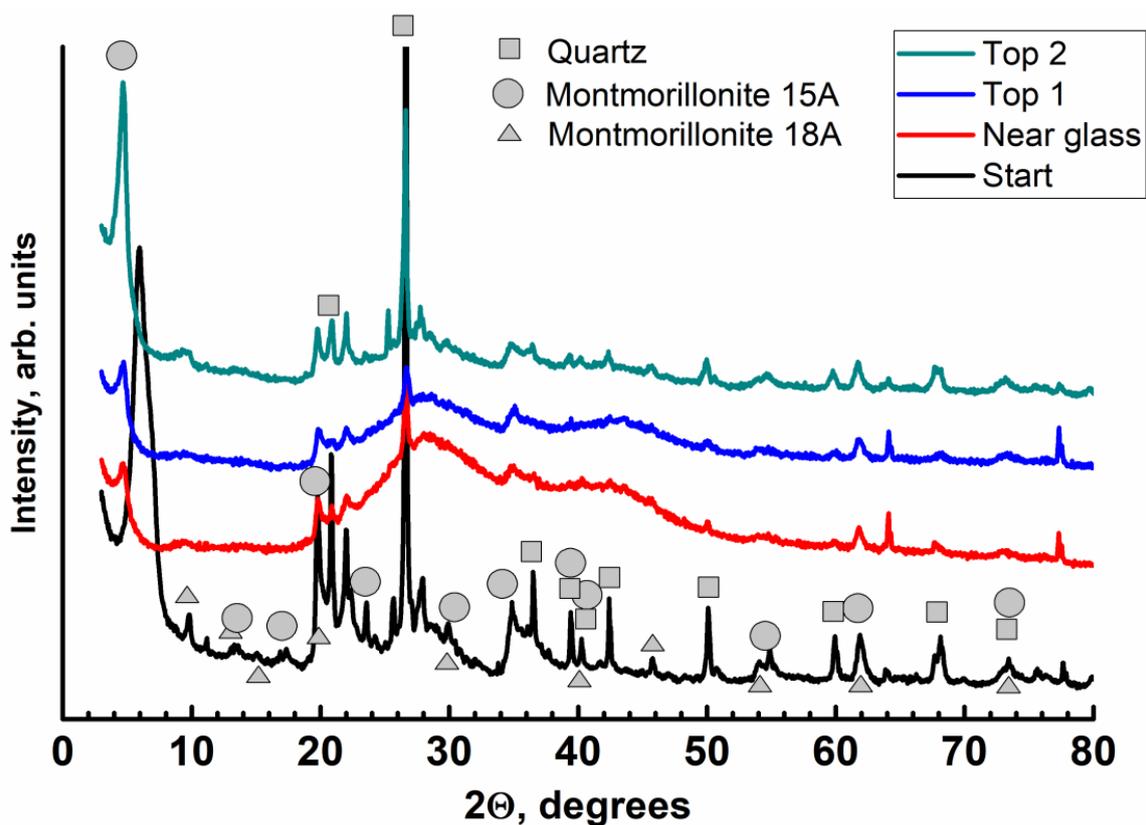


Figure 6. XRD patterns of initial dry bentonite (“start”) and of moist bentonite from different locations inside the granite container (“top1”, “top2”, “near glass”). The 101 quartz reflection ($2\theta = 26.627^\circ$) is off-scale. The curves are displaced vertically for clarity. Main reflections of principal mineral phases (ICDD cards): filled squares—quartz (01-079-1910), circle—montmorillonite 15A (00-013-0135); triangle—montmorillonite 18A (00-012-0219). Other peaks belong to feldspars and layered clay minerals.

For evaluation of the amount of ^{238}Pu adsorbed on bentonite clay, a desorption experiment was performed using a mixture of concentrated nitric acid and hydrofluoric acid.

Before the experiment, a sufficient amount of bentonite clay removed from different layers was placed into a quartz glass cup and dried in air at 40 °C until the constant weight of 14.3 g. The dry sample was brought in contact with the acids solution (10 mL of fluoric acid and 20 mL of nitric acid) for 3 weeks. The acid-resistant residue was less than 5 wt.%. α -spectroscopic measurements of the Pu-containing solution after the desorption showed that the estimated specific activity of ^{238}Pu is 0.41 MBq per gram of dry bentonite. The total amount of ^{238}Pu in the dry bentonite after the experiment makes 0.01–0.02% of initial amount of ^{238}Pu in the glass sample. As shown in Table 4, the Pu specific activity of the solution above the bentonite layer is insignificant in comparison with amount of Pu adsorbed by the clay.

4. Discussion

4.1. Alteration of the Glass Sample

During the first examination using optical microscope, formation of a secondary phase on the glass surface was clearly observed (Figure 7). However, the alteration of the glass observed in wet bentonite medium is much less pronounced than for borosilicate glass in contact with distilled water at temperature 90 °C [9,10]. The reasons for the discrepancy are not yet fully understood, but variations in pH and eventual partial radiation-induced destruction of Teflon™ container with release of fluorine compounds in experiments described in [9] may be responsible. Value of pH of natural bentonite suspension is close to neutral and varies from 5 to 7.2 with average of 6.2, which is comparable with those for the distilled water environment. However, further experiments are needed to reveal how does water radiolysis in a bentonite environment affect the degradation process of a highly radioactive glass. Also, for future research, using real or simulated groundwater seems to be reasonable to make test results more relevant to the actual URF or planned disposal site.

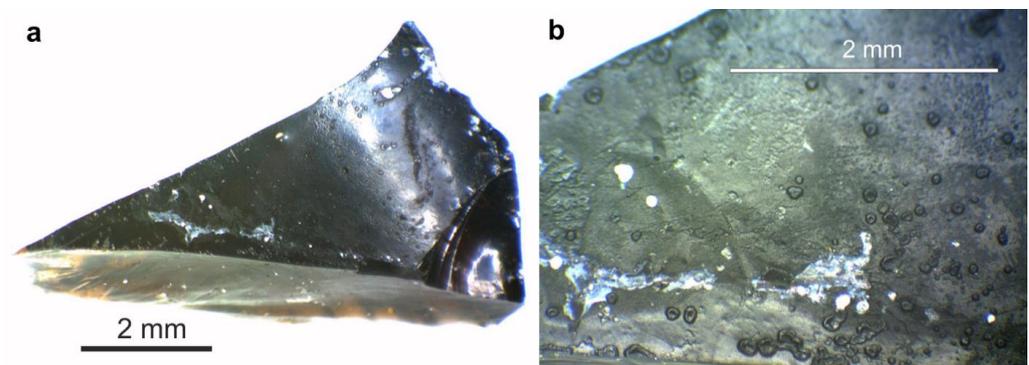


Figure 7. Optical microscopy of the surface of ^{238}Pu -doped borosilicate glass after 2 years of contact with wet bentonite. (a) general view. (b) higher magnification image.

4.2. Bentonite and Granite Alteration

The phase composition of the initial sample is dominated by quartz, different montmorillonite varieties (e.g., 15A, 18A) and feldspars (e.g., anorthoclase). In presence of a thermal gradient, leaching and reprecipitation of constituents from bentonite at different locations in the container may, in long term, induce formation of mineralogically distinct layers. In addition, intense radiolysis may contribute to phase changes. Examination of XRD patterns does not show clear difference between the bentonite samples from different locations in the container. The changes in the patterns are relatively minor and are mostly confined to reduced relative intensity of crystalline peaks, implying partial amorphisation and/or decrease of crystallite sizes. The largest relative changes are observed for the sample from the topmost layer, which demonstrates rather pronounced “amorphous” hump centred at $\sim 28^\circ$ (2θ). This observation might be related to the least stable environment, for example, semi-annual contact with fresh solution and/or air above the clay.

Interestingly, we do not observe formation of abundant crystalline SiO_2 which may form a cement during illitisation of smectites in hydrothermal conditions (see, e.g., reviews [27,28]). Possibly, thermal gradients in our experiments were fairly small, precluding extensive dissolution-precipitation phenomena. According to the XRD patterns, the montmorillonite phase survived after two years of α -irradiation and related radiolysis at a relatively high temperature of 90 °C. It is known, that smectites may undergo structural changes in hydrothermal conditions. Whereas temperatures below 300 °C do not alter dry bentonite structure to noticeable extent [9,28,29], under hydrothermal conditions degrading of the bentonite structure can be observed at 130–150 °C [28] and even at 90 °C (in 3.5% CaCl_2 solution) [30]. That makes impossible to distinguish the effect of α -irradiation of wet bentonite at 90 °C and the effects caused by long-term bentonite-water interaction itself.

Even after 2 years of α -irradiation at 90 °C wet bentonite preserved its barrier function and prevents migration of the adsorbed Pu to the solution. Apparently, the influence of radiolysis and of α -irradiation on structure of comprising minerals is small. For some clay minerals, such as kaolin and attapulgite, significant structural changes were observed during alpha-irradiation by ^{253}Es but even after partial loss of crystallinity these materials were able to prevent Es release into the solution [31].

Autoradiography of the granite sample shows absence of noticeable penetration of Pu in granite rock matrix (Figure 8). It is possible to observe little black colour vein on the bottom of granite container, which is related to penetration of radioactive solution into a small crack caused by mechanical damage of the granite matrix during drilling of the cylindrical hole of the container inner space. Some amount of ^{238}Pu in a small crack can be also explained by contamination during the sawing, since no Pu penetration along grain boundaries was noted. This observation is in a good agreement with previously published data [32], showing that Pu transport in low-porosity granitic rocks from the Beishan site is mostly determined by migration along the fractures (especially in form of colloids [33]) but not by diffusion in granite matrix.



Figure 8. Autoradiography (2 months exposure) of the granite sample from the bottom of experimental granite container: cross section of lower part. Black rectangle appears due to α -particles reaching the film through air gap.

5. Conclusions

The results obtained contribute to laboratory scale safety-case studies of geological disposal for achieving a safe and sustainable way for actinide-bearing waste disposal. Based on experimental results, the following conclusions can be made:

- (1) After two years of contact with ^{238}Pu -doped glass and water at temperature 90 °C Gaomiaozi Na-bentonite remains crystalline; no cementation by crystalline SiO_2 was observed.
- (2) Chemical alteration of ^{238}Pu -doped borosilicate glass after long-term contact with wet bentonite at 90 °C is less extensive than for the identical sample in distilled water.
- (3) The borosilicate glass is slightly altered during the experiment, but leached Pu was quantitatively adsorbed and retained by the surrounding bentonite. The total amount of plutonium adsorbed on bentonite clay for during two years of the experiment did not exceed 0.02% of the initial amount of plutonium in the glass sample.

- (4) Beishan granite remained intact with no evidence of Pu penetration into the granite matrix along mineral grain boundaries.

Author Contributions: Conceptualization and methodology: B.B. and B.Z.; analysis: B.B., B.Z., Y.P. and A.S.; writing—original draft preparation: B.Z., A.S. and B.B.; writing—review and editing: B.Z., A.S., B.B. and X.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: Authors are grateful to Vladimir Garbuzov for his valuable support with the 3D visualization. Authors highly appreciate the technical support of Nina Petrova, Oxana Azarchenko (V. G. Khlopin Radium Institute) and Ksenia Vaganova.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Lutze, W.; Ewing, R.C. *Radioactive Waste Forms for the Future*; North-Holland Physics Publishing: Amsterdam, The Netherlands, 1988; 778p.
- Burakov, B.E.; Ojovan, M.I.; Lee, W.E. *Crystalline Materials for Actinide Immobilisation*; Imperial College Press: London, UK, 2011; 216p. [[CrossRef](#)]
- Ojovan, M.I.; Petrov, V.A.; Yudinsev, S.V. Glass Crystalline Materials as Advanced Nuclear Wasteforms. *Sustainability* **2021**, *13*, 4117. [[CrossRef](#)]
- International Atomic Energy Agency. *Characterization of Swelling Clays as Components of the Engineered Barrier System for Geological Repositories*; IAEA-TECDOC-1718; IAEA: Vienna, Austria, 2013.
- Peuget, S.; Noël, P.-Y.; Loubet, J.-L.; Pavan, S.; Nivet, P.; Chenet, A. Effects of deposited nuclear and electronic energy on the hardness of R7T7-type containment glass. *Nucl. Instrum. Methods Phys. Res.* **2006**, *246*, 379–386. [[CrossRef](#)]
- Peuget, S.; Broudic, V.; Jégou, C.; Frugier, P.; Roudil, D.; Deschanel, X.; Rabiller, H.; Noel, P. Effect of alpha radiation on the leaching behavior of nuclear glass. *J. Nuc. Mater.* **2007**, *362*, 474–479. [[CrossRef](#)]
- Rolland, S.; Tribet, M.; Jégou, C.; Broudic, V.; Magnin, M.; Peuget, S.; Wiss, T.; Janssen, A.; Blondel, A.; Toulhoat, P. 99Tc- and 239Pu-doped glass leaching experiments: Residual alteration rate and radionuclide behavior. *Int. J. Appl. Glass Sci.* **2013**, *4*, 295–306. [[CrossRef](#)]
- Peuget, S.; Delaye, J.-M.; Jégou, C. Specific outcomes of the research on the radiation stability of the French nuclear glass towards alpha decay accumulation. *J. Nuc. Mater.* **2014**, *444*, 76–91. [[CrossRef](#)]
- Zubekhina, B.Y.; Shiryaev, A.; Burakov, B.E.; Vlasova, I.E.; Averin, A.A.; Yapaskurt, V.O.; Petrov, V.G. Chemical alteration of 238Pu-loaded borosilicate glass under saturated leaching conditions. *Radiochim. Acta* **2020**, *108*, 19–27. [[CrossRef](#)]
- Zubekhina, B.Y.; Burakov, B.E.; Ojovan, M.I. Surface alteration of borosilicate and phosphate nuclear waste glasses by hydration and irradiation. *Challenges* **2020**, *11*, 14. [[CrossRef](#)]
- Allen, C.C.; Wood, M.I. Bentonite in nuclear waste disposal: A review of research in support of the basalt waste isolation project. *Appl. Clay Sci.* **1988**, *3*, 11–30. [[CrossRef](#)]
- Parab, H.; Mahadik, P.; Sengupta, P.; Vishwanadh, B.; Kumar, S.D. comparative study on native and gamma irradiated bentonite for cesium ion uptake. *Prog. Nucl. Energy* **2020**, *127*, 103419. [[CrossRef](#)]
- Cheng, J.; Gu, R.; He, P.; Pan, Y.; Leng, Y.; Wang, Y.; Liu, Y.; Zhu, M.; Tuo, X. Effect of high-dose γ -ray irradiation on the structural stability and U(VI) adsorption ability of bentonite. *J. Radioanal. Nucl. Chem.* **2022**, *331*, 339–352. [[CrossRef](#)]
- Nithya, K.; Gandhi, S.; Arnepalli, D.N. Effect of pH on Sorption Characteristics of Bentonite. In Proceedings of the 6th International Congress on Environmental Geotechnics (6ICEG), New Delhi, India, 7–11 November 2010. [[CrossRef](#)]
- Choo, K.Y.; Bai, K. Effects of bentonite concentration and solution pH on the rheological properties and long-term stabilities of bentonite suspensions. *Appl. Clay Sci.* **2015**, *108*, 182–190. [[CrossRef](#)]
- Cui, J.; Zhang, Z.; Han, F. Effects of pH on the gel properties of montmorillonite, palygorskite and montmorillonite-palygorskite composite clay. *Appl. Clay Sci.* **2020**, *190*, 105543. [[CrossRef](#)]
- Jia, S.; Dai, Z.; Yang, Z.; Du, Z.; Zhang, X.; Ershadnia, R.; Soltanian, M.R. Uncertainty quantification of radionuclide migration in fractured granite. *J. Clean. Prod.* **2022**, *366*, 132944. [[CrossRef](#)]
- Ménager, M.-T.; Petit, J.-C.; Brocandel, M. The migration of radionuclides in granite: A review based on natural analogues. *Appl. Geochem.* **1992**, *7*, 217–238. [[CrossRef](#)]

19. Chunli, L.; Zhiming, W.; Shushen, L.; Yuae, Y.; Hong, J.; Bing, L.; Ling, J.; Ling, W.; Dan, L.; Zhongde, D.; et al. The migration of radionuclides ^{237}Np , ^{238}Pu and ^{241}Am in a weak loess aquifer: A field column experiment. *Radiochim. Acta* **2001**, *89*, 519–522. [[CrossRef](#)]
20. Yamaguchi, T.; Nakayama, S.; Vandergraaf, T.T.; Drew, D.J.; Vilks, P. Radionuclide and Colloid Migration Experiments in Quarried Block of Granite under In-Situ Conditions at a Depth of 240 m. *J. Power Energy Syst.* **2008**, *2*, 186–197. [[CrossRef](#)]
21. Aertsens, M.; Maes, N.; Van Ravestyn, L.; Brassinnes, S. Overview of radionuclide migration experiments in the HADES Underground Research Facility at Mol (Belgium). *Clay Miner.* **2013**, *48*, 153–166. [[CrossRef](#)]
22. Begg, J.D.; Zavarin, M.; Tumej, S.J.; Kersting, A.B. Plutonium sorption and desorption behavior on bentonite. *J. Environ. Radioact.* **2015**, *141*, 106–114. [[CrossRef](#)]
23. Wang, J.; Chen, L.; Su, R.; Zhao, X. The Beishan underground research laboratory for geological disposal of high-level radioactive waste in China: Planning, site selection, site characterization and in situ tests. *J. Rock Mech. Geotech. Eng.* **2018**, *10*, 411–435. [[CrossRef](#)]
24. Li, C.; Zheng, Z.; Liu, X.Y.; Chen, T.; Tian, W.Y.; Wang, L.H.; Wang, C.L.; Liu, C.L. The Diffusion of Tc-99 in Beishan Granite—Temperature Effect. *J. Nucl. Sci. Technol.* **2013**, *3*, 33–39. [[CrossRef](#)]
25. Ye, W.M.; Cui, Y.J.; Qian, L.; Chen, B. An experimental study of the water transfer through confined compacted GMZ bentonite. *Eng. Geol.* **2009**, *108*, 169–176. [[CrossRef](#)]
26. Ye, W.M. Investigation on chemical effects on GMZ bentonite used as buffer materials. *E3S Web Conf.* **2016**, *9*, 02001. [[CrossRef](#)]
27. Meunier, A.; Velde, B.; Griffault, L. The reactivity of bentonites: A review. An application to clay barrier stability for nuclear waste storage. *Clay Miner.* **1998**, *33*, 187–196. [[CrossRef](#)]
28. Wersin, P.; Johnson, L.H.; McKinley, I.G. Performance of the bentonite barrier at temperatures beyond 100 °C: A critical review. *Phys. Chem. Earth* **2007**, *32*, 780–788. [[CrossRef](#)]
29. Laine, H.; Karttunen, P. *Long-Term Stability of Bentonite. A Literature Review*; POSIVA Working Report; Posiva WR: Eurajoki, Finland, 2010.
30. Liu, X.; Prikryl, R.; Pusch, R. THMC-testing of three expandable clays of potential use in HLW repositories. *Appl. Clay Sci.* **2011**, *52*, 419–427. [[CrossRef](#)]
31. Haire, R.G.; Beall, G.W. Consequences of radiation from sorbed transplutonium elements on clays selected for waste isolation. *ACS Symp. Ser.* **1979**, *100*, 291–295. [[CrossRef](#)]
32. Zhang, X.; Wang, Z.; Reimus, P.; Ma, F.; Soltanian, M.R.; Xing, B.; Zang, J.; Wang, Y.; Dai, Z. Plutonium reactive transport in fractured granite: Multi-species experiments and simulations. *Water Res.* **2022**, *224*, 119068. [[CrossRef](#)]
33. Malkovsky, V.I.; Petrov, V.A.; Yudinsev, S.V.; Ojovan, M.I.; Poluektov, V.V. Influence of Rock Structure on Migration of Radioactive Colloids from an Underground Repository of High-Level Radioactive Waste. *Sustainability* **2023**, *15*, 882. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.