

SORPTION INFLUENCE ON IODINE-129 RELEASE FROM THE DGR'S NEAR FIELD

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In terms of potential long-term radiation hazard, ^{129}I is seen as a most problematic radionuclide, which is explained by its high mobility and long half-life. The paper explores its forms that may occur in VHLW from SNF reprocessing. It also overviews the studies focused on ^{129}I sorption by engineered barrier materials considered typical for DGR sited in crystalline rocks, namely, bentonite and steel containers for vitrified high-level waste. The paper shows that when considered, the realistic coefficients for the interphase ^{129}I distribution on bentonite and carbon steel corrosion products have little effect on its release beyond the DGR's near field. However, ^{129}I release into the DGR's near field is expected to be retarded in a quite considerable way if the empty space inside the insulating containers is filled with selective sorbents.

Keywords: radionuclide transport, radioiodine, modelling, radioactive waste.

Introduction

Operation of the nuclear power complex generates large radioactive waste (RW) inventories. Among other components, these inventories feature the iodine isotope ^{129}I considered critical when it comes to the safety assessment of underground disposal facilities. Due to its long half-life ($T_{1/2} = 1,57 \cdot 10^7$ years) and high mobility in the cascades of engineered and natural barrier materials, in the long run, its releases from the waste forms disposed of in deep geological formations may turn out to be decisive in terms of the potential radiation hazard levels associated with deep geological repositories (DGR) [1], [2].

Such high mobility is explained by the anionic nature of iodine transfer forms contributing to its low affinity for sorption on the host media, namely, on the mineral phases with their surfaces predominantly having a negative charge. To assess the long-term DGR stability and safety, one should have proper understanding of ^{129}I release pathways, its behavior and transport in the materials of the engineered safety barrier system (EBS). Proper

understanding of mechanisms governing radioiodine absorption by EBS materials is a key to the long-term radiation safety of DGR.

The scientific community has been endeavoring to calculate sorption retardation parameters for ^{129}I during its underground transport. However, the results obtained provided no clear evidence regarding its transport behavior. The interfacial distribution coefficients (K_d) calculated based on the experimental data showed a great deal of variation. The simplest conclusion that could be indicated in the DGR safety assessment was a conservative assumption on zero iodine sorption on EBS materials, which was assumed in [1], [2]. However, two questions arise: how reasonable this approach is and in which way iodine sorption may influence the choice of the EBS concept under the DGR designs developed for the Yeniseiskiy site [3].

This article discusses sorption mechanisms and provides quantitative assessment of K_d influence on ^{129}I release beyond the EBS in the DGR's near field [3]. The reference option considers an

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aluminophosphate waste form (APG) with vitrified high-level waste (VHLW), steel container corrosion products and clay-based bentonite buffer material. It also considers the effect produced on ^{129}I transport in EBS by container gap filling with a selective sorbent.

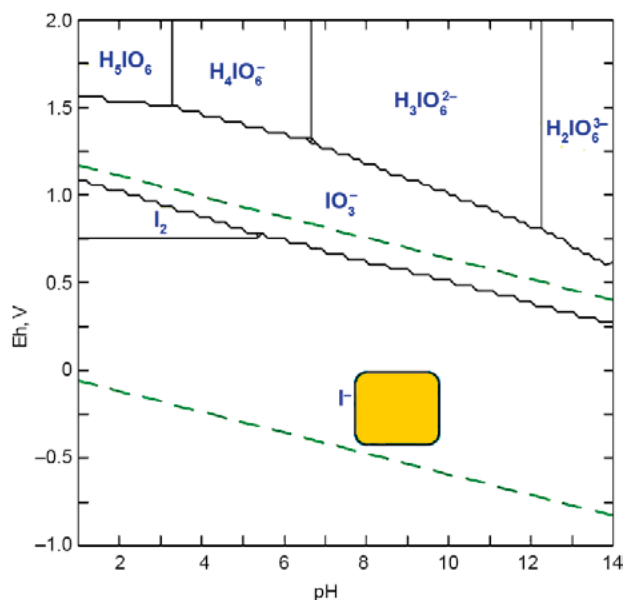
Iodine species expected in VHLW and the aqueous phase of the DGR's near field

SNF reprocessing involves a dissolution stage when concentrated nitric acid is applied to dissolve most of the iodine inventory, which is predominantly represented by the cesium iodide: it is oxidized to molecular iodine with 92–99% of its initial activity being released from the water volume into gas phase [4]–[7]. At the post-dissolution stage after the target component extraction is completed, iodine can still remain in the solution in the form of iodate compounds (IO_3^-) and insoluble species such as colloids of silver iodides [8] or some other metals (for example, Pd [9]) characterized with high fission yields or accounting for their decay products.

To provide reducing environment, some reagents (ethylene glycol and sodium hydroxide) are added to the furnace when sodium aluminophosphate glass (APG) is melted [10], [11]. Iodine (at least partially) transforms into its iodide (I^-) and, to varying degrees, iodate (IO_3^-) species [12]–[14] with the latter ones potentially considered more stable than the former ones [15]. The residual iodine content in VHLW (APG) is conservatively estimated at 4% of its initial content in the reprocessed spent nuclear fuel (SNF) [7]. Formation of soluble iodine species in glasses is evidenced by approximately equal leaching rates calculated both based on iodine and the main components for a variety of waste form materials considered as potential radioactive iodine retainers. However, lower leaching rates have been yet noted for some of the waste forms [16].

Under DGR conditions, iodine behavior is supposed to be strongly dependent on the redox potential of the contacting aqueous solution. The behavior of iodine species in VHLW leaching products largely depends on their interaction with the steel container corrosion products given water radiolysis caused by its interaction with VHLW. Basically, groundwater radiolysis is supposed to contribute to an oxidizing environment (see, for example, [17]) with iodine found in the form of I^- and IO_3^- ions. A similar phenomenon was studied in [18]. Interaction with the reducing bentonite zone is supposed to result predominantly in a iodide form — groundwater conditioned by bentonite is expected to have a pH level of 7.5–9 and iodine (with no account taken of impacts produced by container corrosion products and radiolysis) would transfer into its

iodide form (water composition according to [19], calculation implemented in the Spana software [20], Figure 1). It should be noted that in borosilicate VHLW waste forms, iodine tends to be present in the iodide ion form as well [21].



$T = 25\text{ }^\circ\text{C}$ [I^-]_{sum} = 10 $\mu\text{mol/L}$, [Ca^{2+}] = 1.21 mmol/L, [Na^+] = 1.4 mmol/L, [Mg^{2+}] = 0.49 mmol/L, [CO_3^{2-}] = 3.3 mmol/L, [SO_4^{2-}] = 0.16 mmol/L, [Cl^-] = 0.71 mmol/L, [K^+] = 0.12 mmol/L

Figure 1. Pourbaix diagram for iodine species (plotted in the Spana calculation code [20]; conditions predicted in the DGR zone are highlighted in yellow)

The solid mineral phase of silver iodide (AgI) accounts for most stable underground iodine form: in nature, it is represented by iodargyrite and iodirite minerals [22], [23] that can be viewed as natural analogues when considering the options for slowing down iodide release from VHLW. It should be noted that some literature sources report possible transition of colloidal silver iodide AgI found in VHLW into soluble species prompted by its reaction with natural sulfide ions resulting in very poorly soluble sulfide Ag_2S (as well as selenides) [24]. This phenomenon has been confirmed by our calculations implemented in the PHREEQC calculation code [25] (Table 1).

Table 1. Solubility in water (leachate) / bentonite water, mol/l

| Phase | Ag solubility in water (leachate) / bentonite water, mol/l | Formula |
|---|--|--------------------------|
| Silver phosphate, $\text{Ag}_3\text{PO}_{4(s)}$ | $8.36 \cdot 10^{-4}$ mol/l | Ag_3PO_4 |
| Silver sulfide, acanthite mineral | $3.24 \cdot 10^{-12}$ mol/l | Ag_2S |
| Silver iodide, mineral iodite | $1.0 \cdot 10^{-8}$ mol/l | AgI |

Another potential mechanism responsible for iodine mineralization accounts for its coprecipitation with phosphate minerals (in terms of oxides, phosphate amounts to over 50% of VHLW [11]). This glass type leaches with some considerable phosphate ion inventory (from tens to hundreds of mg/l) being released into solution potentially resulting in calcium phosphate formation upon its interaction with calcium found in bentonite. In radioiodine transport models, one should account for possible halogen-apatite formation ($\text{Ca}_5(\text{PO}_4)_3\text{X}$, X — OH, F, Cl, I), which cannot be excluded since apatites tend to form poorly soluble fluorapatites [26], [27]. Macro components get released from the APG waste form and this process is accompanied by potential secondary reactions occurring in the bentonite barrier mass: calcium get desorbed from bentonite with sodium ion being released from the waste form and hydroxyapatite (and, as mentioned above, probably haloapatites) being formed due to calcium interaction with phosphate ions, which provided the basis for the leaching model development in [28]. The effect produced by APG waste form leachates on the bentonite has been evaluated as well. Table 2 presents the modeling results describing the interaction of NKM water (1 dm³) with 1 kg of 10th Khutor grade bentonite. It can be seen that the saturation index is exceeded only for the hydroxyapatite indicating its potential precipitation upon bentonite — glass leachate interaction.

Table 2. Modelled saturation indices upon bentonite interaction with APG waste form leachates (leachate composition according to [28], PO_4^{3-} concentration — 2 mmol/l)

| Phase | SI | Formula |
|-----------------|---------|--|
| Berlinite | -11.729 | AlPO_4 |
| Brushite | -17.247 | $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ |
| Hydroxylapatite | 4.400 | $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ |
| Strengite | -11.604 | $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ |
| Vivianite | -16.383 | $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ |
| Whitlockite | -0.536 | $\text{Ca}_3(\text{PO}_4)_2$ |

$\text{SI} = \lg\text{PAI} - \lg\text{PR}$. PAI is the current product of ions in solution resulted from the corresponding mineral phase dissolution reaction, PR is the product of the solubility level for the corresponding mineral phase. $\text{SI} > 0$ — mineral phase formation is predicted, $\text{SI} < 0$ — mineral phase dissolution is predicted.

Iodine sorption on EBS materials

Iodine may sorb on the corrosion products of the carbon steel container, i. e., the first engineered

barrier reached by the radionuclides leached from the VHLW waste form. Due to bentonite, the key steel corrosion products account for highly crystallized iron oxyhydroxides, mainly magnetite, Fe_3O_4 [29]—[31].

I^- and IO_3^- ion sorption on hematite (Fe_2O_3) and kaolin was studied in [32]: in the expected pH range, the calculated K_d amounted to 0.6 cm³/g with the I^- sorption intensity being approximately 3,000 times lower than the one of iodate ion. For IO_3^- sorption on kaolin, a $K_d \approx 0.6$ cm³/g was obtained, whereas I^- was practically not sorbed by kaolin (K_d was less than the measurement error).

In near-neutral and slightly alkaline environments, for ferrihydrite, relevant $K_d(\text{I}^-)$ values accounting for its sorption on steel corrosion products varied from 0.2 cm³/g at pH = 7.4 [33] to 31.6 cm³/g at pH = 7 [34], the K_d values for hematite (Fe_2O_3) and goethite (FeOOH) were ranging from a few to tens of cm³/g with a tendency to decrease along with higher pH levels.

For iodate, the $K_d(\text{IO}_3^-)$ values appeared to be much higher, i. e., $n \cdot 10^{1-3}$ cm³/g for iron hydroxides [32], [35], [36]. Moreover, higher crystallization contributed to lower sorption degree. It was shown in [37] that trace amounts of radioactive ¹²⁵I can be effectively retained by illite seen as an accessory admixture commonly found in bentonite. In [38], chloride and iodide ion diffusion was studied assuming different ionic strength levels of the solution (0.01 M and 0.1 M NaClO_4) and different bentonite densities (0.4—1.8 g/cm³) and pH = 8, 2. $K_d(\text{I}^-)$ 2.9 ± 0.8 , 0.36 ± 0.04 and $K_d(\text{Cl}^-)$ 1 ± 0.5 , 0.2 ± 0.08 cm³/g were calculated for 0.01 M and 0.1 M NaClO_4 respectively. It should be noted that the K_d values for I^- appeared to be in good agreement with the data from [39], [40].

Another study [41] was focused on iodide and iodate transport through bentonite: concentrations of these ions varied from tens to hundreds of mg/l, whereas the K_d values were small accounting for only 0—0.03 cm³/g. It was found in [42] that iodine concentration in carbonated clays accounted for units of mg/kg with its concentration in water ranging from 20 to 40 μmol/l yielding a K_d of 0.2—2 cm³/g [43]. It should be also noted that higher iodine sorption on metallic copper can be expected in case of copper and copper-coated VHLW containers. In this case, K_d values are expected to range from 0.4 to 190 cm³/g [44].

Having considered the above factors, iodine released from VHLW may interact with the near field materials as shown in Figure 2.

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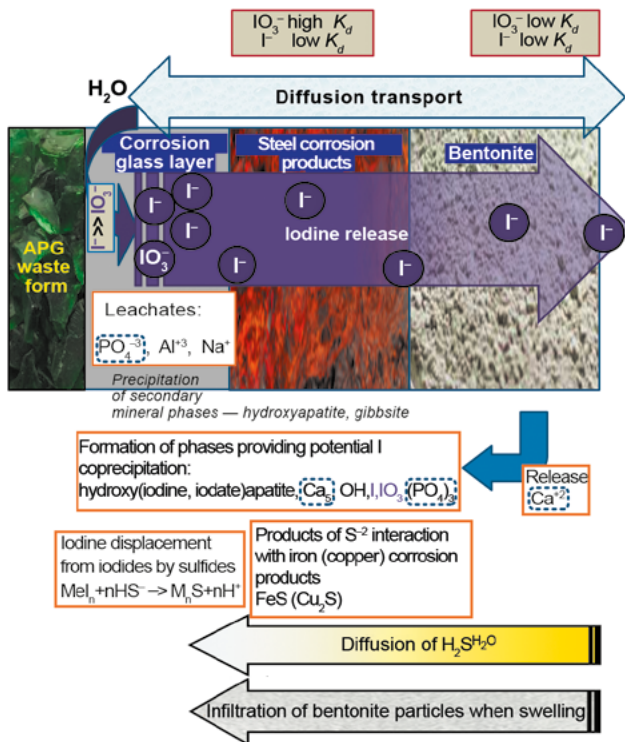


Figure 2. Interaction of iodine released from VHLW with near-field materials

Conclusions regarding the $K_d(^{129}\text{I})$ expected on the EBS materials

Iodine concentrations in VHLW and its species depend on iodine species present in SNF and the redox processes driven by SNF reprocessing and VHLW vitrification into APG waste form. Iodide is expected to account for the main iodine form in glasses. VHLW leaching provides for complex leachate interaction with container corrosion products and bentonite buffer occurring under radiolysis conditions with iodine potentially emerging in the form of both poorly sorbed iodides and relatively well sorbed iodates, the ratios between which are still unknown.

Assuming the above data, the $K_d(\text{I})$ expected in the near field of the Yeniseiskiy DGR may amount to $n \cdot (10^{-2} \dots 1) \text{ cm}^3/\text{g}$ with its reference value of $0.1 \text{ cm}^3/\text{g}$ assumed under further safety assessments.

Quantitative estimates of K_d influence on ^{129}I release beyond EBS

Sorption on buffer material (reference option)

An EBS typical for a DGR sited in crystalline rocks was considered in the assessments (Figure 3). The only exception was the VHLW container produced entirely of a carbon steel material. A hypothetical term source with ^{129}I specific activity of 10^6 Bq/kg weighting 1,500 kg was considered in the

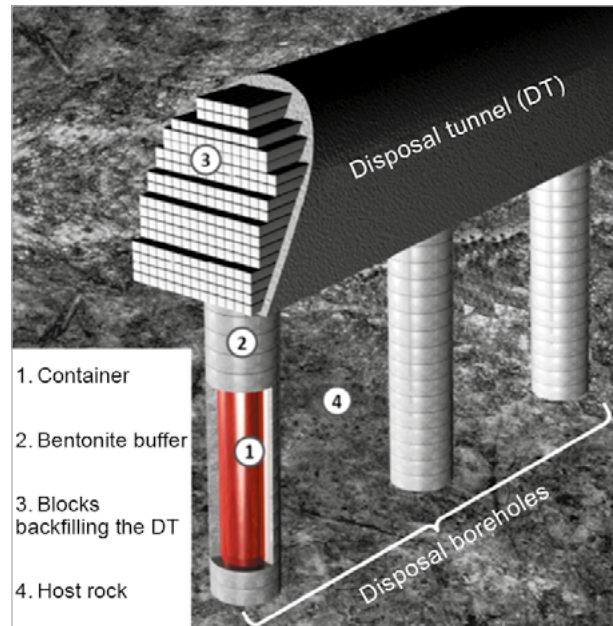


Figure 3. Illustration of the KBS-3V concept for SNF disposal in crystalline rocks [45]

assessment: it was assumed that it provided radioiodine release into a water layer filling the voids in the container at a constant rate of $1.3 \cdot 10^{-4} \text{ year}^{-1}$ (expected constant time of radioactivity release from the APG assuming the parameters of original VHLW packages considered for disposal¹). It was believed that the buffer density was sufficient to neglect the advective flow with the consideration given exclusively to the diffusion flow. Buffer characteristics were assumed as follows:

- thickness: 40 cm;
- dry density: $1,600 \text{ kg/m}^3$;
- open porosity: 0.044 by volume;
- effective diffusion coefficient: $3 \cdot 10^{-11} \text{ m}^2/\text{s}$.

In the calculation model, the bentonite buffer was divided into six concentric layers of equal thicknesses. Zero ^{129}I concentration was assumed for the outer surface of the bentonite buffer, i. e., iodine was totally released to the bentonite barrier surface getting instantly dissipated in the massif. Thus, the model excluded the influence that could be produced by the natural barrier, i. e., the host rock, on ^{129}I release. Figure 4 shows the ^{129}I released beyond the buffer.

It can be seen that assuming the K_d values in the range from 0 to $10 \text{ cm}^3/\text{g}$ considered for the buffer (with no selective sorbents being added), changes

¹ Assumed were the parameters of an integral model being currently developed by the Nuclear Safety Institute for the long-term DGR safety assessments. Model description and analysis go beyond the scope of this article. The results presented tend to be illustrative in their nature and are thought to provide comparative assessments of ^{129}I release beyond the bentonite buffer considering the observed K_d values.

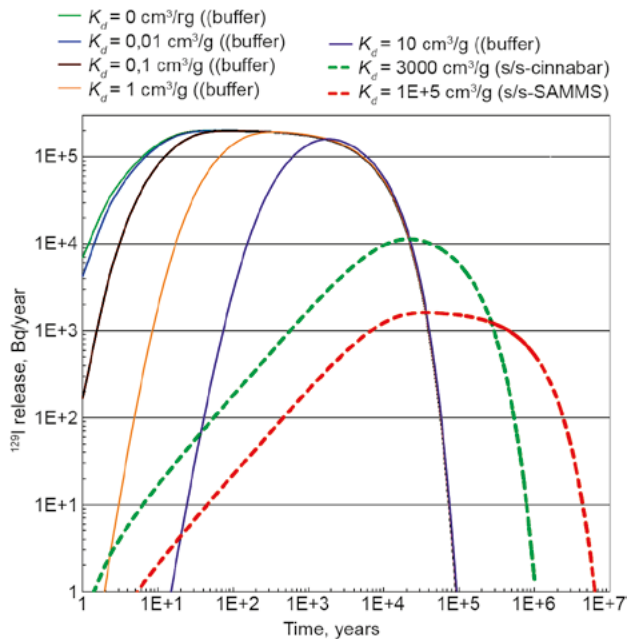


Figure 4. Time dependence for ^{129}I release beyond the bentonite buffer assuming different K_d values for the buffer and the selective sorbent (s/s)

in the maximum ^{129}I release responsible for the maximum potential exposure doses from the DGR were small amounting to approximately $\pm 30\%$ of the average value. In this case, given the long half-life of ^{129}I ($T_{1/2} = 1.57 \cdot 10^7$ years), sorption retardation of iodine releases by the bentonite buffer (by approximately 2,000 years assuming the maximum K_d value) appeared to be insignificant.

Considerations regarding the use of selective ^{129}I sorbents

The risks inherent in long-lived weakly sorbed radionuclides contributing to DGR radiation hazards in the long-term perspective have been recognized quite a long time ago with relative studies still ongoing to identify proper selective sorbents. Such materials should have the following characteristics:

- high interphase distribution coefficients for the selected nuclide and sufficient sorption capacity assuming its activities expected in the DGR;
- long-term stability under physical and chemical operating conditions assumed for a specific DGR;
- technically feasible methods providing material introduction into EBS;
- acceptable cost.

The gap volume available in a container intended for VHLW disposal in a DGR may vary depending on the engineering designs (2 or 3 cans with VHLW, waste disposal in old canisters or re-packaging), nevertheless amounting to no less than 100 liters. The option providing for such gap filling with a selective sorbent having a consistency similar to

the one of sand is being currently studied. Silver-activated bentonites [46], mercury (II) sulfide (cinnabar), mesoporous ceramic substrates or the so-called mesoporous quartz with self-assembled monolayers on mesoporous silica (SAMMS) can be used as selective sorbents for iodine retention [47]–[50]. The latter material contains quartz particles with a specific surface area of some $1,000 \text{ m}^2/\text{g}$ and a pore size of $2 \cdot 10^{-9}$ – $1 \cdot 10^{-8} \text{ m}$ being chemically modified by functional groups having high affinity for sorbed complexes or ions. $K_d(^{129}\text{I})$ values considered typical for cinnabar account for $\sim 3,000 \text{ cm}^3/\text{g}$; for SAMMS – 10^5 – $10^6 \text{ cm}^3/\text{g}$.

At present time, no data are available on the permeabilities of a backfill based on cinnabar and SAMMS. However, as a good approximation, one may assume that for these materials the effective diffusion coefficient of the aqueous phase would be close to the one of sand amounting to some $5 \cdot 10^{-10} \text{ m}^2/\text{s}$ given a porosity of 0.3. The bulk density of cinnabar would amount to $5,700 \text{ kg}/\text{m}^3$, the one of SAMMS – to $1,400 \text{ kg}/\text{m}^3$.

Time dependency for ^{129}I release beyond the bentonite buffer was repeatedly calculated for the same model assuming the container voids filled not with water, but with a saturated selective sorbent with K_d values of $3,000 \text{ cm}^3/\text{g}$ (cinnabar) and $10^5 \text{ cm}^3/\text{g}$ (SAMMS). The results obtained are also shown in Figure 4.

Figure 4 shows that under long-term DGR conditions, selective sorbent added to a VHLW package may considerably reduce ^{129}I release into the environment. In this case, the maximum ^{129}I release can be reduced by approximately 2 orders of magnitude compared to the option providing for the void filling with water. However, to demonstrate the feasibility of selective sorbent application in EBS elements, one should further study their durability and compatibility with other materials assuming various physicochemical and biological influences expected in a particular DGR.

Chemical stability of a cinnabar-based sorbent can be judged by natural minerals having similar chemical composition, for example, pyrites and chalcopyrites. These sulfide rocks can undergo oxidation resulting in highly soluble compounds, which in turn may prompt the release of the sorbed iodine. The oxidation rate depends on the activity of dissolved oxygen and ferric ions and appears to be much higher in the presence of an aqueous phase. Assuming sorbent emplacement into VHLW containers, aqueous phase radiolysis should be considered with its products also contributing to higher oxidizing ability of the medium.

However, the VHLW acceptability criteria for disposal suggest that the initial liquid phase content

in a container is extremely small. In the absence of extreme external influences, natural water inflow into the internal space of a package is expected only in a long-term perspective (not earlier than in 10,000 years even considering the least resistant steel container designs [51]), when the residual VHLW radioactivity and the oxygen content preserved in the DGR at the post-closure stage is supposed to drop considerably. Therefore, no considerable ^{129}I release from the packages is expected in the long term.

The long-term chemical stability of the new SAMMS-type materials has not been specifically studied. However, based on the following facts it can be basically expected that their chemical stability should not be inferior to those of mineral sulfides [47]:

- the inert quartz waste form appears to be insensitive to changing redox properties of the environment;
- functional molecular SAMMS layers have sufficiently high stability given slight changes in the pH levels of the environment;
- SAMMS functional groups are contained in small-diameter pores being inaccessible to microbial activity.

Moreover, the use of bentonite may virtually eliminate the inflows of hazardous chemical compounds and biota into containers with groundwater flows given its matrix density contributing to a swelling pressure of over 1.65–2 MPa [52], [53].

Conclusion

Low sorption coefficients identified for steel container corrosion products and the bentonite buffer provide no considerable ^{129}I retardation nor decrease the rate of its release beyond the engineered barrier system. However, specifically selected selective sorbents with their interphase distribution coefficients being several orders of magnitude greater may nevertheless considerably reduce ^{129}I releases beyond the EBS. Their use in DGR EBS designs seems yet restrained by the required demonstration of their long-term stability. However, preliminary studies have revealed certain prospects in this area and the feasibility of further research assuming the conditions expected in a DGR.

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