

Nuclear Waste Management: Recycling and Long-term Safe Storage

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Abstract

Nuclear energy production generates nuclear waste. Nuclear and radioactive waste, especially high level waste (HLW) and intermediate level waste (ILW), require special long-term safe management solutions. One part of the solution involves recycling through reprocessing of spent nuclear fuel. Recycling reduces the volume of nuclear waste and allows for the reuse of some of its components. This can be achieved through methods such as adsorption, ion exchange, coagulation, flotation, filtration, chemical precipitation, reverse osmosis, and solvent extraction, like the PUREX process. Another possible future solution involves partitioning and transmutation technology, which can reduce the production of nuclear waste. The best long-term solution is the immobilisation of HLW and ILW in a solid matrix. Materials used for this purpose include glasses, cements, bitumen, geopolymers, concrete, and ceramics as a promising material. While cementation is still the most commonly used immobilisation method due to its low cost and simplicity, vitrification is a more permanent long-term solution. Deep geological disposal in combination with vitrification and a robust multi-barrier system is considered the most acceptable solution for safe nuclear waste isolation. This review provides insight into the mostly commonly used and promising immobilisation materials, as well as the most effective methods and technologies currently in use and under development for the management of HLW and ILW in nuclear waste management.

Keywords

Nuclear waste, cementation, vitrification, deep geological disposal, recycling, PUREX

1 Introduction

The demand for and consumption of energy is constantly growing with the technological progress of society. In most countries, environmental impact, such as pollution and CO₂ emissions, plays a significant role in the choice of energy production methods. Uranium mining and milling do produce certain CO₂ emissions, but the overall amount per kWh of nuclear energy produced is negligible.¹ The main uranium producers are Kazakhstan, Canada, Australia, Namibia, Niger, Russia, Uzbekistan, China, Ukraine, and USA. Other significant advantages of nuclear energy, when compared to clean forms of renewable energy like solar, wind, hydropower, marine, and geothermal, are that it is well-controlled, sustainable, not dependent on environmental conditions, and does not require a large area. The major disadvantage of nuclear energy is that it generates nuclear waste, although the amount is considerably smaller than, for example, the waste generated by coal power stations.² At the moment, between 10 and 20 % of electrical energy produced originates from nuclear energy, with most nuclear reactors using oxide-based fuels, such as uranium oxide (UOX), and mixed uranium and plutonium oxide (MOX). Countries with the largest number of nuclear power plants (NPP) are the USA (93 + 2 under construction), France (56 + 1 under construction), China (54 + 14 under construction), Russia (38 + 4 under construction), Japan (33 + 2 under construction), India (23 + 6 under construction), Canada (19), Ukraine (15 + 2 under construction),

and the UK (11 + 2 under construction). The Republic of Croatia is at the bottom of this list, sharing ownership of the Krško NPP with Slovenia. More than 60 % of all nuclear power plants are over 30 years old and nearing the end of their operational life and the decommissioning process.³ This requires adequate nuclear waste management solutions and future plans for construction of efficient next-generation nuclear reactors that will produce less or no nuclear waste.

2 Nuclear waste

Nuclear waste is classified into three categories: high level waste (HLW) that originates from nuclear fuel use and nuclear weapons production (U, Pu and ³H) and has very high activity and produces heat; intermediate level waste (ILW), which also has significantly high activity and, like HLW, requires special handling and processing considerations (usually including nuclear reactor components, contaminated parts left over after decommissioning, different contaminated by-products and parts like sludge, resins, filters, decontamination residues, etc.); and low level waste (LLW) which has low activity, produces no heat and requires no special considerations (usually originating from research laboratories, hospitals, industry, and military defence use).^{2,4} In the spirit of responsible usage of limited resources and achievement of sustainability, spent nuclear fuel and other radioactive waste should be partially recycled as much as possible, allowing for their efficient reuse, be it

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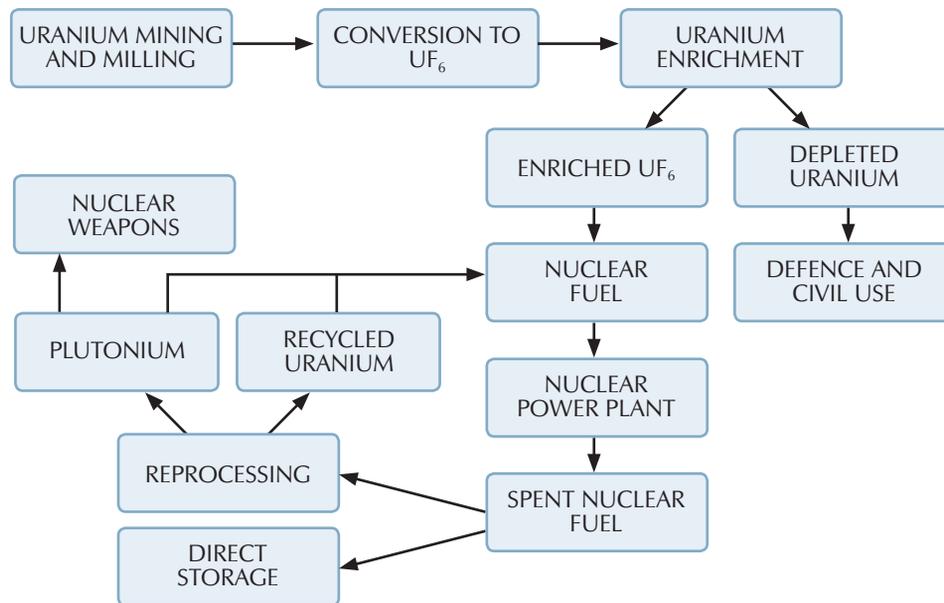


Fig. 1 – Nuclear fuel cycle⁵

Slika 1 – Nuklearni gorivni ciklus⁵

for energy production or other applications like research, industry, medicine, and more. Recycling spent nuclear fuel can reduce waste volume up to 6 % and decrease isolation time of residual waste by a factor of 100.³ The downside of nuclear waste recycling is the resulting HLW, which necessitates proper management. Fig. 1 shows the nuclear fuel cycle and the possibilities for its reuse and exploitation.

Besides HLW, there is also a significant amount of other ILW and LLW produced as a result of growing worldwide use of a wide range of different radioisotopes (such as in medicine, industry, agriculture, research, military, new technologies, etc.). All such residual radioactive waste requires adequate solutions for long-term safe management. In accordance with the European Union (EU) Council Directive 2011/70/Euratom of 19 July 2011, establishing a Community framework for the responsible and safe management of spent fuel and radioactive waste, all EU states should have in place a national policy and programmes for spent nuclear fuel and radioactive waste management.⁶ In the Republic of Croatia, there are currently approximately 13 m³ of various used low and intermediate-activity, short and long-lived radioactive sources, as well as institutional radioactive waste. By the year 2060, this volume is expected to reach 100 m³. As a solution, the Republic of Croatia has established the *Centre for the Disposal of Radioactive Waste*, which is intended to store only LLW and ILW from industry, hospitals, research laboratories, and Krško NPP. This Centre is not intended for the storage or disposal of spent nuclear fuel from Krško NPP.⁷ After the end of the Krško NPP's operational life, the Republic of Croatia is responsible for the disposal of 50 % of its HLW (around 3000 m³ of waste from reactor operation and future decommissioning). Therefore, it is necessary to find a solution for this problem as soon as possible.⁸

3 Recycling of spent nuclear fuel

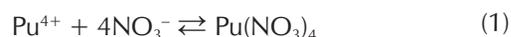
Spent nuclear fuel, after cooling, can be either directly disposed of in a repository for nuclear waste (open fuel cycle) or it can be processed and reused (closed and advanced fuel cycles). Conventional methods used for removal of heavy metals, lanthanides, and actinides from nuclear waste aqueous solutions include adsorption, ion exchange, coagulation, flotation, filtration, chemical precipitation, and reverse osmosis.⁹ Natural and synthetic zeolites (aluminosilicates) exhibit good properties for removal of radionuclides from aqueous solutions by ion exchange.^{9,10} An example of this application is the use of chabazite-type zeolite, which was successfully employed for the removal of ¹³⁴Cs, ¹³⁵Cs, and ¹³⁷Cs from contaminated water after the accident at the Fukushima Daiichi NPP. Kimura *et al.* demonstrated that the remaining zeolite with adsorbed Cs could be successfully vitrified in borosilicate glass containing H₃BO₃, Na₂CO₃ or Na₂B₄O₇ modifiers.¹¹ The downside of this kind of vitrification is the partial release of Cs due to its volatile nature, as demonstrated by Charpin *et al.*, who showed that, during vitrification, aggregated nano- and micro-sized particles containing Cs are formed in the melter.¹² Activated carbon exhibits a good nuclear waste adsorption capacity, and due to their properties, metal-organic frameworks (MOFs) also show excellent potential for the removal of lanthanides and actinides. MOF is a relatively new material that consists of an inorganic core with metal ion centres connected to organic ligands forming a branched network. By varying the metal ions and ligands, MOFs with different cavity sizes and properties can be synthesised. Properties like high porosity and very large surface area make MOFs an excellent selective adsorption material.¹³ The positive aspect of adsorption is that, unlike various extraction processes that will be described

later, it does not require the use of (hazardous) organic solvents which generate additional radioactive waste that needs appropriate disposal. Additional good properties of these molecular trap adsorbents are that they are relatively cheap and reusable without losing their capacity.¹⁴ The mechanism of radionuclides adsorption in MOFs occurs either by cation exchange with the metal ion centre, coordination to organic ligands, or capture within the MOF cavities.¹⁵ UiO-66, ZIF (zeolitic imidazolate framework), and MIL (Materials of Institute Lavoisier) based MOFs are just a few examples studied for radionuclide separation application.¹⁶ *Elsaidi et al.* researched a set of SIFSIX-3-M (M = Zn, Cu, Ni, Co, Fe) MOFs. They demonstrated that SIFSIX-3-Cu has good β and γ stability for absorbed doses up to 50 kGy, and significantly high potential for ⁸⁵Kr separation.¹⁷ A study by *Li et al.* showed that molecular trap adsorbents based on MIL-101-Cr MOF, functionalised by grafting with different tertiary amine groups, demonstrate good potential for radioactive organic iodide adsorption on the industrial scale. *Feng et al.* inserted silver nanoparticles (AgNP) in UiO-66 MOF, and showed that the resulting MOF also had good adsorption properties for radioactive iodine removal.¹⁸ *Shen et al.* proposed a solution for the removal of very problematic volatile long-lived β emitter ⁹⁹Tc, which is in aqueous solution mainly present in ⁹⁹TcO₄⁻ form. They synthesised 2D cationic SCU-103 based MOF with Ni²⁺ ions and nitrogen ligand tris[4-(1H-imidazol-1-yl)-phenyl]amine, and showed that it is very stable in highly alkaline media, resistant to high doses of β and γ ionising radiation, and has excellent selective adsorption properties for ⁹⁹TcO₄⁻ removal.¹⁹ Another material considered for radionuclides removal is carbon nanotubes (CNTs) due to their capability to retain a wide range of different substances (water, aqueous solutions, biomolecules, polymers, nanoparticles, etc.). Although CNTs present a promising material for preconcentration and solidification of nuclear waste, further research regarding CNT behaviour and properties is needed to confirm their actual application.⁹

Some countries reprocess spent nuclear fuel using the most commonly employed PUREX (plutonium uranium refining by extraction) process based on liquid-liquid solvent extraction. Through this process, both U and Pu are recycled into a mixed oxide (MOX) form, namely UO₂ and PuO₂, and can be reused in light water and fast reactors. The obtained MOX accounts for approx. 5 % of the total new nuclear fuel produced. The main producers of MOX fuel are France, Russia, India, and Japan.^{3,20,21} The challenging aspect of MOX fuel is the generation of ²⁴¹Am from ²⁴¹Pu, resulting in slightly higher activity of MOX fuel compared to initial UOX fuel activity.²

Prior to the PUREX process, spent nuclear fuel is cooled for a minimum of 5 years. The first step in the process involves dissolving the fuel in aqueous nitric acid. The resulting nitrate solution contains U, Pu, minor actinides and fission products. This solution is then processed to attain the desired U concentration, acidity, and Pu valency. In addition, I, Kr, and Xe isotopes undergo off-gassing treatment. During this step, some fission products, along with a certain amount of fuel, remain undissolved. The second step involves solvent extraction, in which a separation occurs between the aqueous nitric acid and organic tri-*n*-butyl phos-

phate diluted with *n*-paraffin phases. The result of this step is the separation of U(VI) and Pu(IV) in the form of nitrate complexes from fission products and minor actinides.^{21–23}



The organic phase containing U and Pu is further processed facilitating their separation. During this step, Pu(IV) is reduced to Pu(III) using U(IV) and transfers to the aqueous phase, while U(VI) remains in the organic phase.



To prevent oxidation of the formed Pu³⁺ by nitric acid, a scavenger, hydrazine, is added.

The obtained U solution undergoes a thermal denitration process, while the Pu solution is subjected to oxalate precipitation and calcination to produce solid forms. Soluble nonradioactive compounds are removed from the sludge, and the remaining HLW solution, which contains fission products, minor actinides, corrosion products, process additives, fuel additives, residual coating material, and other impurities, is concentrated through evaporation. Afterward, it is vitrified along with the undissolved fission products and fuel. The vitrification process will be discussed later herein. Additionally, formic acid is used for the removal of organic material. If chosen, recovery of ¹³⁷Cs, ¹³⁵Cs, and ⁹⁹Tc isotopes can be achieved through filtration after precipitation with sodium tetraphenylborate in combination with sodium titanate, which adsorbs any remaining Pu and Sr.^{21–25} Apart from PUREX, other separation processes are also utilised. Examples of both established and still-developing separation processes for actinides and lanthanides include: DIAMEX (extractant: malonamide), TRUOX (extractant: octyl-phenyl-di-isobutyl-carbamoylmethyl-phosphine-oxide), SANEX (extractant: dialkyldithiophosphinic acid), TRPO (extractant: mixture of tri-alkyl phosphine oxides), TALSPEAK (extractant: di-2-ethyl-hexyl-phosphoric acid; complexing agent: diethylene-triamine-penta-acetic acid), SESAME (oxidising agent ammonium persulphate or heteropolyanions as catalyst; extractant: tri-*n*-butyl phosphate), DIDPA (extractant: di-*iso*-decyl phosphoric acid), HDEHP (extractant: di-2-ethyl-hexyl-phosphoric acid), TPTZ (extractant: tripyridyltriazine with di-nonyl-naphthalenesulfonic acid), CYANEX (extractant: mixture of phosphonic and phosphinic acids), SREX (extractant: dicyclohexano 18-crown-6 ether), and TRAMEX (extractant: tertiary amine). The primary concern with the PUREX process is the acquisition of Pu, which could be misused for nuclear weapons production. To address this problem, various separation processes, such as COEX (combined U and Pu extraction), GANEX (grouped actinide extraction), and UREX (uranium extraction) are being developed.^{26–35}

Alongside the separation process, partitioning and transmutation technology is one of the potential future solutions for nuclear waste management. This technology is based on the quantitative recycling of long-lived and highly radiotoxic nuclides through pyrometallurgical processing to create new fuel for use in advanced fast-neutron reactors.

The result is a significant reduction in radiotoxicity by a factor of 100 to 200 and a decrease in the amount of produced nuclear waste. However, this promising technology is still in the research and development phase. Currently, the most feasible technical solution involves aqueous reprocessing and sodium-cooled fast reactor technology. However, numerous challenges have yet to be addressed for the partitioning and transmutation technology to transition from the laboratory to an industrial and commercial scale.^{28,29,36}

4 Materials for nuclear waste immobilisation in a solid matrix

Immobilisation in a solid matrix is the most acceptable long-term solution for HLW and ILW management. The choice of material for this purpose depends on the composition of nuclear waste. Nuclear waste composition depends on the physical and chemical properties of the initial nuclear fuel and on the duration of its use in a nuclear reactor, where prolonged use produces unstable isotopes.³ Desirable properties of an ideal HLW immobilisation matrix include thermal stability, high immobilisation capacity (up to 45 wt. %) to minimise waste volume, long physical and chemical stability, existence of natural analogues confirming long-term durability, resistance to ionising radiation and corrosion, chemical compatibility with a wide range of components and with other materials in contact, simple, safe, and cost-effective industrial-scale production, and the formation of a solid material that is easy to transport and store.^{2,37–39} The most commonly used immobilization materials for HLW include glasses, ceramics, and metal containers. For ILW, materials include glasses, bitumen, cements, geopolymers, high-integrity containers, concrete, and metal containers. LLW utilises the same materials as ILW with the exception of glasses.³⁸ Bitumen is used to immobilise more than 200 000 m³ of radioactive waste (mostly sludge and resins). Polymers are less frequently used, while ceramics are an emerging material with significant potential, and will be discussed further herein.^{39,40}

The main techniques used for immobilisation of various hazardous waste are physical containment as a short-term solution, cost-effective solidification/stabilisation methods like cementation as a medium-term solution, and vitrification as a more expensive but permanent solution.⁴¹ Worldwide, the most commonly used immobilisation methods for nuclear waste management are cementation and vitrification.

4.1 Cements and cementation process

While the vitrification technique has several advantages, as we will discuss later, the most commonly used method for nuclear waste management remains pouring concrete around nuclear waste placed in encapsulating containers or mixing nuclear waste and cement, usually in a 1 : 1 ratio. Nuclear waste is either chemically fixed in an insoluble form, physically adsorbed or physically trapped (encapsulated) in a cement matrix.^{4,42} In the case of pour-

ing concrete around nuclear waste placed in a container, it is important to consider possible corrosion of the container. *Duffó et al.* showed that steel containers corrode when in contact with used cation-exchange resins due to sulphate ions formed by radiolysis, and also when in contact with incineration ashes containing corrosive chloride ions.⁴³ At Krško NPP, nuclear waste management primarily involves solidification (immobilization) by cementation, together with radioactive waste processing that includes filtering, evaporation and barrel drying, burning (performed abroad), and barrel supercompaction.⁴⁴ The main advantages of this method are its low cost and simplicity for a wide range of nuclear wastes, as well as its effective radiation shielding. The disadvantages of cementation include increased waste volume, weak mechanical durability, potential corrosion when exposed to environmental conditions, and large amounts of CO₂ emissions during cement production.^{2,4,38,42} Portland cement is most commonly used for nuclear waste cementation. It consists of a Ca, Al, and Si matrix and includes different combinations of ground clinker mixed with limestone or granulated blast furnace slag, gypsum, and other additives. The most commonly used cement types include CEM I, CEM III and CEM V.^{2,45} The addition or presence of different compounds can have both positive and negative impacts on cement. For example, metal cations Zn²⁺, Pb²⁺, Cd²⁺, and Cr³⁺ reduce the strength of cement. Na and K salts, Na₂SiO₄ and thiosulphate act as accelerators. Carbonates, hydroxides, aluminates, silicates, and H₃BO₃ accelerate setting but retard solidification. CaCl₂ acts as a retarder, Li salts (except Li₂BO₂) and sulfuric acid are accelerators. CaSO₄ anhydrite acts as retarder, and hemihydrate as an accelerator. Small quantities (< 0.1 %) of alkali carbonates retard setting while larger quantities cause rapid setting. Conversely, ZnSO₄ at small quantities (< 2.5 %) acts as an accelerator and at larger quantities (2.5–5.5 %) as a retarder. Chlorides, sulphates, carbonates, increased quantities of MgO, and formation of gas can destroy the cement matrix. Sugars and triethanolamine can act as both retarders and accelerators, and polar organic solvents are larger retarders than non-polar ones.⁴ In addition to modified Portland cements, other researched materials that show good potential for nuclear waste cementation include calcium aluminate cement (CAC), calcium sulphotoaluminate cements (CSAC), magnesium potassium phosphate cement (MKPC), magnesium phosphate cement (MPC), calcium phosphate cement (CPC), magnesium silicate cement (M-S-H) and alkali-activated cement (geopolymer concrete made by mixing aluminosilicate from natural or waste byproduct sources like fly ash, ground granulated blast furnace slag (GGBFS), and metakaolin with alkaline activator).^{4,42,46–48}

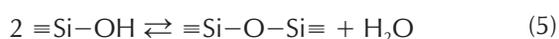
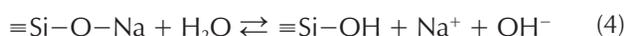
4.2 Glasses and the vitrification process

Because glasses closely meet all required properties, they provide a very good matrix for nuclear waste management. The main requirements for glass intended for immobilisation are long durability (thousands of years), good solubility for a wide range of nuclear waste components, relatively low melting temperatures, and resistance to corrosion from the melter system. Borosilicate glasses fulfil all these requirements and are suitable for the technological

process.^{24,49} Adding alkaline oxides to borosilicate glasses transforms $[\text{BO}_3]$ groups into more stable $[\text{BO}_4]$ groups, resulting in a stronger glass network and greater durability. This effect can be also achieved by adding PbO , and in the case of SrTiO_3 alumina borate glasses, by adding P_2O_5 .³⁸ There is an initiative to standardise the composition of glass used for HLW immobilisation. The proposed standard borosilicate glass to be used internationally is called International Simple Glass (ISG), and has the following composition (in mol %): 60.2 % SiO_2 , 16.0 % B_2O_3 , 12.6 % Na_2O , 3.8 % Al_2O_3 , 5.7 % CaO , and 1.7 % ZrO_2 .⁵⁰ Elements that are problematic to incorporate into the borosilicate glass matrix include Mo, S, rare earth elements, Ru, Rh, and Pd.⁵¹ *Krishnamurthy and Kroeker* showed that Mo and S cause their crystalline separation in the form of molybdates and sulphates from aluminoborosilicate glasses. However, when P_2O_5 is added to the glass, they become fully integrated into the glass matrix.⁵² In general, conducted studies show a link between oxidation state of cations and solubility in aluminoborosilicate glasses, with a higher oxidation state resulting in lower solubility. Examples of such cations include Mo^{6+} , Tc^{4+} , Tc^{7+} , S^{6+} , Ce^{4+} , Pu^{4+} , U^{4+} , Th^{4+} , Np^{4+} , Am^{3+} , and Cm^{3+} . Besides cations, elemental metals such as Ru, Pd, Rh, Ag, Mo, as well as anions Cl^- , I^- , also exhibit low solubility.⁵³ Apart from the most commonly used borosilicate, other glass compositions are also being considered for nuclear waste immobilisation. For example, *Erdogan et al.* studied $\text{PbO}-\text{B}_2\text{O}_3$ glasses and found that a composition with a high 80 % PbO content has good potential as a vitrification matrix.⁵⁴ Another example with great potential is iron polyphosphate glasses.⁵⁵

The drawback of glasses, regardless of their composition, is that they are partially prone to dissolution in aqueous solutions. Glass corrosion in the presence of water is an important factor that needs to be considered in case of a multi-barrier system breach so that the behaviour and possible negative consequences could be predicted and prevented. This glass corrosion process is referred to as leaching and results in a hydrated surface layer that is several dozen nm thick. It involves the diffusion of water, changes in $\text{Si}-\text{O}-\text{M}$ bonds ($\text{M} = \text{Si}, \text{Al}, \text{Zr}, \text{Fe}, \text{Zn}, \text{etc.}$), and proton ion exchange processes of $\text{Si}-\text{O}-\text{Si}$ network modifiers like alkali ions (e.g., Na), alkaline earth ions (e.g., Ca, Mg), and Al, resulting in an increased pH value of the solution. Ion exchange of alkali ions is faster than in the case of alkaline earth ions and Al, and depending on the amount of these modifiers, the pH can reach values from 9 up to 12.^{50,56-58} As a result of ion exchange during leaching, immobilised alkaline radionuclides ^{135}Cs and ^{137}Cs , and alkaline earth radionuclide ^{90}Sr , are also removed from the glass surface layer. Other radionuclides can also be affected by this process, such as europium, where $\text{Eu}-\text{O}-\text{B}$ bonds transform into $\text{Eu}-\text{O}-\text{Al}$ bonds.⁵⁸

Chemical processes that occur during leaching are proton ion exchange and acid-base reaction with diffused water.^{57,58} Example for glass containing sodium is given.



During this process when one sodium (alkali) ion is released, three hydrogen ions are incorporated into the glass network. The number of water molecules that will diffuse into the glass depends on the number of released sodium (alkali) ions. Formed $\text{Si}-\text{O}-\text{Si}$ bonds will stabilize the hydrated surface layer and release water molecules.⁵⁸

Besides direct contact with liquid water, the presence of unsaturated water vapour should also be considered because it reacts with the glass surface and affects leaching.⁵⁷ Exposure to unsaturated water vapour in deep geological disposal depots is highly probable, and if the multi-barrier system is inadequate after a long period of exposure, this could have a negative impact on glass durability. *Chaou et al.* found that, in the case of increased temperatures and relative humidity, the hydration of glass increases, resulting in the formation of a gel layer on the surface and release of glass modifiers (in their case study, alkali ions).⁵⁹

The effects of glass corrosion highly depend on the conditions, but the end results are a consequence of four corrosion stages with different kinetic regimes: initial dissolution rate, rate drop, residual rate, and alteration resumption (Fig. 2).⁶⁰ As seen in Fig. 2, diffusion of water and ion exchange rates relatively quickly decrease and transition to stable state, where equilibrium is reached between diffusion, ion exchange, and dissolution.⁵⁸ Some scientists do not consider rate drop as a separate corrosion stage (kinetic regime), but as a transition between initial dissolution and residual rate.²⁵

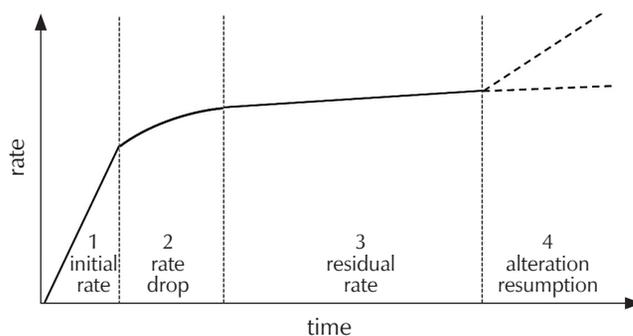


Fig. 2 – Kinetics of glass corrosion process⁵⁰

Slika 2 – Kinetika procesa korozije stakla⁵⁰

Rate of leaching in glass is calculated by the following equation:³⁸

$$L = \frac{m_0 - m_t}{S \cdot t} \quad (6)$$

where m_0 is initial sample mass, m_t is final sample mass after leaching, S is sample surface area, and t is duration of leaching. Leaching rate is usually expressed in $[\text{g m}^{-2} \text{ day}^{-1}]$ unit. Ranges of leaching rates for different materials used for nuclear waste immobilisation are shown in Table 1.

Table 1 – Leaching rates of different immobilisation materials³⁹
 Tablica 1 – Brzine ispiranja različitih materijala za imobilizaciju³⁹

Material	Approximate range of normalised leaching rates/g cm ⁻² day ⁻¹
calcine	10 ⁻¹ –10 ⁻²
cements	10 ⁻¹ –10 ⁻⁵
ceramics	10 ⁻² –10 ⁻⁸
bitumen	10 ⁻³ –10 ⁻⁶
borosilicate glasses	10 ⁻⁴ –10 ⁻⁷
phosphate glasses	10 ⁻⁴ –10 ⁻⁸

The leaching process is highly complex in multicomponent silicate glass systems.⁶¹ This includes glasses used for nuclear waste immobilisation, which in addition to the main Si and B components, contain more than 30 other elements from various sources, such as Li, Na, K, Ca, Zn, Al, S; fission products and actinides like Cs, Sr, Tc, La, Nd, Pr, Mo, Zr, Np, etc.; corrosion products like Fe, Mn, Co, Cr, Ni; residual coating material like Mg, Al, Fe, Zr; and additives for oxide fuel reprocessing like Gd). Studies have shown that high concentrations of elements Si, Zr, Al, and Ln have a positive impact on increasing glass durability, whereas high concentrations of alkali elements B and Mg, have a negative impact, reducing glass durability. For some elements, the impact depends on their concentration and conditions. The best example is Al, which has a negative impact when present in excessively high concentrations.^{62,63}

The average value of the equivalent dose rate at the surface of the spent nuclear fuel exceeds 100 Sv h⁻¹, or in other words, spent nuclear fuel has six orders of magnitude greater activity than the initial UOX fuel.^{2,3} The most hazardous radionuclides in spent nuclear fuel come from elements such as Pu, Np, Am, Cm, I, and Tc.⁶⁴ If these radionuclides enter in an organism, they will mainly cause bone, liver or lung cancer.⁶⁵ When deposited in glass, radionuclides will form chemical bonds with oxygen atoms in the glass network, creating an amorphous so-called gel layer at the glass surface, forming crystalline phases or remaining in aqueous form.^{50,57} Like any other material, ionising radiation (α , β , and γ) produced by nuclear decay products will cause certain damage to the glass. Ionising radiation can cause volume change, radiolytic decomposition, formation of oxygen and helium bubbles, decreased hardness, and increased fractures.⁶⁶ The most destructive effects are caused by α decay, especially by long-lived actinides like Am, U, Np, Pu, and Cm, and can cause amorphisation and swelling, leading to microfractures. Fission products that produce β and γ radiation also have a negative impact inducing bond ruptures, electron excitation, causing changes in valence and ionic mobility, as well as the formation of oxygen bubbles, and at very high doses, phase separation.^{67,68} McGann *et al.* showed that γ -radiation, up to absorbed doses of 8 MGy, had no significant effect on the glass network and mechanical properties of the selected high Fe-content alkali-borosilicate glasses. They attributed this mainly to oxidation of Fe²⁺ to Fe³⁺ as a result of γ -radi-

ation-created electron-holes annihilation, where Fe acts as a self-healing element for the glass.⁶⁸ This effect is not seen in low Fe-content alkali-borosilicate glasses, but the results that Jiménez *et al.* obtained after 0.95 MGy γ -irradiation of ISG nuclear waste, glass simulants with low Fe content indicated no significant changes in structural, chemical, and thermal properties.⁶⁹ On the other hand, Zhang *et al.* showed that when exposed to γ -radiation, borosilicate glasses remain stable up to absorbed doses of 800 kGy, but at higher doses, structural changes occur as a result of bond ruptures and surface particle release. In their case, they observed the release of Na, O, and B, but the type of particles released depends on the glass composition.⁷⁰ The resulting damage to the glass network caused by ionising radiation can have a negative impact on the leaching rate of the glass material, especially if fractures appear on the glass surface. Therefore, glass composition (including immobilised HLW) and structural state, in combination with chemical and physical leaching conditions like temperature and pH, play a crucial role.^{50,61,62,71–73} For example, Ledieu *et al.* showed that the leaching rate in sodium borosilicate glasses strongly depends on the content of boron and sodium oxides.⁶²

Some important mechanical properties of glasses used for nuclear waste include Young's modulus, Poisson's ratio, hardness, toughness, and brittleness.⁷⁴ Chen *et al.* studied sodium borosilicate glasses with different compositions and ISG glass, and found that after a certain dose, ionising radiation no longer had an impact on the hardness, Young's modulus, and volume changes. This impact is the same regardless of glass composition, except in the case of volume change.⁷² Previous studies have shown that alpha decay causes ± 1.2 % volume changes.⁶⁶ Wang *et al.* showed that ionising radiation causes an increased number of non-bridging oxygens, resulting in defects in the glass structure.⁷⁵ On the other hand, Chen *et al.* showed that crack resistance greatly increases after irradiation. In addition, they found that structural changes occur mainly because of the boron, as a result of [BO₄] transformation into [BO₃].⁷² In addition to glass, the impact of ionising radiation, especially of γ , should be considered if groundwater is present in vicinity of the deep geological disposal. Radiolysis of water exposed to γ radiation will form free radicals •OH, •H and •HO₂, hydrated electrons, H₃O⁺, OH⁻, and molecular species H₂ and H₂O₂, which can subsequently react with other species in contact.^{76,77}

The temperature in the centre of the container where the HLW is initially placed reaches around 290 °C, and drops to around 140 °C after 80 years.⁶⁷ Heat produced by decay of ¹³⁴Cs, ¹³⁷Cs, ⁹⁰Sr, and transuranics can cause phase changes in glass if values close to glass transition temperature are reached. In conditions of elevated temperature, ionising radiation can induce chemical decomposition, phase separation (most often at microscopic scale), and formation of bubbles. As a result, in addition to the dose rate, the heat produced by decay is the limiting factor for maximum immobilisation capacity.^{67,78} This issue must especially be considered for containers in which glass is placed to ensure the proper dispersion of decay-generated heat or self-heating that will last for at least 600 years.⁶⁷ On the other hand, it has been shown that borosilicate

glasses exhibit self-healing properties when exposed to α , β , and γ ionising radiation, and there is a possibility that high β and γ doses may significantly reduce glass transition temperature.^{60,78}

Finally, it should be emphasised that there are still many unknown mechanisms regarding how glasses behave under certain conditions, and there are some contradictory results in studies. All of the predicted estimates are a result of examples of glass present in nature, and experiments in simulated conditions combined with kinetic and geochemical models simulations.^{58,79}

4.2.1 Vitrification

Vitrification is primarily used for HLW immobilisation, but it recently showed potential for ILW immobilisation as well.^{80,81} In this process, glass frit is melted with nuclear waste, and at the end of the vitrification process, radionuclides are chemically immobilized within the glass network.² Problematic elements for the vitrification process include I, Xe, Kr, Cs, and especially Tc, because they are volatile at high temperatures. To prevent their release into the environment, if possible, they should be separated before vitrification.¹⁶ The basic technologies being used for the vitrification process include Joule heated ceramic melter (JHCM), hot-wall induction melter (HWIM) or hot crucible induction melter (HCIM), and additionally relatively recently, cold-crucible induction melter (CCIM). These designs have been improved over the years, and now include more efficient new-generation melters. In addition to these, other technologies like in-can melting, stirred melters, submerged combustion melters, cyclone combustion melters, microwave melters, plasma melters, and directed energy melters are also being considered for nuclear waste management. Although these are promising new technologies, they are still not fully developed for commercial industrial-scale use.^{53,78,82}

A good example to illustrate this is the two-stage calcination-melting vitrification process of HLW remaining after the PUREX process. At the beginning of this process, the remaining highly radioactive concentrated solution is mixed with a sugar solution to reduce volatility of Ru and increase denitration. The solution is then introduced into a calciner cylinder that rotates inside an electrically heated furnace. During the calcination stage, the solution is denitrated and evaporated, and the resulting product is a dry powder. The dry powder is then mixed with glass frit, introduced into an induction-heated melter and heated to temperatures between 1000 and 1250 °C, depending on the technology used. These relatively low temperatures help reduce the volatility of ⁹⁹Tc, ¹³⁷Cs, and ¹²⁹I. At the end of the melting stage, the resulting liquid glass is poured into corrosion-resistant stainless-steel cylinders, typically 1.3 m high. Various materials have been examined for this use but stainless-steel is still the standard. The cylinders are cooled for 24 h and then sealed by welding. Before storage, the surface of the cylinders is decontaminated. During storage, the cylinders are passively cooled to avoid

approaching temperatures close to the glass transition temperature.^{3,21,53,83}

The rate of the vitrification process (waste throughput rate) is defined as the waste loading in glass multiplied by the glass melting rate.⁴⁹ The main factors that limit the vitrification process are crystallisation and accumulation in the melter in the case of Fe-rich wastes (containing 35 wt. % Fe₂O₃, 25 wt. % Al₂O₃, 15 wt. % Na₂O, and 25 wt. % other oxides), Al-rich wastes (containing 50–80 wt. % Al₂O₃), Th- and Zr-rich wastes (containing > 7 wt. % ThO₂ or ZrO₂), P, Bi, and Cr-rich wastes; chemical durability of the produced glass in the case of Na-rich wastes (> 70 wt. % Na₂O); molten salt accumulation at the melter surface, and formation of a water soluble phase in the case of sulphur and halide-rich wastes (containing Na₂O with 5–20 wt. % SO₃ + Cl + F + CrO₃ + MoO₃).⁷⁸ All of these factors can negatively impact melter operation, especially when dense crystals are formed.⁴⁹ Due to all these negative factors, corrosion of the melter refractory lining must be carefully predicted and monitored. *Jin et al.* showed how this could be done in the case of Monofrax[®] K-3 refractory with a composition of 58.6 wt. % Al₂O₃, 27.1 wt. % Cr₂O₃, 5.9 wt. % Fe₂O₃, 6.1 wt. % MgO, and 1.6 wt. % SiO₂.⁸⁴

Vitrification facilities for HLW and ILW disposal operate in Belgium (1), China (1), France (2), Germany (1), India (2), Japan (1), Korea (1), Slovakia (1), Russia (2), UK (1), and the USA (2).^{25,50,58} Among these, France and the UK are the leading countries depositing in glass more than 90 % of spent nuclear fuel and HLW remaining after fuel reprocessing: fission products (Cs, Ba, I, Sr, Mo, Zr, Tc, Ru, Rh, Pd, rare earth elements), and residual minor actinides with long half-life times (Np, Am, Cm).^{37,50} All the listed countries use alkali-borosilicate glass matrix, except Russia, which uses alkali-aluminophosphate glass and new sodium-aluminum-iron phosphate based glass.⁸⁵ Both types of glasses are very similar, although they have slightly different solubilities for nuclear waste elements, and aluminophosphate glasses can be more corrosive to metallic glass contact materials.⁷⁸ Borosilicate glass can immobilise around 15–20 wt. % of HLW, while aluminophosphate glass only 3–5 wt. %.³⁷ Some elements like Pd, Ru, Rh, and ¹²⁹I are challenging to immobilise in a glass matrix because they are insoluble in this type of matrix.⁵⁸

4.3 Ceramics

Although borosilicate glasses through decades of use have shown adequate properties, new materials and compositions for nuclear waste immobilisation are still under research. Ceramics and glass-ceramics that are very stable and durable are also being considered as promising materials for HLW deposition, as studies have shown that most fission products and minor actinides remaining after reprocessing can be immobilised in a large number of polycrystalline phases with different composition and structures.^{20,37,38,86} A list of some studied examples is given in Table 2.

Table 2 – List of some polycrystalline phases suitable for nuclear and radioactive waste immobilisation^{20,37,38,53,86}Tablica 2 – Popis nekih polikristalnih faza koje su pogodne za imobilizaciju nuklearnog i radioaktivnog otpada^{20,37,38,53,86}

Mineral	Formula
zirconia (baddeleyite)	ZrO ₂
zirconium silicate	ZrSiO ₄
zirconolite	CaZrTi ₂ O ₇
perovskite	CaTiO ₃
pyrochlore	(Na,Ca,U) ₂ (Nb,Ti,Ta) ₂ O ₆
brannerite	(U,Ln,Ca)Ti ₂ O ₆
lovingite	(Ca,Ce,U)(Ti,Fe,Cr,Mg) ₂₁ O ₃₈
murataite	(Y,Na) ₆ Zn(Zn,Fe ³⁺) ₄ (Ti,Nb,Na) ₁₂ O ₂₉ (O,F,OH) ₁₀ F ₄
hollandite	BaTi ₈ O ₁₆
spinel	MgAl ₂ O ₄
zircon	ZrSiO ₄
thorite	ThSiO ₄
britholite	(Ca,Ce) ₅ (SiO ₄) ₃ (OH,F)
titanite	CaTiSiO ₄ O
monazite	LnPO ₄
xenotime	YPO ₄
NZP	NaZr ₂ (PO ₄) ₃
<i>p</i> -zirconium phosphate	HZr ₂ (PO ₄) ₃
Th-pyrophosphate	Th ₄ (PO ₄) ₄ P ₂ O ₇
monazite	(Ce,La,Nd,Th)PO ₄
kosnarite	(K,Na)Zr ₂ (PO ₄) ₃
vituseite	Na ₃ Ce(PO ₄) ₂
powellite	(Ca,Sr)MoO ₄
apatite	M ₁₀ (XO ₄) ₆ Y ₂ where M is divalent cation (e.g. Ca ²⁺ , Pb ²⁺ , Ba ²⁺), XO ₄ is trivalent anion (e.g. PO ₄ ³⁻ , VO ₄ ³⁻ , SiO ₄ ³⁻), and Y is monovalent anion (e.g. F ⁻ , Cl ⁻ , OH ⁻ , Br ⁻)
garnet	A ₃ B ₂ Si ₃ O ₁₂ where A is divalent cation (e.g. Fe ²⁺ , Ca ²⁺ , Mg ²⁺ , Mn ²⁺), and B is trivalent cation (e.g. Fe ³⁺ , Al ³⁺ , Cr ³⁺)

This suitability for nuclear waste immobilisation is confirmed by studies in which lanthanides with similar ionic radii are used to simulate actinides (e.g., Ce³⁺ simulates Pu³⁺; Nd³⁺ and Eu³⁺ simulate Cm³⁺ and Am³⁺; Th⁴⁺ and Hf⁴⁺ can also simulate Np and Pu; Nd³⁺ is a simulant for rare earth elements). These simulants are used to study how incorporation into the crystal structure occurs and its impact on the resulting structure, physical and chemical properties like stability in water (leaching), density, porosity, glass transition temperature, heat capacity, thermal conductivity, stability to ionising radiation, mechanical durability, coefficients of linear and volume expansion, capacity of the crystal structure, etc.³⁷ The limiting factor, due to volatile radioisotopes, is the melting temperature which is above 2000 °C for most ceramics. However, the positive aspect of higher melting temperatures is that they enable incorporation of species that are difficult to dissolve.

5 Deep geological disposal

Deep geological disposal is a method for managing HLW and ILW using deep underground depots comprising a system of chambers within suitable stable geological formations, connected by tunnels and shafts with surface facilities.⁸⁷ While near-surface depots at depths between 15 to 200 m are adequate for LLW, the storage of HLW requires greater depths.²⁵ When considering deep geological disposal, some limiting factors to be taken into account include groundwater, earthquake and volcanic activity zones, impact of weather conditions, proximity to populated areas, and geological formations. Acceptable host rock formations include crystalline and volcanic rocks, clay, granite, basalt, salt, and tuff.^{88–90} The most significant limiting factor in terms of potential pollution is groundwater, as it could lead to leakage and the spread of radioisotopes into the environment, and consequently, the food chain.³⁸ Ongoing research is still being conducted to assess the long-term safety and impact on humans and the envi-

ronment in both crystalline and sedimentary host rock formations. However, the prevailing conclusion is that deep geological disposal, with borehole depths ranging from a few hundred meters up to a few kilometres in combination with vitrification, a robust multi-barrier system (natural and artificial), and continuous monitoring is considered the most suitable solution for safe isolation of nuclear waste. The multi-barrier system consists of solidified waste placed in an appropriate container, a buffer barrier layer between the container and the sidewalls of the chamber to contain the spread of radionuclides in the event of a release from the container, a backfill to stabilise and prevent rock damage, and a stable geological formation. Because HLW generates heat, it requires a different system from that used for ILW. The general layout of a multi-barrier system for HLW and ILW is shown in Table 3. The buffer material, primarily intended for heat-producing HLW, is bentonite, but at higher temperatures, there is a possibility that bentonite will transform into illite, which is a different clay mineral. Due to this limitation, the design temperature for buffer materials is set below 100 °C. However, *Yoon et al.* studied the thermal conductivity of Ca-type bentonite and found that the values had not significantly changed in the temperature range from room temperature to 150 °C. This research suggests that higher design temperatures can be used, meaning that a greater amount of waste could be deposited in a smaller area.⁹¹

Table 3 – Examples of multi-barrier system setup^{87,91}
 Tablica 3 – Primjeri strukture sustava višestrukih barijera^{87,91}

Type of nuclear waste	HLW	ILW
solidification form	vitrification	cementation
type of container	Cu or Ni alloy, steel	carbon/stainless steel, concrete
type of buffer	clay (bentonite)	cement
type of backfill	crushed host rock, concrete, excavated rock, chemical buffering materials	
type of geological formation	stable rock	

Currently, deep geological disposal is the best proposed comprehensive long-term solution for HLW originating from commercial civil use and military defence programmes (weapons and equipment). Leading countries that have accepted this concept and initiated its implementation include Canada, China, Finland, France, Sweden, Switzerland, and the USA.^{3,87,92}

6 Conclusion

As a result of the widespread and continuously expanding use of nuclear energy for various peaceful civil purposes,

such as electrical power production, medical isotopes, research, and industry, as well as for military defence purposes, significant amounts of nuclear waste are generated. This necessitates implementation of responsible and safe nuclear waste management solutions. One part of the solution is nuclear waste recycling, which can decrease waste volume and isolation time. For the remaining HLW and ILW, the most acceptable long-term solution is immobilisation in a solid matrix. No research can provide an actual long-term projection of how these solid matrices will behave, as it is impossible to include all possible parameters in experimental conditions. However, examples present in nature, 70 years of practical use, and the results of numerous studies confirm that glasses are excellent materials for immobilising nuclear waste. In addition to glasses, the most promising new emerging material investigated for HLW immobilisation is ceramics. Although the initial costs of vitrification are higher, it should be considered a feasible long-term option for HLW management. This approach to radioactive waste management has the advantage of being well-investigated, constantly improving, generating significantly less waste volume than the initially cheaper cementation process, and exhibiting great chemical and mechanical durability over decades of use. In combination with deep geological disposal, vitrification presents the optimal long-term solution for nuclear waste management.

List of abbreviations Popis kratica

CCIM	– cold-crucible induction melter
CNT	– carbon nanotubes
COEX	– combined U and Pu extraction
EU	– European Union
GANEX	– grouped actinide extraction
GGBFS	– ground granulated blast furnace slag
HCIM	– hot crucible induction melter
HLW	– high level waste
HWIM	– hot-wall induction melter
ILW	– intermediate level waste
ISG	– international simple glass
JHCM	– Joule heated ceramic melter
LLW	– low level waste
MIL	– Materials of Institute Lavoisier
MKPC	– magnesium potassium phosphate cement
MOF	– metal-organic frameworks
MOX	– mixed uranium and plutonium oxide
NPP	– nuclear power plants
PUREX	– plutonium uranium refining by extraction
UOX	– uranium oxide
UREX	– uranium extraction
ZIF	– zeolitic imidazolate framework

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SAŽETAK

Gospodarenje nuklearnim otpadom: recikliranje i dugoročno sigurno skladištenje

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Nuklearni otpad nastaje kao rezultat uporabe nuklearne energije. Nuklearni i radioaktivni otpad, posebno visoko radioaktivni otpad (engl. *high level waste*, HLW) i srednje radioaktivni otpad (engl. *intermediate level waste*, ILW), zahtijevaju posebna dugoročna i sigurna rješenja za gospodarenje. Djelomično rješenje je recikliranje preradom istrošenog nuklearnog goriva. Recikliranjem se smanjuje volumen nuklearnog otpada, a neke njegove komponente mogu se ponovno upotrijebiti. To se može postići adsorpcijom, ionskom izmjenom, koagulacijom, flotacijom, filtracijom, kemijskim taloženjem, reverznom osmozom i ekstrakcijom otapalima poput PUREX procesa. Još jedno moguće buduće rješenje je tehnologija razdvajanja i transmutacije, kojom će se proizvoditi manje nuklearnog otpada. Najbolje dugoročno rješenje je imobilizacija HLW i ILW u čvrstoj matrici. Materijali koji se u tu svrhu upotrebljavaju uključuju stakla, cemente, bitumen, geopolimere, beton i keramiku kao obećavajući materijal. Iako je cementiranje još uvijek najčešće primjenjivana metoda imobilizacije jer je jeftina i jednostavna tehnika, vitrifikacija predstavlja trajno dugoročno rješenje. Duboko geološko odlaganje u kombinaciji s vitrifikacijom i robusnim sustavom višestrukih barijera smatra se najprihvatljivijim rješenjem za sigurnu izolaciju nuklearnog otpada. Ovaj pregledni rad daje uvid u najčešće upotrebljavane i najperspektivnije materijale za imobilizaciju te u najučinkovitije metode i tehnologije za gospodarenje HLW i ILW nuklearnim otpadom koje se primjenjuju ili su u razvoju.

Ključne riječi

Nuklearni otpad, cementiranje, vitrifikacija, duboka geološka odlagališta, recikliranje, PUREX

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