



3.1.4 Bituminized waste, polymers (Other waste forms), Domain Insight

Authors: Denise Ricard (Andra)

Reviewers: Elie Valcke

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Overview

The immobilisation of radioactive waste may be done through solidification, embedding or encapsulation. The immobilised wasteform can be produced by chemical incorporation of the waste species into the structure of a suitable matrix so that the radioactive species are atomistically bound in the structure, or by encapsulation of waste, achieved by physically surrounding the waste with or in a material so the waste particles are isolated, and radionuclides are retained. Bitumen and polymers materials are typically employed for the encapsulation/embedding of low-level or intermediate-level waste (LL-ILW) as an alternative to the cementation. Other materials, such as geopolymers, an emerging class of materials based on alkali-activated aluminosilicate, have also been developed in the last years as a promising material for the encapsulation of radioactive waste. This class of materials is not discussed in the present document. The polymers described are organic materials, in which the primary backbone of the molecular chain is composed of carbon atoms.

Immobilisation of radioactive waste with bitumen has been used in several countries including Belgium, Czech Republic, Denmark, Finland, France, Japan, Sweden, Switzerland, Ukraine and USA. Two types of bitumen are most used for the immobilisation of diverse types of wastes, such as evaporator concentrates, ion exchange resins and spent filter cartridges: direct distillation products, also called soft bitumen, and oxidised (or blown) bitumen, also called hard bitumen.

Polymer matrices have only been used to a limited extent for immobilisation of radioactive waste. The polymers most used are polyethylene, epoxy resins, and polyester resins (IAEA, 1988; WPSGD, 2015). In France, epoxy resin immobilisation has been applied since 1996 for the conditioning of ion exchange resins from the primary circuits of nuclear power stations. The epoxy resin immobilisation process has also been tested on evaporator concentrates, filters, and dismantled reactor components. An epoxy resin-based immobilisation process is under consideration in England for the conditioning Magnox fuel element debris. Polyester resins, and vinyl ester resins especially, have been employed in the immobilisation of radioactive waste in several countries, particularly in the USA, to a lesser extent in the UK and France.

The physical and (radio-)chemical properties of the immobilised wasteforms have to be adequate to meet storage, transport, disposal facilities conditions and regulatory requirements. Safety of disposal is based on the use of multiple barriers to prevent or restrict the migration of radionuclides. The immobilised waste could provide a primary barrier preventing the release of radionuclides in the environment during storage and transportation while during post-closure disposal, the wasteform can contribute to reduce the release of radionuclides and toxics.

The wasteform requirement depends on the acceptance criteria for a given final disposal site, and it can differ from one country to another. Requirements are related to the leaching properties, flammability, chemical and radiation stability, gas production, durability issues, etc. Therefore, the knowledge of properties, performance and long-term behaviour of wasteforms is an important issue that has been studied for bituminized wastes (IAEA, 1993; Mariën et al., 2013; CEA, 2017; Valcke et al., 2022) and some polymer encapsulation materials (IAEA, 1988; Damian et al. 2001; WPSGD, 2015).

Keywords

Waste immobilisation, bitumen, polymers, chemical and physical properties, long-lived behaviour.

1. Typical overall goals and activities in the domain of bituminized waste, polymers (Other wasteforms)

This section provides the overall goal for this domain, extracted from the [EURAD Roadmap goals breakdown structure \(GBS\)](#). This is supplemented by typical activities, according to phase of implementation, needed to achieve the domain goal. Activities are generic and are common to most geological disposal programmes.

Domain Goal	
Identify or confirm composition, properties, behaviour and evolution under storage and disposal conditions of wasteforms immobilised with organic materials (bitumen and polymers).	
Domain Activities	
Phase 1: Programme Initiation and DGR Site Identification	Conduct initial analysis of inventory of immobilised waste and future inventory susceptible to be immobilised with organic materials. Preliminary assessment of properties of immobilised materials.
Phase 3: DGR Site Characterisation	Evaluate impact of disposal conditions on behaviour of wasteforms. Perform studies about wasteform degradation (gas production, durability, release of degraded molecules, etc.) and the effects on disposal safety (interaction with disposal materials, RN complexation and migration).
Phase 4: DGR Construction	Confirm performance and behaviour of immobilised materials to support repository license application.
Phase 5: DGR Operation and Closure	Confirm and preserve documentation for the emplaced disposal containers for licence application for operation/closure.

2. Properties of bitumen and polymer wasteforms

The long-term behaviour of bituminized and polymer waste is of importance for the safety assessment of the disposal systems and hence for the criteria for acceptance of the wasteform in individual disposal sites. Depending on the site, other properties may need consideration, such as:

- (a) Radiation effects and stability,
- (b) Thermal effects and stability,
- (c) Dimensional and mechanical stability,
- (d) Chemical stability,
- (e) Long-term sedimentation and homogeneity,
- (f) Interaction with surrounding disposal media,
- (g) Gas generation and effects,
- (h) Leach resistance,
- (i) Microbial stability.

2.1 Bituminized waste

Bitumen is considered to have favourable chemical and physical properties to act as encapsulation material for radioactive waste. It has been used for solidifying low and intermediate-level waste such as sludges, liquid concentrates, and ion exchange resins. Sludges are generated when liquid waste streams are treated by chemical precipitation or flocculation to reduce the volume of waste contaminated with radionuclides. Sludges contain variable contents in soluble and less soluble salts, such as nitrates, sulphates, phosphates, etc.

The diffusion of radionuclides in bitumen is insignificant and the diffusion of water vapour and water in bitumen is slow. However, during interim storage and subsequent disposal the bitumen properties may change primarily due to radio-oxidation. This may influence the behaviour of the wasteform and/or other barriers in a repository, which has to be considered in a safety assessment (SKB, 2001). Processes normally studied are:

- Radiolytic effects
- Ageing
- Water uptake
- Leaching
- Flammability and thermal stability
- Biodegradation

2.1.1 Radiolytic gas production and swelling

The self-irradiation associated to the presence of radionuclides in the waste leads to the production and emission of radiolytic gases. In absence of oxygen, the predominant gas is hydrogen with only minor contribution (up to 5% of the produced volume of hydrogen) coming from carbon monoxide, carbon dioxide and hydrocarbons (IAEA, 1993; SKB, 2001). Radiolysis of bitumen in air results in consumption of oxygen and generation of carbon dioxide and carbon monoxide in addition to hydrogen (Burnay, 1985). The amount of gas released depends on the type and amount of bitumen and the activity incorporated in the waste. In France, for example, the hydrogen production rate was estimated for bituminized waste (sludge embedded in direct distillation bitumen) destined for geological disposal. The hydrogen rate would be up to 10 L/year per primary waste package (CEA, 2017).

The gases generated by radiolysis may lead to the swelling of bituminized waste (Burnay, 1987; IAEA, 1993; SKB 2001; Mouazen et al., 2013; Marchal et al., 2016). The swelling results from a higher gas generation rate than the gas removal rate from the waste. The swelling level is dependent on several parameters such as dose rate, the total dose, the bitumen type, the nature of the waste and the loading, (IAEA, 1993; SKB 2001). Some works have shown that irradiation of distilled bitumen led to bubble formation and that oxidised bitumen is more prone to form pores or cracks when gamma irradiated than distilled bitumen (Phillips et al., 1984). Several models have been developed to predict this phenomenon.

2.1.2 Water uptake and leaching

Although pure bitumen is poorly permeable to water and dissolved species, the presence of hygroscopic salts or ion exchange resins favours water uptake and subsequent swelling or expansion of the waste. Since this phenomenon might affect the integrity of the waste package containment and even disturb the performance of the disposal host formation, numerous studies have been carried out in recent years on bituminized waste, mainly bituminised dried evaporator concentrates and precipitation sludge (Valcke et al., 2010; Mariën et al., 2013; Bleyen et al., 2016; Irisawa & Meguro, 2017; Bleyen et al., 2022).

The process of water uptake and swelling depends on the amount of waste in the matrix, the waste composition, and the type of bitumen. Other factors affecting water uptake are related to the repository conditions, for instance temperature, material surrounding the matrix, and available volume for swelling.

2.1.2.1 Bituminized waste (dried evaporator concentrates and precipitation sludge embedded in bitumen)

The water uptake and swelling process in this type of bituminised waste is due to the semi-permeable membrane function of bitumen surrounding the waste particles. This means that water can diffuse slowly but easily through the bitumen membrane whereas the dissolved salts cannot (i.e. osmosis) unless the membrane is damaged, for instance by swelling. In geological disposal, free swelling conditions are possible during an initial phase, until the free volume in the drum is filled with swollen bituminized waste. Once there is no more space for further swelling, the swelling waste could exert osmosis-induced pressure, initially on the concrete secondary container, but eventually also on the surrounding clay formation.

The phenomenology of the water uptake, swelling, and salt leaching processes in free swelling conditions is reasonably well understood (Gwinner et al., 2006; Sercombe et al., 2006; Bleyen et al., 2016). On contact with water, the soluble salts are dissolved locally. Formation of saline solution bags results in porosity developing, which facilitates the migration of dissolved species (radionuclide and salts).

Some studies have shown that the kinetics of water uptake and the release of the most soluble salts in free swelling conditions follow a diffusion mechanism (Gwinner et al., 2006; Sercombe et al., 2006; CEA, 2009). In these studies, the release of radionuclides has been associated with the release of high-solubility salts, which is a penalising approach: it has been demonstrated that radionuclide release rates are two to four orders of magnitude lower than those of tracer salts.

The swelling in confined conditions has been extensively studied in the last years (Valcke et al., 2010; Mariën et al., 2013; Irisawa & Meguro, 2017; Bleyen et al., 2022). Nearly-constant-volume water uptake tests with simulated Belgian Eurobitum bituminized waste have shown pressures up to 20 MPa after about four years of hydration (Mariën et al., 2013). For two different simulated French bituminized waste products, pressures up to 28 and 34 MPa were measured (Bleyen et al., 2022).

In Belgium, compatibility studies have investigated the chemo-hydro-mechanical (CHM) interaction between swelling Eurobitum and the Boom Clay. These studies include the laboratory water uptake tests and the development of a fully coupled CHM formulation for Eurobitum (Mokni et al., 2010; Mariën et al., 2013).

Another important issue associated to this type of bituminized waste is the leaching of nitrates and sulphates. Large amounts of nitrate and other soluble salts in the host rock can influence the geochemistry (redox, increase of the ionic strength, etc.) in the vicinity of the near field and influence the migration of radionuclides, especially redox-sensitive radionuclides (Abrahamsen et al., 2015; Bleyen et al., 2018).

2.1.2.2 Ion exchange resins encapsulated in bitumen

The water uptake results in a volume increase to the dried resin beads that in turn thins the bitumen membrane and allows water to pass more quickly to the other dehydrated resins. The more resin in the product, the more rapid is the change in the product dimensions. Water uptake by bitumen-resin products is significantly reduced at lower loadings. Again, as with bituminized salts, water diffusion is the controlling factor (IAEA, 1993). The ionic state of the resin affects the swelling ability, H⁺ and OH⁻ results in the largest swelling (SKB, 2001). On the other hand, bituminized wastes containing cationic ion exchangers saturated with multi-valent cations show a considerably lower tendency to swell.

2.1.3 Ageing and release of organic soluble species

In dry conditions, like in interim storage conditions, the self-irradiation associated to the presence of radionuclides in the waste also leads to ageing of the bitumen (i.e. radio-oxidation). Especially in the presence of oxygen, the radio-oxidation of blown bitumen results in a hardened and brittle material, comprising many small fissures, which in turn facilitate the ingress of oxygen deeper in the waste (Valcke et al., 2009). The consequences of this embrittlement and fissuring on process like water uptake and swelling are not well known yet.

Radiolytic and chemical degradation of the bitumen in contact with water can lead to the release of water-soluble organic species. The related safety issues are to assure that the presence of the radiolytic and chemical degradation products will not increase the radionuclide migration rate by increasing their solubility and/or reducing their sorption.

Radiolytic degradation of blown bitumen gamma-irradiated in the range of 1 to 10 MGy had not shown significant degradation (Kagawa et al., 2000). The main water-soluble organic component by radiolytic degradation was oxalic acid. Some monocarboxylic acids and high molecular components were detected. Additionally, the chemical degradation of bitumen in alkaline solution under aerobic and reducing conditions showed that the release of soluble species increased under aerobic conditions. Formic acetic and high molecular weight components were measured in solution.

For distilled bitumen, degradation by radiolysis (gamma-irradiation) followed by hydrolysis in alkaline solutions led to the formation of the following soluble species: oxalic acid, phthalic acid, acetylacetic acid and the dibutylester of phthalic acid (Van Loon & Kopajtic, 1991).

In addition to degradation products from bitumen, other organic species initially present in the waste (TBP, EDTA, etc.) might leach from the bituminized waste.

2.1.4 Flammability and thermal stability

The salts contained in bituminized waste can present an exothermic reactivity following interactions that can occur with the bituminous matrix and/or between different species in the waste. It is therefore necessary to bring elements of knowledge to the safety study related to the risk of fire inherent in the bituminous waste.

The study of the thermal behaviour of simplified bitumen incorporating nitrate salts (of sodium or magnesium) under anaerobic conditions has revealed an exothermic reactivity (Matta, 2023). This exothermicity is higher for bitumen containing sodium nitrate. The bitumen incorporating low sodium nitrate content shows a behaviour similar to that of pure bitumen under anaerobic conditions. As the nitrate content increases and nitrates are available to be engaged in redox reactions, bituminous mixes exhibit a behaviour similar to that of pure bitumen stressed under aerobic conditions, i.e. with sufficient availability of oxygen.

2.1.5 Biodegradation

Even though it has been concluded that a repository environment (low temperature, high salinity, high alkalinity, radiation) is far from ideal for promoting growth of micro-organisms (Buckley et al., 1985), there are micro-organisms which are well adapted to this environment. Their activity is, however, limited to spots where there is sufficient space to grow and where the repository conditions are less hostile.

The biodegradation of bitumen is dependent on type and availability of the microbial community, on environmental factors that facilitate or impede microbial growth and on the chemical composition of bitumen waste.

The microbial activity has been described for pure bitumen or simulated bituminized waste (IAEA, 1993; Libert et al., 1997; SKB, 2001; Mijndonckx et al, 2015; Mijndonckx et al, 2020). The biodegradation rates of bitumen are very low. In aerobic conditions, biodegradation rates are higher compared to anaerobic conditions; in both conditions gas production (nitrogen and carbon dioxide) was observed. It was also observed that organic degradation products leached from the bitumen were degraded by microorganisms (Libert et al., 1997; Mijndonckx et al, 2020).

The results from (Mijndonckx et al., 2020 and 2022; Bleyen et al., 2017) have also shown that microbial nitrate reduction can occur with leached organic Eurobitum degradation products as electron donor, possibly decreasing the oxidative impact of the nitrate plume on the host formation.

2.2 Polymer wasteforms

Polymer matrices have only been used to a limited extent for immobilisation of waste. The matrices most extensively investigated and used in the immobilisation of ILW radioactive waste are:

- Thermoplastic polymers: Polyethylene
- Thermosetting polymers: Epoxy resins, polyester resins, urea-formaldehyde

The polymers described have low water permeability, leading to wasteforms with low radionuclide leaching. One of the key advantages of organic polymers for the conditioning of radioactive waste is their general compatibility with a variety of waste materials including reactive metals. There is little information about the evolution/performance of wasteforms in the long term. To our knowledge, most of the information available comes from experiments conducted through short-time standard test.

Polymer matrices can evolve with time in repository conditions under the effect of irradiation (auto-irradiation associated the presence of radionuclides), of temperature, in presence of water (after saturation of the disposal site), etc. The main issues of degradation of polymer matrices are the gas release, release of soluble organic molecules and their potential effects on radionuclide migration, and durability/lifetime of encapsulation properties.

2.2.1 Polyethylene

Polyethylene has been studied as an immobilisation medium for radioactive waste, and a number of industrial scale processes have been operated, immobilising liquid concentrates, sludges and ion exchange resins in countries such as the Netherlands, Argentina and Japan. The Brookhaven National Laboratory (BNL) in the USA actively markets polyethylene immobilisation processes and has a full-scale demonstration facility for a polymer-waste mixing and extrusion process (Shaulis, 1997; WPSGD, 2015). The Japan Atomic Energy Research Institute (JAERI) together with Niigata Engineering Co. has developed a polyethylene system for immobilisation of dried waste (IAEA, 1988).

2.2.1.1 Properties and performance

Some properties such as compressive strength, resistance to thermal cycling and resistance to leaching (tests performed according to standard methods for polyethylene wasteforms containing sodium nitrate) are described in IAEA, 1988; Kalb et al., 1993 and Shaulis, 1997.

Accelerated leach tests of full-scale polyethylene forms containing nitrate salt waste were performed to model cumulative fraction releases of waste after 300 years of leaching under fully saturated conditions (Shaulis, 1997). The limitation of this model is the assumption that the waste remained structurally stable during that time interval. The results indicate that approximately 5% – 17% of the contaminant source will be leached after 300 years of exposure to saturated conditions.

2.2.1.2 Evolution and degradation

Radiolysis of polyethylene produces considerable quantities of gas. In the absence of oxygen, hydrogen is the main radiolysis gas produced. Radiolysis of polyethylene in air results in consumption of oxygen and generation of carbon dioxide and carbon monoxide in addition to hydrogen.

Results from experiments involving the irradiation of polyethylene-based wasteforms seem also to indicate that doses up to 1 MGy result in increased strength, lower permeability and leachability, and better chemical resistance (Kalb et al., 1993; WPSGD, 2015).

Radiolytic and chemical degradation of polyethylene can lead to formation and release of soluble organic species. Studies conducted on polyethylene films irradiated to integrated doses of 2 to 10 MGy followed by leaching in alkaline solution (hydrolysis) lead to the release of mono- and dicarboxylic acids (glycolic, acetic, formic, propionic, glyoxylic, 6-hydroxy hexanoic, glutaric, succinic, malonic, adipic, oxalic and pimelic acid) (Ferry et al., 2020). The films only exposed to alkaline solution did not show significant degradation.

ASTM normalised experiments conducted after 28 days incubation of polyethylene wasteforms containing sodium nitrates, boric acid, incinerator ash and ion exchange resins showed no fungal or bacterial growth (Kalb et al., 1993; Shaulis, 1997).

2.2.2 Epoxy resins

A wide range of epoxy resins are available commercially with different properties. This makes them very versatile as potential immobilisation agents for radioactive wastes, but also means that care needs to be taken in selecting a material with the right properties.

Epoxy resin immobilisation has been applied in France since 1996 to the conditioning of ion exchange resins from the primary circuits of nuclear power stations. The epoxy matrix is composed by crosslinking network based on diglycidyl ether of bisphenol-A (DGEBA) and the aromatic diamine diamino diphenylmethane (DDM). The basic epoxy resin immobilisation process has also been tested on evaporator concentrates, filters and dismantled reactor components (WPSGD, 2015). The process developed called Mercure is suitable for treating resins containing short-lived radionuclides (^{58}Co , ^{60}Co , ^{110}Ag , ^{54}Mn , ^{57}Co , ^{134}Cs , ^{137}Cs , etc) for surface disposal (Abrahamsen et al., 2015).

2.2.2.1 Properties and performance

The properties of epoxy wasteforms (such as compressive strength, leaching behaviour, flammability and thermal stability) for dry sodium borate (powder), wet ion exchange resins and Magnox fuel element debris are reported in (IAEA, 1988).

2.2.2.2 Ageing and evolution of properties

Three types of ageing (thermal oxidation, radio-chemical ageing and hydrolytic ageing) were studied on different epoxy-amine networks based on BGEBA/DDM for the embedding of low activity radioactive waste (Damian et al. 2001). The effects of radiochemical ageing in the studied experimental conditions are very low compared to the effects of thermal oxidation ageing. No significant degradation is noticed for irradiation up to 3.4 MGy. Hydrolytic ageing led to leaching of plasticiser and the hydrolysed species.

Radiolytic damage has been observed at > 1 MGy for wet ion exchange resins immobilised in epoxy resin. Irradiation of epoxy resin-based wasteforms results in the generation of modest amounts of gas (hydrogen and carbon dioxide) (IAEA, 1988).

2.2.3 Polyester resins

There is a wide range of commercially available polyesters made from different acids, glycols and monomers, all having varying properties and performance that can be tailored to specific applications. A type of polyester resin that has found particular use in the immobilisation of radioactive waste is vinyl ester resin. Polyester resins have been employed in the immobilisation of radioactive waste in several countries (USA, France, Japan, UK) (IAEA, 1988). The immobilised waste includes concentrated waste, ion exchange resins and zircaloy swarf.

2.2.3.1 Properties and performance

The wasteform properties (compressive strength, leaching behaviour, flammability, thermal stability) for simulated sodium sulphate, bead resin and powdered resin wastes are reported in IAEA (1988). It is noticed that cured polyester resin-based wasteforms can have (very) high compressive strengths (up to 80 MPa). Consequently, however, the resins have an inability to deform plastically and generally exhibit brittle fracture characteristics.

2.2.3.2 Evolution and degradation

The use of styrene as the cross-linking agent for polyester resins imparts greater radiation tolerance. Wasteforms produced from the immobilisation of sodium sulphate waste in polyester resin have been

shown to increase in compressive strength when exposed to doses of up to 10 MGy. The main radiolysis product was CO₂ (WPSGD, 2015).

Resistance of polyester wasteforms to microbial activity was evaluated by using an ASTM normalised experiments after 28 days incubation. No changes in surface appearance, weight, size, compressive strength or surface hardness were observed.

2.2.4 Urea-Formaldehyde resins

Urea formaldehyde is no longer used as an immobilisation agent for radioactive wastes, principally because of problems encountered with the generation of corrosive free liquids during curing. Water is produced during the curing of the resin and, while this is largely incorporated into the resin matrix, some freestanding water can be produced. Despite these drawbacks, urea formaldehyde resin was the main organic immobilisation agent used in the USA between 1970 and 1980. The adoption of regulations regarding the presence of free liquids in waste packages meant, however, that the use of urea formaldehyde resins was phased out (IAEA, 1988; WPSGD, 2015).

3. International examples of bituminized waste studies

Water uptake and swelling of bituminized waste have been extensively studied:

- Free swelling process and modelling of French bituminized waste (Gwinner et al., 2006; Sercombe et al., 2006).
- Water uptake, swelling processes in confined conditions for Eurobitum and possible effect on the Boom Clay formation has been studied in Belgium (Valcke E. et al., 2010; Mokni et al., 2010; Mariën et al., 2013. The same methodology has been applied to study water uptake and related processes in the French bituminized waste (Bleyen et al., 2022).

4. Critical background information

- Swelling by osmosis-induced water uptake of bituminized waste and the potential effect on the near-field of the host formation for deep geological disposal. These topics have been extensively studied in the last decades.
- Data on the flammability and exothermic reactivity of bituminized waste products are needed for safety assessments of possible fire incidents. Research efforts have much dealt with the consequences of a fire, and not with the mechanisms that could lead to an ignition. Recently, the thermal behaviour and exothermic reactions in the French bituminized waste have been studied.

4.1 Challenges and innovations

New polymer matrices have been developed in the last years for encapsulation of LLW, such as Nochar (Kelley & Campbell, 2020) or new epoxy-resin based materials. Knowledge of these materials is less mature and the understanding of their long-term performance and durability under disposal conditions is required to consider them for the conditioning of specific wastes and obtain final wasteforms, which can meet the WAC of the disposal facilities.

4.2 Past and ongoing (RD&D) projects related to bitumen and polymer

Past (RD&D) Projects:

- Microbiology in nuclear Disposal - European Project MIND (2015 - 2019) (Abrahamsen et al., 2015; Mijndonckx et al, 2015)
- Eurad WP 3 CORI – Cement-Organic-Radionuclide Interaction (2019-2024) (Eurad, 2021)

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