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Behaviour of mercury and mercury compounds at the underground disposal in salt formations and their potential mobilisation by saline solutions

by

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Kurzbeschreibung

In den kommenden 40 Jahren sind in der Europäischen Union etwa 11 000 t metallisches Quecksilber zu beseitigen, das in der Chlor-Alkali-Industrie nicht mehr genutzt wird oder bei der Nichteisenmetallproduktion sowie der Gasreinigung anfällt. Eine Option zur Beseitigung ist die dauerhafte Ablagerung in Untertagedeponien (UTD) im Salzgestein. Bislang war metallisches Quecksilber als Flüssigkeit von einer Ablagerung in UTD ausgeschlossen.

Vor einer Zulassung ist es notwendig, die besonderen Herausforderungen zu untersuchen, die sich aus den spezifischen Eigenschaften des metallischen Quecksilbers (flüssiger Zustand, Bildung toxischer Gase, aufwendige Reinigung kontaminierter Flächen) für die Entsorgungspraxis ergeben.

Auf Basis des heutigen Kenntnisstandes ist eine sichere Dauerlagerung von metallischem Quecksilber in Untertagedeponien im Salzgestein grundsätzlich machbar. Im Normalbetrieb der UTD ist nicht mit einer Beeinträchtigung der Betriebssicherheit zu rechnen. Es sind jedoch zusätzliche technische und organisatorische Maßnahmen zu treffen, um das Risiko einer Freisetzung flüssigen und gasförmigen Quecksilbers im Zuge von Unfällen zu minimieren. Eine Beeinträchtigung der Betriebssicherheit sollte nicht zu besorgen sein. Empfohlene Maßnahmen beinhalten eine für die Betriebsphase störfallsichere Auslegung der Transport- und Lagerbehälter und eine Auslagerung der stofflichen Eingangskontrolle zum Abfallerzeuger. Empfohlen werden zudem eine kampagnenweise Einlagerung von Behältern und der unverzügliche Verschluss von Einlagerungsabschnitten. Nach Verschluss der gesamten Untertagedeponie gehen bei planmäßiger Entwicklung des UTD-Gesamtsystems vom abgelagerten Quecksilber keine spezifischen Umweltrisiken aus. Im hypothetischen Fall eines Lösungszuflusses wirkt die niedrige Löslichkeit reinen metallischen Quecksilbers als innere Barriere.

Abstract

Within the next 40 years, in the European Union approximately 11,000 t of metallic mercury has to be disposed that is no longer used in the chlor-alkali industry or is gained from non-ferrous metal production or the cleaning of natural gas. One disposal option is permanent storage in underground storage sites in salt rock. As a liquid, metallic mercury has been excluded from this disposal option so far. Prior to a permit, it is necessary to investigate the particular challenges for the disposal practice that originate from the specific properties of metallic mercury (liquid state, formation of toxic gases, laborious clean-up of contaminated areas).

On the base of present knowledge a safe permanent storage of metallic mercury in underground storage sites is principally feasible. Under the conditions of a normal operation it is expected that the operational safety is not affected. However, additional technical and organisational measures have to be taken, in order to minimize the risk of a release of liquid or gaseous mercury in case of an accident. There should be no reason to fear a deterioration of operational safety. Recommended measures include constructing the transport and storage containers in a way that they withstand hazardous incidents, shifting the material acceptance control to the waste producer, emplacement of containers in distinct campaigns with subsequent closure of disposal sectors. After sealing the complete underground storage facility and assuming a normal development of the integral system of the underground storage site, disposed mercury does not pose a specific environmental risk. In the hypothetical case of a fluid intrusion, the low solubility of pure metallic mercury represents an inner barrier.

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List of Abbreviations

ABBergV	Allgemeine Bundesbergverordnung. English: German Federal General Mining Ordinance
ADN	Accord européen relatif au transport international des marchandises dangereuses par voie de navigation intérieure. English: European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways
ADR	Accord européen relatif au transport international des marchandises Dangereuses par Route. English: European Agreement concerning the International Carriage of Dangerous Goods by Road
BAM	Bundesanstalt für Materialforschung und –prüfung. English: Federal Institute for Materials Research and Testing
BfR	Bundesinstitut für Risikobewertung. English: Federal Institute for Risk Assessment
BfS	Bundesamt für Strahlenschutz. English: Federal Office for Radiation Protection
DepV	Verordnung über Deponien und Langzeitlager (Deponieverordnung). English: Landfill Ordinance
ERAM	Endlager für radioaktive Abfälle Morsleben. English: Morsleben Repository for Radioactive Waste
EU	European Union
FEP	Features, Events, Processes
GefStoffV	Verordnung zum Schutz vor Gefahrstoffen (Gefahrstoffverordnung - GefStoffV). English: German Hazardous Substances Ordinance
GGVSEB	Verordnung über die innerstaatliche und grenzüberschreitende Beförderung gefährlicher Güter auf der Straße, mit Eisenbahnen und auf Binnengewässern (Gefahrgutverordnung Straße, Eisenbahn und Binnenschifffahrt - GGVSEB). English: German Ordinance on the Carriage of Dangerous Goods by Road, Rail and Inland Waterways
RID	Règlement concernant le transport international ferroviaire des marchandises dangereuses. English: Regulation Concerning the International Carriage of Dangerous Goods by Rail
TA Luft	Erste Allgemeine Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz (Technische Anleitung zur Reinhaltung der Luft – TA Luft). English: Technical Instructions on Air Quality Control
UN	United Nations

1 Introduction

1.1 The disposal of surplus mercury

Mercury is a toxic heavy metal that can cause severe damage to human health with excessive exposure. People whose dietary habits include a lot of fish that is contaminated with mercury are particularly affected. This involves the particularly toxic transformation product methylmercury, which can cause irreversible damage to the nervous system primarily in unborn babies (WHO 1991). Mercury is released into the environment by such human activities as mining, combustion processes, chemical processes and the use and disposal of mercurial products.

In light of the health risks, the European Commission agreed in 2005 on a Community Strategy Concerning Mercury with the goal of reducing the concentration of mercury in the environment. To this end, measures already taken to reduce mercury input in the environment are to be further reviewed and reinforced (European Commission 2005). The strategy contains a series of measures which the European Commission and the member states are to take to achieve the goal of reducing the mercury levels in the environment and human exposure. A ban on exports of mercury from the Community borders is proposed as measure no. 5. As a result, the EU Parliament and the Council agreed on a mercury ban regulation. It contains the following four key issues:

- The export from the EU of elemental mercury, mercury ore, mercury(I) chloride, mercury(II) oxide and other substances with a mercury level above 95% weight by weight is prohibited from March 15th, 2011.
- Metallic mercury, which is produced from the extraction of cinnabar ore or which is no longer used in the chlor-alkali industry or which accrues during the cleaning of natural gas and the production of non-ferrous metals, is to be classified as waste which must be disposed of.
- By way of derogation from the ban on disposing of liquid waste in landfills in the Landfill Directive, metallic mercury may be stored in specially adapted salt mines or in facilities in solid rock for longer than one year or permanently.
- Prior to final disposal, the facilities require a special safety assessment and approval in which the particular risks arising from the nature of mercury are taken into account. The specific requirements must first be defined in the annexes of the Landfill Directive.

Based on a study by BiPRO (2010), the European Commission has compiled criteria for the temporary storage of mercury. They were agreed on by the Council as Directive 2011/97/EU. Up to now, there was no adequate scientifically supported basis which would allow criteria to be derived for the permanent storage of metallic mercury. Thus the Commission has deferred the submission of a relevant directive for permanent storage pending further research results[1]. As long as this directive is not formulated and approved, a disposal of metallic mercury may not take place.

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[1] Proposals for relevant requirements in the aforementioned BiPRO report were only taken notice of so far.

This does not affect the disposal of stabilised mercury. Most technical stabilisation processes involve mercury sulphide, which originates as a product of the chemical conversion of metallic mercury with sulphur. As solid waste, it may be disposed of in underground storage according to the applicable law. Solidification is mentioned as an option in the mercury ban regulations, but is not further assessed in light of ongoing research.

Overall, approx. 11 000 tonnes of mercury are to be expected from European sources by 2040, which must be disposed of. Residual amounts of mercury still existing in the electrolytic cells of the chlor-alkali industry comprise the bulk of this total (approx. 7 400 tonnes), while approx. 83 tonnes from non-ferrous production (especially zinc) and gas purification (see section 2.1) are added to this annually.

Only the five underground storage which are in operation in Europe are eligible for final disposal. Except for a facility in the UK, which can accept only a few selected types of waste, all eligible underground storages are in Germany.

1.2 Objective: Requirements for the permanent storage of mercury underground

The objective of the investigations conducted as part of this project was to obtain information and experimental data on the chemical and physical behaviour of mercury, selected mercury compounds and mercury waste during the operational phase[2] and the post-operational phase of an underground storage. On this basis, potential risks are to be identified for operational safety and long-term safety and recommendations are to be developed for additional technical and organisational requirements for the permanent storage of elemental and stabilised mercury in an underground storage.

In particular, the study had the task of investigating three aspects of the safety of underground storage:

- Safety during the operational phase: Representation of important chemical and physical properties of liquid and stabilised mercury (mercury sulphide) in contact with air and analysis of the resultant risks when operating a underground storage - development of proposals for technical and organisational measures to prevent accidents and to reduce risks.
- Description of the likely behaviour of liquid and stabilised mercury (mercury sulphide) in the salt rock after achieving complete enclosure while taking into account a failure of containers and other technical barriers.
- Behaviour of metallic mercury and mercury sulphide upon completion of the operational phase of an underground storage in the event of a hypothetical solution inflow: experimental determination of the solubility of elemental mercury, mercury oxide and mercury sulphide in relevant saline solutions as well as expected solution concentrations when leaching mercury waste. To allow a quantitative comparison with already stored waste types, the experimental studies were also extended to selected mercury waste.

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[2] "Operational phase" indicates the period from the installation of the underground storage to the end of the waste disposal operations. It follows the decommissioning phase in which the mine is closed. The "post-operational phase" then starts and describes the unaffected geological further development of the underground storageunderground storage system.

1.3 Methodology

In accordance with the objective, the completion of the task took place in five stages:

1. Behaviour of mercury and stabilised mercury under normal conditions and under hypothetical accident conditions

In preparation for the derivation of risks for operational and long-term safety, physical and chemical data from the literature was compiled and assessed. This concerned in particular the stability of mercury and stabilised mercury (mercury sulphide) in contact with air and salt rock as well as exposure to heat, e.g. in the event of a fire.

2. Chemical and physical long-term behaviour of mercury and stabilised mercury in contact with salt rock and saline solutions

The assessment involved the chemical compatibility of mercury with salt rock and also the long-term chemical behaviour of mercury, selected mercury compounds and mercury wastes in contact with saline solutions. For this purpose, the dissolution behaviour of mercury, mercury oxide (as an example of pollution of elemental mercury), and mercury sulphide was investigated experimentally and compared with selected mercury wastes in selected saline solutions. The work was supplemented by thermodynamic modelling. To assess the alternative option of a disposal of mercury sulphide in above-ground landfills, the long-term behaviour of mercury sulphide in such facilities was discussed.

3. Analysis of results which can lead to a release of mercury during the operational phase

To be able to assess which risks are involved in dealing with metallic mercury in the underground storage operation, events that can lead to a release of mercury during above-ground and underground operation were identified and analysed (risk analysis). The studies assumed normal operation of an underground storage, but also took potential accidents into account.

4. Development of recommendations for technical and organisational measures to prevent the release of mercury and the endangerment of occupational safety during the operational phase.

After identifying the specific risks, the goal now was to develop proposals for technical and organisational measures which could eliminate or reduce the risk of the release of mercury even in the hypothetical event of an accident. The recommendations were developed both for the permanent storage of metallic mercury as well as mercury sulphide.

5. Analysis as to whether mercury-specific risks must be dealt with for the post-operational phase

Finally, the question as to whether there are mercury specific risks for the long-term safety of underground storage was investigated. In this case, the likely behaviour of stored liquid mercury in the post-operational phase assuming various development scenarios was derived based on experimental and theoretical work.

2 Origin, quantities and disposal of mercury

2.1 Origin and quantities of the mercury to be disposed of in the EU

The largest amount of mercury that will have to be disposed of in the course of the next decades is expected to come from the area of the chlor-alkali industry. The European chlorine industry has voluntarily undertaken to opt out of the mercury cell technology-based production of chlorine and alkali hydroxides by 2020. Mercury was and is used as an electrode to electrolyse saline solutions and to separate them into chlorine and alkali hydroxides. At the end of 2011, there were still 7 164 tonnes of mercury in European chlor-alkali facilities (European Commission 2012), which must be disposed of by 2020. 171 tonnes were already in facilities for temporary or permanent storage. Furthermore, approx. 83 tonnes of mercury are expected annually and continuously from non-ferrous production (especially zinc production) and gas purification (Concorde 2006). Extrapolated over 40 years, this results in almost 11 000 tonnes of mercury for which a disposal option is sought. The fourth source specified in the regulation (extraction of mercury from cinnabar) has no more practical relevance after mining was discontinued in Almadén (Spain).

Tab. 1: Surplus mercury in five regions of the world

Region	Forecast quantity [tonnes]	First possible occurrence of a surplus	Period	Source
South, Southeast and East Asia	5 500 - 7 500	2017	2010 - 2050	Concorde (2009)
Latin America and the Caribbean	2 000 - 8 000	2013	2010 - 2050	UNEP (2009)
Eastern Europe (excluding the EU) and Central Asia	2 300 - 10 000	2011	2010 - 2050	UNEP (2010)
USA	7 500 – 10 000[3] DOE storage: 1 200 DNSC storage: 4 436	2013 DOE/DNSC: already exists	2013 - 2042	US EPA (2007) DNSC (2003) US DOE (2009)
EU	10 700	2011	2011 - 2050	This work based on Concorde (2006), European Commission (2012)
Total	34 000 - 52 000			

DOE: Department of Energy; DNSC: Defense National Stockpile Center

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[3] The higher value (10 000 t) includes imports from Latin America. These are not considered in the sum total to avoid counting them twice.

Mercury from other sources (recycling, soil remediation) is currently not classified as waste by the mercury ban regulation. If, however, the European demand for mercury, e.g. for the production of dental amalgam or energy-saving lamps, is permanently lower than the supply from the specified sources, the need to dispose of it is also to be expected here. The amount of mercury contained in contaminated areas in the EU27+2 is estimated, for example, at 11 000 – 20 000 tonnes, of which only about 900 to 1 900 tonnes are regarded as extractable (COWI 2008). In the next 40 years, between 34 000 and 52 000 tonnes of metallic mercury could be pending disposal worldwide (Tab. 1), whereby disposal concepts are also being examined in other regions[4].

2.2 Disposal of metallic mercury

In accordance with the EU regulation on the mercury export ban, metallic mercury, which is classified as waste, must be disposed of permanently. Only adapted salt mines or, alternatively, deep rock formations, which offer an equivalent level of safety and containment, are permitted in principle as storage locations for the disposal of metallic mercury. There are currently five underground disposal facilities for hazardous, non-radioactive waste in operation in the EU (Tab. 2). They are only in salt formations, one of which is in Great Britain and the other four are in Germany. Facilities in solid rock are not in operation at present and are not planned either according to current knowledge. A previous project of the Swedish government to establish its own underground storage specifically for mercury in Sweden was abandoned in favour of a more cost-effective disposal in other European countries (Naturvårdsverkets 2001, Swedish Ministry of the Environment 2009). None of the five underground storages operated in the European Union are approved for the disposal of metallic mercury.

Tab. 2: Underground storage in Europe

Country	Facility	Operator
Germany	Herfa-Neurode, Hessen	K+S Entsorgung
Germany	Zielitz, Sachsen-Anhalt	K+S Entsorgung
Germany	Sondershausen, Thüringen	Glückauf Sondershausen Entwicklungs- und Sicherungsgesellschaft mbH (GSES)
Germany	Heilbronn, Baden-Württemberg	UEV - Umwelt, Entsorgung und Verwertung GmbH
Great Britain	Minosus, Cheshire	Veolia Environmental Services

Elemental mercury currently may not be disposed of directly in an underground storage because, as a liquid, it is excluded from disposal in accordance with Landfill Directive 1999/31/EC and the waste acceptance criteria in the Council Decision 2003/33/EC. Only the acceptance of mercury waste has been allowed so far. According to the practice to date,

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[4] Reference is made to the various projects supported by UNEP in Asia and Latin America. http://www.unep.org/hazardoussubstances/Mercury/PrioritiesforAction/SupplyandStorage/Activities/tabid/4505/language/en-US/Default.aspx

however, this also includes solid waste which contains liquid mercury, e.g. rubble, soils or old measuring devices.

The disposal of up to 10 000 tonnes of elemental mercury entails specific risks. Thus EU Regulation 1102/2008 prescribes the determination of specific requirements for the facilities and special acceptance criteria for metallic mercury to be stored before a facility may start storing mercury.

2.3 Disposal of stabilised mercury

Additional requirements are not legally required, however, if elemental mercury is chemically stabilised, i.e. converted to a thermodynamically stable mercury compound, e.g. mercury sulphide. Various processes for stabilising elemental mercury have been developed worldwide. Most of them are based on a conversion to mercury sulphide (Hagemann 2009). As far as is known, there are currently only two processes available that are either already in use on an industrial scale (DELA, Germany) or are prepared for industrial use (MAYASA, Spain).

The DELA process is based on a gas phase reaction of elemental mercury (min. 99.9% purity) with sulphur at high temperatures. The reaction is performed in batches in a large vacuum mixer. It leads to the formation of pure cinnabar powder (α-HgS). Approx. 800 kg of mercury can be stabilised per batch. The annual capacity of the facility is 4 000 tonnes of mercury (DELA 2009, Kummel 2011). According to the company, 280 tonnes of elemental mercury were stabilised in total up to September 2012[5]. The cost of stabilisation including disposal is specified as 2,000 euros per tonne (DELA 2010).

In contrast, the MAYASA process consists of two stages. In the first stage, elemental mercury is pulverised with sulphur so that black metacinnabar (β-HgS) is obtained. In the second stage, the product is melted at <140°C with a mixture of sulphur, gravel, sand, calcium carbonate and a sulphurous polymer into a monolithic mass (López et al. 2009, MAYASA 2010, López-Delgado et al. 2012a, b)[6]. The construction of a facility with a daily capacity of 2.5 tonnes is planned, whereby the price for the stabilisation should be about 2,000 euros per tonne (González 2011, Ramos 2012).

Almost all other stabilisation processes discussed or developed worldwide can be traced back to one of these two types of production. Processes for the solidification of mercury as amalgam (preferably as a zinc or copper amalgam) are an exception. The produced amalgams (= alloys with mercury) are soft solids, which have the same mercury vapour pressure as pure mercury. There were no advantages as a result in terms of handling, thus the development of these processes was discontinued worldwide, apart from the special case of radioactive mercury for which there are no alternatives otherwise (Hagemann 2009). The analysis in this report is thus restricted to the products of DELA and MAYASA.

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[5] S. Kummel (DELA), personal communication, 24.9.2012

[6] There are reports elsewhere of a more advanced process variant in which aggregates such as gravel, sand and calcium carbonate are omitted (González 2011, Ramos 2012).

According to the European Commission (European Commission 2012), 171.1 tonnes of mercury were delivered up to 31.12.2011 from the chlor-alkali industry to facilities for temporary or permanent storage. 166 tonnes of this were stabilised at DELA and taken to a salt mine. Gas and non-ferrous metal production reported 18.8 tonnes, 12.4 tonnes of which were stabilised at DELA and disposed of in the Sondershausen underground storage. 1.9 tonnes were processed by BATREC (Switzerland) and exported to Germany for permanent storage. The final whereabouts of the remaining quantity is not exactly clear.

There are currently no analyses of the specific risks of underground disposal of stabilised mercury. These are to be investigated and necessary requirements formulated for operational practice if necessary.

3 Specific properties of mercury

3.1 Toxicity and exposure

The heavy metal mercury and its compounds are highly toxic for humans and ecosystems. It re-enters the biosphere in small quantities (500 t/a) by such natural processes as volcanism and erosion and is immobilised to the same extent by sedimentation and other processes (Selin et al. 2008a, b). As a result, mercury was always present in small quantities in all environmental media. Since the 16th century, however, man has also mobilised significant quantities of mercury by mining mercury ores specifically. Mercury has been used in products and processes since then and is also released during the combustion of coal and processing of ores. Since 1500, about one million tonnes of mercury in total have been obtained from mining, used and released into the biosphere (Hylander and Meili 2003). Currently, approx. 3 400 tonnes of mercury are released annually into the biosphere due to human activities (Selin et al. 2008a,b). This additional input has led to much higher concentrations of mercury in soils, sediments, oceans and rural bodies of water. A simulation by Selin et al. (2008b) showed that only about 32% of the Hg precipitation in the US region is caused by natural primary emissions, about 42% is based on anthropogenic primary emissions, while 20% is based on anthropogenic re-emissions.

Mercury is emitted in elemental (Hg^0) or ionic form (Hg^{2+} or Hg_2^{2+}), but it can also be converted by specific bacteria to methylmercury as a by-product of sulphate reduction in environmental media (Gilmour and Henry 1991). This methylmercury can be absorbed by plants and animals, and fish in particular. As a lipophilic substance, it accumulates similar to persistent organic pollutants in the food chain. The highest concentrations are found in large predatory fish, for example, shark, tuna and swordfish, as well as in fish which are found in the Arctic. In this region, the deposition of mercury from the atmosphere into seawater is particularly high. People who consume a large amount of fish have a higher risk of being exposed to increased mercury levels. Even with average eating habits, however, fish consumption beside releases from dental amalgam represent the most important source of mercury exposure of the general population (IPCS 1991, UBA 1999, European Commission 2001, BfR 2010). It should however be noted that contaminated fish contains the much more toxic methylmercury, while dental amalgam primarily releases only elemental mercury.

Increased exposure to mercury can lead to severe damage to health, especially in the unborn and infants. When subjected to high doses, patients mainly complain of headaches, dizziness, nervousness and bad memory; metallic taste, vomiting and diarrhoea persist. Pulmonary oedema and slight trembling of the hands occur in extreme cases. If such symptoms have manifested themselves once, patients suffer from them for years (WHO 1991, WHO 2003, Mergler et al. 2007).

The signs of the disease manifested themselves particularly drastically in the inhabitants of Minamata Bay (Japan). In the 1950s, methylmercury was discharged with the wastewater of a chemical plant directly into the sea and contaminated seawater, sediments and fish. As a result, many of the residents of the coastal region became ill with mysterious diseases that were only able to be associated years later with the wastewater discharges, the mercury contained in the wastewater and the accumulation of mercury in the food chain (MOE Japan 2002).

3.2 Specific properties of elemental mercury

The following Tab. 3 lists important specific properties of elemental mercury which may be of importance for its permanent underground storage. The information is taken from the “Mercury Data Sheet” (Hillenbrand et al. 2006) and other sources specified in the table.

Tab. 3: Properties of metallic mercury and implications for its handling in underground storage (operational phase)

Characteristic	Property	Assessment/ consequences for handling in underground storages (operational phase)
Melting point	-38 °C [1]	Liquid at room temperature: Prevention of leakage, provision of collecting basins
Boiling point	357 °C [1]	Depending on the temperature, mercury may be completely converted to a gas: Prevention of a thermal impact[7]
Vapour pressure	0.25 Pa at 25°C (20 mg/m^3) 0.54 Pa at 30°C 37 Pa at 100°C 2 660 Pa at 205°C 53 300 Pa at 323°C [2]	Already forms significant partial pressure at room temperature. Exponential increase in partial pressure when temperature is increased; possibly exceeding the occupational exposure limit (0.02 mg/m^3) at room temperature: Prevention of a thermal impact, use of tightly closed and pressure-resistant containers
Density	13.5 g/cm✣ at 25°C [1]	Leaking liquids and vapours are heavier than air / dispersed droplets sink into the smallest cracks, crevices (permanent source of contamination): Prevention of leakage from a container (decontamination is very difficult or impossible) Monitoring the mine air and exhaust used air at floor level
Mobility	Very mobile due to high surface tension, forms very small droplets	Prevention of leakage from a container, provision of collecting basins
Flammability	Non-flammable [1]	No special extinguishing agents required
Water solubility	0.06 mg/l at 25°C [2] Practically insoluble in water	No special measures required
Formation of alloys	Forms amalgams with a number of metals (e.g. copper, silver, gold, aluminium) [3]	Avoidance of direct contact of mercury with container materials which contain these metals
Chemical reactivity	Chemically stable under normal conditions, reacts very slowly with atmospheric oxygen [4], but faster in the presence of water [5]. Can be converted via intermediate steps to methylmercury in soils, sediments and bodies of water [6]	No special measures required in an underground storage, only highly oxidising compounds (e.g. chlorates, chromates, nitric acid) should be avoided. Depositing mercury waste in above-ground landfills should be avoided because it would be a potential long-term source of methylmercury
Corrosion resistance	At room temperature, no reaction or very slow reaction with iron, unalloyed steel or stainless steel [7]. Corrosion only at higher temperatures or in the presence of other reagents (water, gases, salts) [7] [8]	These materials can be used as container materials or as parts of the container. Corrosive contaminants should be avoided
Human toxicity	Toxic after intake via food, inhalation or	Prevention of leakage from a container

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[7] Thermal impact: intentional or accidental heating of an object above the ambient temperature

Characteristic	Property	Assessment/ consequences for handling in underground storages (operational phase)
	skin contact) [1]. Acute and chronic neurological effects, especially in the unborn and infants.	Avoidance of direct contact, especially avoidance of inhalation of vapours
Biodegradability	Not biodegradable, water hazard class 3 [1]	Prevention of leakage from a container Prevention of penetrating the surface water or groundwater

[1] Hillenbrand et al. (2006); [2] Clever (1987); [3] Greenwood and Earnshaw (1990), [4] Hollemann and Wiberg (1984); [5] Amyot et al (2005); [6] Han et al. (2008); [7] Conde et al. (2007), [8] Leeper (1980)

The vapour pressure of elemental mercury at 25°C is $2.5 \cdot 10^{-3}$ hPa = 20.6 mg/m^3 (Clever 1987). This value far exceeds the maximum occupational exposure limit which is specified as 0.02 mg/m^3 by the Technical Rules for Hazardous Substances (TRGS 900). The vapour pressure increases exponentially with the temperature. At 30°C, the value is already at 31.1 mg/m^3 (Clever, 1987). A release of mercury may lead to impermissible concentrations, especially in enclosed and poorly ventilated areas. Less knowledge is available on the kinetic behaviour of liquid mercury, thus on the evaporation speed of mercury and on the behaviour of mercury gas in mine air.

In summary, the following specific properties are to be considered in particular in a risk analysis:

- As a liquid, leaking mercury can spread easily over a large area, especially if there is a slope.
- Liquid mercury releases toxic gaseous mercury that can already reach a gas concentration at 25°C which is far beyond the permitted concentration in the workplace.
- As a gas, mercury can be transported over long distances and can cause secondary contamination.
- Mercury droplets easily penetrate underground pores and cracks due to their high specific weight. This results in contamination which is difficult to clean and which constantly forms a secondary emission source.

3.3 Specific properties of stabilised mercury

“Stabilised mercury” means solid products which result from a chemical reaction of liquid metallic mercury with suitable reagents. All processes[8] that are applied on a large scale worldwide to stabilise mercury lead to the formation of mercury sulphide, thus the following discussion is focused on this chemical compound. Mercury sulphide occurs in various modifications (black metacinnabar β-HgS and red cinnabar α-HgS) with different crystal structures, but whose physical and chemical properties differ only slightly from each other. The presentation of the properties of mercury sulphide in Tab. 4 thus applies for both modifications as well as for mercury sulphide, which was mixed with other materials. Further details on the most important stabilisation process can be found in section 2.3.

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[8] With the exception of some special processes for the solidification of radioactive mercury (Hagemann 2009)

Tab. 4: Properties of mercury sulphide and their implications for its handling in underground storage (operational phase)

Characteristic	Property	Assessment/ Consequences for Handling in underground storages (operational phase)
Melting point	Under normal pressure, there is no melting point, but decomposition occurs until equilibrium is reached with gaseous mercury and sulphur. From 585°C, the decomposition pressure exceeds 1 bar (atmospheric pressure) [1]	At ambient temperature: no special measures required
Boiling point	None because decomposition occurs beforehand [1]	
Degradation pressure (Hg)	25°C: $7 \cdot 10^{-12}$ hPa 100°C: $2 \cdot 10^{-7}$ hPa 300°C: 0.24 hPa 500°C: 222 hPa 565°C: 1 011 hPa (own calculations on the basis of [1])	For dry storage: flame-proof design of containers, prevention of a thermal impact
Density	8.1 g/cm✥ at 25 °C [2]	No special measures required
Mobility	Heavy solid (powder or monolith)	No special precautionary measures required Provision of respiratory protection
Flammability	From 250-300°C and with a sufficient supply of air, a conversion to Hg and SO_2 occurs [4,7]. According to MAYASA, their product is non-flammable in accordance with EN ISO 11925-2:2002 [3].	Adapt extinguishing agent to surrounding fire Self-contained breathing apparatus and chemical protective suit. Condense escaping vapours with water [5]. Prevention of a thermal impact
Water solubility	Pure product: around $2 \cdot 10^{-5}$ mg/l at 25°C (estimate: [6]	No special measures required
Reactivity with container materials	Metals. Plastics, glass: none known	No special measures required
Chemical reactivity	Chemically stable under normal conditions, virtually does not react with atmospheric oxygen under dry conditions. No reaction at room temperature with the addition of air and water [7]	No special measures required
Corrosion resistance	No known reaction with steels or plastics	These materials can be used as container materials or as parts of the container or packaging
Human toxicity	Toxic after intake via food, inhalation or skin contact) [1]. Acute and chronic neurological effects, especially in the unborn and infants, and also organ damage [8] [9]	Prevention of leakage from a container Avoidance of direct contact, especially avoidance of inhalation of dust
Biodegradability	Not biodegradable, water hazard class 3	Prevention of leakage from a container Prevention of penetrating the surface water or groundwater

[1] Leckey and Nulf (1994); [2] Lide (1991); [3] MAYASA (2010); [4] Habashi (1997); [5] Kremer Pigmente (2008); [6] Dyrssen and Wedborg (1991); [7] Wells et al. (1958) [8] UBA (1999) [9] Liu et al.(2008)

In comparison to elemental mercury, mercury sulphide demonstrates only negligible vapour pressure at room temperature. It is also solid, which greatly simplifies handling. Only minor risks are involved with a release of mercury sulphide compared to elemental mercury. The assessment looks otherwise when it comes to a thermal load. Mercury sulphide is not thermally stable at fire temperatures, but decomposes into the elements in the absence of oxygen or is oxidised to mercury and sulphur dioxide in the presence of atmospheric oxygen. This is not in contradiction to the findings of MAYASA (2010) and López-Delgado et al. (2012b) that the product produced by them is non-flammable. The results of the studies indicate only that their product does not continue to burn by itself after a propane gas flame is applied. A more detailed discussion of thermal stability is found in section 4.3.5.

Toxicologically, mercury sulphide is usually treated as part of the group of inorganic mercury compounds, even though it is resorbed less due to its low solubility in comparison to other compounds (oxide, chloride). Continuous exposure can lead to damage to the nervous system and organs, as with other mercury compounds (Liu et al. 2008). Thus both elemental mercury and mercury sulphide are to be regarded as toxic to humans.

In summary, the following specific properties are to be noted:

- Mercury sulphide can be easily handled in solid form.
- Open handling of mercury sulphide dust should be avoided to prevent ingestion and inhalation.
- Mercury sulphide decomposes at increased temperatures and is oxidised by air from approx. 250°C.

4 Long-term chemical behaviour of mercury, mercury compounds and mercury waste

4.1 Solution types which may occur in salt formations

An underground storage may be established only if a permanent isolation of the stored waste from the biosphere can be demonstrated as part of a long-term safety assessment (§ 3 DepV (landfill ordinance) in conjunction with Annex 2). This is achieved only if the geological barrier of the salt rock as well as the technical barriers (shaft and drift seals[9]) remain permanently intact so that an inflow of groundwater from the overburden[10] cannot occur. The inflow of solutions from the deposit areas is to be viewed as a hypothetical sequence of events which is not assumed in the planned long-term development of the salt formation. If a solution inflow nevertheless occurs, the source of the inflow may be the salt formation itself (limited inflow of isolated solutions without hydraulic contact with the overburden) or the overburden (potentially unlimited inflow with hydraulic contact with the overburden). In both cases, typical solution compositions (or combination thereof) are to be expected, which result from the reaction of infiltrating solutions with the natural salt rocks. Of these, the following compositions can be regarded as typical for many salt deposits (Herbert 2000):

- Saturated NaCl solution: Saturated solution which results from the dissolution of pure halite (NaCl).
- IP9 solution. Solution which results from the dissolution of polyhalitic rock salt (Herbert 2000). This rock type consists of the minerals halite, anhydrite ($CaSO_4$) and polyhalite ($K_2Ca_2Mg[SO_4]_4{\cdot}2H_2O$). IP9 solution is in equilibrium with the minerals anhydrite, glauberite, ($Na_2Ca(SO_4)_2$), halite, polyhalite and syngenite ($K_2Ca[SO_4]_2{\cdot}H_2O$) (Harvie et al. 1982).
- IP21 solution: Solution which results from the dissolution of the potash rock carnallitite or some hard salts. Carnallitite consists of the minerals carnallite ($KMgCl_3{\cdot}6H_2O$), kieserite ($MgSO_4{\cdot}H_2O$) and halite. Hard salts consist of sylvite (KCl), halite and at least one other mineral (e.g. kieserite or anhydrite). The most common type is kieseritic hard rock (sylvite, halite, kieserite and possibly anhydrite, Herbert 2000). IP21 solution is in equilibrium with the minerals halite, sylvite, kainite ($KMgClSO_4{\cdot}3H_2O$), carnallite and polyhalite (Harvie et al. 1982). The Q solution has an almost identical composition. In contrast to the IP21 solution, however, it does not contain any calcium and is not saturated with polyhalite.

The behaviour of mercury, mercury compounds and mercury wastes in contact with these solution types is the object of the research in this study. The experiments simulate the hypothetical case of a solution inflow in the post-operational phase. The aforementioned solutions were produced synthetically in the laboratory for this purpose. Naturally-occurring IP21 solutions contain trace elements in addition to the ions Na, K, Mg, Ca, Cl and SO_4. Depending on the place of origin, these can be bromine (as bromide), iron (as Fe^{2+}), manganese (as Mn^{2+}),

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[9] The horizontal mine workings are known as drifts in a mine

[10] The rock stratum overlaying the salt formation is known as the overburden

strontium (as Sr^{2+}), lithium (Li^+) or other elements (Herbert 2000, Herbert and Schwand 2007). A solution that occurred during a borehole test in the carnallitite rock in the Asse II mine near Remlingen (Lower Saxony, Germany) was selected as an example. Its composition is similar to IP21, but it contains the minor elements which occur in the natural carnallitite rock. The composition of the equilibrium solutions depends on the temperature. 25°C is generally used as a reference temperature. If solutions are produced or obtained at 25°C, precipitation may occur when heating or cooling these solutions. Naturally-occurring solutions may differ in their composition from those solutions produced by laboratory experiments. This may be due to many causes. For example, naturally-occurring salt solutions are not always in complete thermodynamic and thermal equilibrium with the salt minerals which are present. Reasons for this may be that the contact time has been too short or not enough of a certain mineral was available along the flow path to achieve complete saturation. Super-saturations are often described because the formation of new minerals is delayed (e.g. kainite). The selection of a certain composition of a solution can thus never illustrate all of the solutions occurring in potash and rock salt deposits, but are only exemplary. On the other hand, one can assume that the fluctuations in the natural compositions are not significant in terms of the solubility of mercury and mercury compounds since this is determined essentially by the concentration of the main elements.

Production and composition of the solutions used in the laboratory experiments

The aforementioned solutions were produced as follows:

- Saturated sodium chloride solution was obtained by dissolving sodium (p.a.) in deionised water up to saturation.
- Synthetic IP9 solution is produced according to the GRS process “LA006”. Here, various sodium, potassium and magnesium salts are dissolved successively in water; the solution is not obtained immediately, but one must wait until equilibrium is reached by stirring for a long time. The production is successful if the density lies within a narrow range. Otherwise, it must be lowered by adding water or adapted by adding sodium chloride. The final control is done by chemical analysis.
- Synthetic IP21 solution is produced according to the GRS process “LA007”. Here, various sodium, potassium and magnesium and calcium salts are dissolved successively in specific amounts of water; the solution is not obtained immediately, but one must wait until equilibrium is reached by stirring for a long time. The production is successful if the density lies within a narrow range. Otherwise, it must be lowered by adding water or adapted by adding synthetic carnallite. The final control is done by chemical analysis.
- Quasi-natural IP21 solution: The starting point for the production of this solution was a solution composition which developed during an in-situ borehole test in carnallitite rock in the Asse mine (carnallitite solvation experiment CLV, laboratory no. 5132, sample name CLV2/35 of 9.9.1986, Herbert 2000). Its composition is similar to IP21. It is characterised primarily by a higher level of bromide, lithium and rubidium than the IP21 solution. Its production was similar to the synthetic IP21 solution, but with the addition of sodium bromide, rubidium chloride and lithium chloride.
- So-called mixing solution (German “Anmachlösung”): A $MgCl_2$ solution which is produced by dissolving halite (NaCl), carnallite ($KMgCl_3*6H_2O$) and kieserite ($MgSO_4H_2O$), and which lies near the point R.

The composition of the solutions was determined by means of ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry), ICP-MS (Inductively Coupled Plasma – Mass Spectrometry) as well as potentiometric titration (Cl) (Tab. 5).

Tab. 5: Composition of the solutions

	Saturated NaCl solution	Synthetic IP9 solution	Synthetic IP21 solution	$MgCl_2$ solution, so-called "mixing solution" for Asse	IP21 solution according to Asse CLV experiment
Na [mg/l]	125 200	82 790	7 259	1 077	7 433
K [mg/l]	-	31 537	14 953	579	10 947
Mg [mg/l]	-	22 857	90 130	105 400	94 993
Ca [mg/l]	-	<LoQ	4.26	34.6	<LoQ
Cl [mg/l]	190 363	196 897	269 193	294 723	273 500
SO_4 [mg/l]	-	35 795	26 825	19 997	34 267
Br [mg/l]	-	-	-	4 091	3 189
Mn [mg/l]	-	-	-	8.45	-
Li [mg/l]					0.2833
Sr [mg/l]					0.1033
Zn [mg/l]					2.743
BO_2 [mg/l]					22.49
Density	1.1976	1.2425	1.2913	1.3043	

LoQ: limit of quantification

An uncontrolled inflow of solution during the operational or decommissioning phase is not assumed and not further investigated. However, the conditions of some partial experiments (mercury in contact with solutions and atmospheric oxygen) correspond in principle to the conditions that could be expected in such a case.

4.2 Experimental methods for determining the solubility of mercury and mercury compounds in saline solutions

4.2.1 Solubility of elemental mercury in saline solutions

Consumption of oxygen is to be expected in an underground storage in the long term due to corrosion and other oxidation processes. For this reason, the solubility experiments were primarily conducted in an argon atmosphere without oxygen.

The study of the solubility of elemental mercury in aqueous solutions necessitates special requirements in terms of the purity of raw materials, the exclusion of atmospheric oxygen and the analysis.

A bead of highly pure mercury was presented in a 250 ml gas and liquid-proof screw cap jar in a glove box flushed with argon (Merck Suprapur 99.9999%). Then, approximately 200 ml of the relevant solution as well as hydrazine hydrate were added as a reducing agent (6 mg per 100 ml). These formulations were stirred by means of a magnetic stirrer. The experiments were conducted in the glove box to avoid any subsequent contamination by atmospheric oxygen due to leaks. The temperature in the glove box was between 23 and 25°C. Solubility depends only slightly on the temperature within this narrow temperature range. Glew and Hames (1972) found that the solubility in a saturated NaCl solution increased by approx. 5% per degree at temperatures around 25°C. This is less than the measurement scatter which they found at these temperatures. Further temperature control was thus unnecessary for the purposes of this project.

Experiments with air

Some comparative experiments were intended to indicate the effect of atmospheric oxygen on equilibrium concentrations. To this end, elemental mercury, solution and stirring bar were placed in a 250 ml glass vial in contact with air.

Overview of all experiments, sampling and analysis

The following experiments were conducted:

1. Solubility of elemental mercury in saturated NaCl solution
2. As previously, but in the presence of atmospheric oxygen
3. Solubility of elemental mercury in synthetic IP9 solution
4. As previously, but in the presence of atmospheric oxygen
5. Solubility of elemental mercury in synthetic IP21 solution
6. As previously, but in the presence of atmospheric oxygen
7. Solubility of technical mercury in saturated NaCl solution
8. Solubility of technical mercury in synthetic Q solution
9. Solubility of technical mercury in synthetic IP9 solution

The solubility of contaminated mercury in saline solutions was also investigated (see section 4.3.4). A sample provided by DELA GmbH (Essen) served as technical mercury.

The sampling took place in an argon atmosphere in a glove box after the stirrer had been switched off for at least two hours. By means of a pipette syringe, an aliquot of the supernatant was removed and transferred to a sample which contained 1 ml 2% $K_2Cr_2O_7$ and 1 ml 20% H_2SO_4 as an oxidising agent. As a result, existing elemental mercury was transferred in its non-volatile oxidised form. There was no filtration in order to avoid sorption of dissolved mercury in the filter material. The solutions were filled up to the calibration mark after the addition of nitric acid (1%). Their analysis was conducted after diluting 1:1 000 by means of ICP-MS. The lower limit of quantification of the mercury concentration in the analysis solution was 0.8 µg/l.

All experiments were conducted in three parallel batches. The sampling in the first batch was conducted after one, two and three weeks. If the concentrations were stable, samples were also taken from the parallel batches.

4.2.2 Potential contaminants in metallic mercury

As mercury can oxidise in the air and a complete exclusion of air cannot be permanently guaranteed during technical handling of mercury, mercury oxide is a contaminant that cannot be avoided. Mercury can contain other contaminants depending on its usage and origin.

For the chlor-alkali industry it is known that the used high-purity mercury is contaminated during the operation of the cells by the addition of raw materials, especially by sodium chloride (or potassium chloride), and by the contact of the mercury with the facility components. Primarily, iron as well as chromium and vanadium (Klotz 1973) or calcium and molybdenum (O´Grady 1970) arise as metallic contaminants. There are also reports of copper, nickel and lead. The higher the concentration of metallic contaminants in mercury, the lower is its viscosity. The terms amalgam butter or mercury butter are used to describe such a state. Iron concentrations in the order of 0.2 to 0.5% by weight were found in the amalgam butter (O'Grady 1970). Added to this are ionic contaminants which float on the mercury due to their lower density. These can be mercury compounds, but also iron oxides and other substances. The metals dissolved in mercury are removed in the chlor-alkali facility by various processes, e.g. by electrolysis (Solvay 1974) or by reacting with saline solutions. Residual metal concentrations below 10^{-5}% by weight are achieved at the same time (Klotz 1973, O'Grady 1970).

Mercury obtained from natural gas extraction is a highly contaminated raw product which can contain water as well as greasy and oily substances in addition to metallic contaminants (Rudolf and Knoche 1982). Depending on the level of foreign matter, it is also occurs as sludge. This mercury cannot be stored directly on a long-term or permanent basis. It must be treated in advance, whereby the recyclers use a multi-stage process in which the mercury is first evaporated from the waste, condensed and then distilled one or more times for purification[11]. However, the literature also contains processes which are based on a reaction with aqueous solutions with which most of the contaminants are removed and purities of 99.9% or higher are achieved (Rudolf and Knoche 1982).

Mercury residues from gas extraction (drilling fluids and scales) may also contain radioactive contaminants.. Currently, there is little quantitative information about the final disposal of these wastes. A part of it is treated by specialized companies (Gellermann et al. 2003).

No information was available on the purity of the mercury from the extraction of non-ferrous metals. It must be assumed that, depending on the type of processed ore, it still contains amounts of the volatile elements zinc and cadmium and possibly lead, and does not achieve the purity of 99.9%, thus would still have to be purified. Distillation, electrochemical and wet chemical processes can be considered for this purpose, as they are also used in the chlor-alkali industry.

In the following studies, mercury oxide (HgO) is used as a model substance for soluble ionic mercury compounds.

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[11] Cf. e. g. Presentation of GMR Leipzig http://www.gmr-leipzig.de/pdf/schema.pdf

4.2.3 Solubility of mercury oxide in saline solutions

The following experiments were intended to indicate the solubility of mercury oxide (HgO) in relevant saline solutions.

To this end, approx. 3 g HgO (Alfa Aesar Puratronic 99.998%) were mixed in each case in a PTFA screw cap bottle with about 45 g of solution and were turned upside down and shaken. The use of plastic containers is necessary because high pH values occur during the dissolution of HgO, which can corrode glass containers. Samples were taken at intervals of about 4 weeks. The analysis was conducted with ICP-MS. The last sampling was conducted after 6.5 months.

The following experiments were conducted:

1. Solubility of mercury oxide in saturated NaCl solution
2. Solubility of mercury oxide in synthetic IP9 solution
3. Solubility of mercury oxide in synthetic IP21 solution
4. Solubility of mercury oxide in $MgCl_2$ “mixing solution”
5. Solubility of mercury oxide in IP21 solution (Asse CLV)

The analysis of the filtered solutions took place due to the high mercury concentrations achieved with ICP-OES.

4.2.4 Solubility of mercury sulphide in saline solutions

Mercury sulphide occurs in three variations. Only the red (α-HgS, cinnabar / vermilion) and the black (β-HgS, metacinnabar) are relevant for technical and natural processes. Cinnabar is the more thermodynamically stable of the two variations. However, reactions at room temperature always yield metacinnabar.

The solubility of mercury sulphide in neutral, aqueous solutions was estimated to be about 10^{-10} mol/l (Dyrssen and Wedborg 1991). Experiments with such low solution concentrations must be conducted with great care to avoid the formation of colloids or more soluble minute crystals. The experiment was conducted in a latent manner, that is, neither solid nor solution was agitated to avoid crystal abrasion.

10 g of mercury sulphide were filled into a 5 ml glass vial in a glove box flushed with argon. The solution was then added drop by drop until the mercury sulphide was just covered with it. This was the case with the 7 ml solution. The very high solid to solution ratio enabled an accelerated equilibrium to be reached in the process. The glass vials were not shaken, tilted or turned upside down. Their temperature was controlled at 25±1 °C in the climatic chamber. The subsequent sampling was conducted in a glove box. The extracted solution was filtered with 0.02 µm filters, the first drops of the filtrate were discarded in the process. The sample was placed in a volumetric flask with 1 ml 2% $K_2Cr_2O_7$ and 1 ml 20% H_2SO_4 and the amount of the sample was weighed. The mercury sulphide in the experimental container was then re-filled with salt solution to enable subsequent sampling.

25 g of mercury sulphide and IP21 solution were used in a comparative experiment. Here, sampling was conducted after 2 weeks as well as after 1, 2, 3 and 4 months. The decision as to when sampling would be conducted for the other experiments was based on the results of this experiment.

Two modifications of mercury sulphide were used for the experiments: black mercury sulphide (Alfa Aeasar 13783) and red mercury sulphide (DELA GmbH). Experiments were also conducted with a stabilised mercury waste (mercury sulphide in matrix) of the Spanish company MAYASA (see section 4.3.4).

Both mercury sulphides reached equilibrium with the following solutions:

1. Saturated NaCl solution
2. Synthetic IP9 solution
3. Synthetic IP21 solution
4. $MgCl_2$ mixing solution
5. IP21 solution (Asse CLV)

4.2.5 Determining concentration of dissolved mercury after contact of selected mercury waste with saline solutions

The objective of these experiments was to determine the mercury concentrations which result from the hypothetical contact of waste with saline solutions. The experiments also serve as a comparison for the classification of results with elemental mercury and mercury sulphide. If such a reaction should occur, a slow penetration of the waste by the solution and practically negligible flow rates can be expected. The system would thus be stationary. The shaking and leaching experiments regularly used when studying waste (e.g. DEV S4/ DIN 38414 part 4) do not reflect these conditions. They are a suitable method for obtaining a quick impression of the leachability of certain pollutants. However, their objective is not to determine the maximum achievable pollutant concentrations which occur with the hypothetical inflow of saline solutions. To achieve this experimentally, consideration must be given to the fact that a storage chamber filled with salt grit must be backfilled to a level of 50 - 80% (Herbert and Mönig 1996). This results in a ratio of solid to solution of 1:1 at most, which increases further due to subsequent convergence (DIN 38414 part 4 provides 1:10 in contrast). On the other hand, the physiccal and thus also the physico-chemical properties of the waste can change significantly by the intensive movement (shaking upside down), which can lead, among other things, to colloid formation and artificially inflated pollutant concentrations. However, such a backmix reactor is not to be expected in an underground storage.

Thus, a process was applied with which neither the waste nor the solution phase are moved. A 100 ml glass container was filled to approx. 4/5 with untreated waste. Solution was added until the waste was just covered with it. The experimental formulations were stored at 24±1 °C. A sampling took place once a month in argon. The analysis was conducted as for the experiments with elemental mercury.

The investigated waste types are summarised in Tab. 6. They include, among others, a stabilised mercury waste of the Spanish company MAYASA (CA 1009). This involves a black mercury sulphide, which was brought into a solid concrete-like form by dissolving in a liquid sulphur/sand/polymer blend.

Tab. 6: Tested mercury wastes

GRS waste no.	Description	Mercury level [mg/kg]
CA 545	Electrolysis residue (pace), mercurial	0.5 to 6.0 (inhomogeneous material)
CA 1005	Mercurial sludge	20 900
CA 1006	Mercurial KU catalyst (natural gas production)	59 300
CA 1007	Elemental mercury, contaminated / low degree of purity	996 000
CA 1008	Mercurial activated carbon	575 000
CA 1009	Stabilised mercury waste from MAYASA	325 000

Solubility experiments were conducted with the following solutions:

1. Synthetic IP9 solution
2. Synthetic IP21 solution
3. $MgCl_2$ mixing solution
4. IP21 solution (Asse CLV): only stabilised mercury waste from MAYASA

4.3 Chemical stability of elemental mercury and mercury sulphide in contact with salt rock, air and aqueous solutions

4.3.1 Stability of elemental mercury in contact with atmospheric oxygen

Metallic mercury, Hg(0), can react with atmospheric oxygen (O_2) in accordance with

$$2Hg(0) + O_2(g) = 2HgO(s) + \Delta G_R = -113.2\ kJ/mol^{12}\ (\Delta H = -452\ kJ/kg\ Hg)$$

to become mercury oxide (montroydite). The formation is exothermic and should proceed spontaneously. However, it was observed that pure mercury does not indicate any oxidation reaction, but remains blank and does not indicate any formation of an oxide layer. Instead, oxidation is reported only for contaminated mercury (Hollemann and Wiberg 1985). The exact causes are unclear, but kinetic effects can be assumed. Contaminants could act as a catalyst for the oxidation reaction.

4.3.2 Stability of elemental mercury in contact with salt rock

There is no need to be concerned about a reaction of elemental mercury with the salt rock (NaCl or potassium salts such as KCl). The hypothetical reaction

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[12] This and all other reaction enthalpies were calculated on the basis of the free enthalpies of formation of the reactants from Barin (1989). In cases where atmospheric oxygen was involved in the reaction, consideration was given to the fact that air only has an oxygen content of 21% by volume. The free reaction enthalpies are then slightly higher.

$$2Hg(0) + 2NaCl(s) = Hg_2Cl_2(s) + 2Na(s)\ \Delta GR = +557{,}5\ kJ/mol$$

is extremely endothermic (thus energy consuming) and does not proceed spontaneously. The same applies to other relevant salt minerals. Mercury thus remains permanently stable in addition to salt minerals.

4.3.3 Stability of elemental mercury in contact with aqueous solutions

4.3.3.1 Dissolution in water

Elemental mercury may dissolve in water via three processes:

- Reaction with dissolved oxygen,
- Oxidative dissolution of mercury by reaction with water,
- Molecular dissolution of mercury (without changing the oxidation state).

Mercury is a relatively noble metal. It is not attacked by pure water in the absence of oxygen. The equilibrium of the reaction

$$Hg(0) + 2H^+(aq) = Hg^{2+}(aq) + H_2(g)\ \Delta G_R = 164.8\ kJ/mol$$

is entirely on the side of the raw materials, thus a conversion does not occur. It is also made more difficult by the phenomenon of over-voltage. Accordingly, the formation of hydrogen on a mercury surface is kinetically inhibited, even if it were thermodynamically possible (Ackermann et al. 1988).

4.3.3.2 Reaction with dissolved oxygen

However, dissolution can take place in the presence of atmospheric oxygen. According to the reaction

$$2\,Hg(0) + O_2(g) + 4H^+(aq) = 2\,Hg^{2+}(aq) + 2H_2O\ \Delta G_R = -470.41\ kJ/mol$$

mercury is transferred into an oxidised form. Amyot et al. (2005) found that the oxidation rate is increased significantly if small quantities of chloride are present. Depending on the pH value and the presence of other ions, mercury remains as Hg^{2+} in solution or precipitates in the form of insoluble compounds such as mercury oxide or mercury sulphide. Under certain redox conditions and in the presence of chloride, the reaction can also lead to mercury(I) chloride (calomel).

$$4\,Hg(0) + O_2(g) + 4H^+(aq) + 4\,Cl^-(aq) = 2\,Hg_2Cl_2(s) + 2H_2O\ \Delta G_R = -891.5\ kJ/mol$$

The formation of calomel is to be expected in particular if there is an excess of elemental mercury. Divalent Hg^{2+} which may have formed would react with elemental mercury to become calomel:

$$Hg^{2+}(aq) + Hg(0) + 2\,Cl^-(aq) = Hg_2Cl_2(s)$$

The following diagram describes the stability of the various mercury species depending on the redox potential (Eh) and the pH value (Fig. 1). It was generated by using the code Geochemist's

Workbench and the “thermo.dat V8.R6” database[13]. Elemental mercury is the most stable species over wide Eh/pH ranges. Oxidised compounds such as Hg^{2+}, Hg_2^{2+} or mercury oxide (montroydite) are formed only with high redox potentials, as are possible in the presence of oxidising agents or atmospheric oxygen.

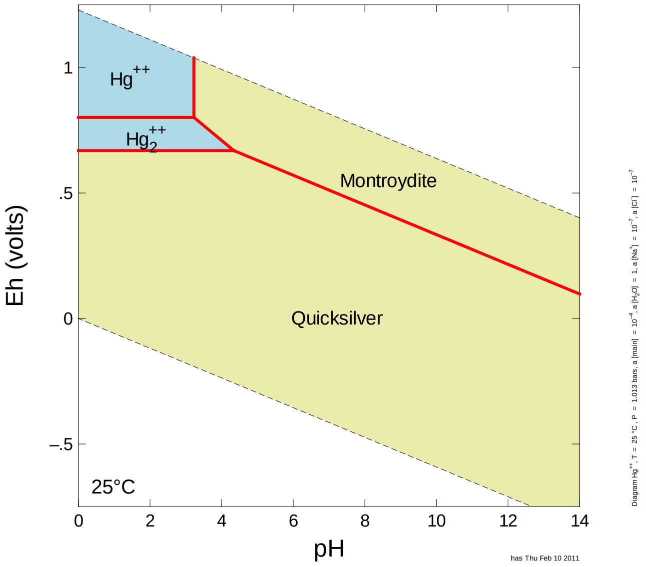

Fig. 1: pH/redox equilibrium in the Hg-H_2O system

If the systems are in contact with air (20.95% by volume O_2) under normal pressure, the redox potential thus lies near the upper dotted line of the diagram (the upper stability limit of water). Deep groundwater generally has low redox values well below 0 mV since the oxygen available in the near-surface zones is degraded by the degradation of humic substances and reaction with minerals (e.g. Fe(II) compounds or sulphides) (Grenthe et al. 1992).

4.3.3.3 Dissolution in saline solutions

If aqueous solutions contain chelating agents which can reduce the concentration of the free mercury ions, the aforementioned redox equilibria thus move to the side of the oxidation products. Chloride is a strong chelating agent for mercury, which leads to the formation of chloro complexes:

$$Hg^{2+} + n\,Cl^{-} = [HgCl_n]^{2-n} \; (n = \; 1 \ldots 4)$$

The complex $[HgCl_4]^{2-}$ is to be found primarily in the saturated NaCl solution (Hagemann et al 2013). The oxidative dissolution can be described with the following formula:

$$Hg(0) \; + \; 2H^{+} \; + 4Cl^{-} = \; [HgCl_4]^{2-} \; + \; H_2(g)$$

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[13] This database was originally derived from the GEMBOCHS database for the calculation codes EQ3/6. The complex formation constants for HgCl2(aq) and HgCl42- from Powell et al. (2005) were added for this modelling. In the Eh/pH diagrams, the calculation of the stability limits between various forms of oxidation in highly concentrated saline solutions is somewhat uncertain because the calculation code and the database for low concentrated solutions work with a simple Debye-Hückel formula. The Eh/pH diagrams thus have more of an indicative character, but still reflect the fundamental conditions sufficiently well according to previous experience with similar systems.

The reaction with oxygen proceeds according to

$$2\,Hg(0) + O_2(aq) + 8\,Cl^- + 4H^+ = 2\,[HgCl_4]^{2-} + 2H_2O$$

It is possible to calculate this effect for sodium chloride solutions. The thermodynamic database developed by GRS for mercury in a previous research project can be used as the data basis (Hagemann et al. 2013). This was derived from a combination of literature and laboratory data on the solubility and the vapour pressure of mercurial (II) saline solutions. The calculation results can be found in Fig. 2 (on the left). They show that an oxidation to dissolved mercury can already take place in a concentrated NaCl solution under weak oxidising conditions and at low pH values. It must be noted that weak oxidising conditions only last as long as oxidising agents (e.g. oxygen) can be supplied. Otherwise, the oxidation of mercury quickly leads to a decrease in the redox potential and to the end of the dissolution reaction.

The existing residual oxygen (from the enclosed mine air) would be the limiting value for the hypothetical case of a solution inflow to the stored waste of an underground storage.

The behaviour of elemental mercury in an IP21 solution currently cannot be predicted with certainty. The database derived from Hagemann et al (2013) is not applicable for this solution type. It is conceivable that the even higher concentration of chloride in an IP21 solution in combination with the present sulphate enables dissolution of mercury at least in very acidic solutions. According to the modelling for very acidic solutions, there could be a very narrow pH range (pH<0) in which mercury is dissolved without inflow of oxygen at least in the saturated $MgCl_2$ solution, which is quite similar to the IP21 solution (Fig. 2 on the right).

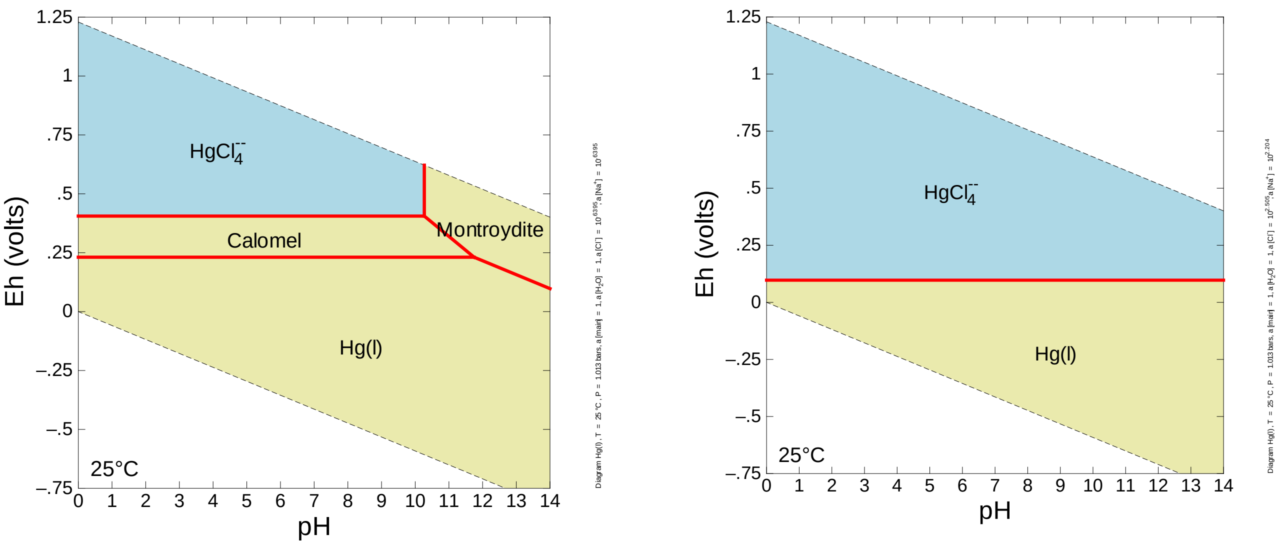

Fig. 2: **pH/redox equilibrium in the system Hg-Cl-H_2O in saturated NaCl solutions (c_{NaCl}=6.1 mol/kg) (on the left) and in saturated $MgCl_2$ solution (5.7 mol/kg) (on the right)**

However, there is no reason to assume that an inflowing solution has such low pH values because all relevant salt minerals that contribute to the composition of the solution are chemically neutral. They do not contain strongly alkaline nor strongly acidic reacting ingredients. There are no naturally-occurring solutions in salt rocks which have such a low pH value. Instead, one can expect solutions which are either neutral or which react slightly acidic due to the hydrolysis of the magnesium and calcium content. A dissolution of the mercury under the formation of hydrogen is thus not to be expected in the IP21 solution.

4.3.3.4 Extent of the dissolution of mercury for a hypothetical solution inflow

Since the oxidation of mercury uses oxygen, the reaction should come to a standstill once the existing oxygen supplies have been used up if the oxygen supply is missing. After the closure of an underground storage, only the oxygen of the remaining mine air is available if this has not already been used up to a large extent by other reactions, e.g. corrosion of metals from container materials or oxidation of iron(II) compounds in potash rock, fill and barrier materials. It must also be borne in mind that only the atmospheric oxygen in the immediate vicinity of the waste is eligible for oxidation reactions because other parts of the mine are separated after backfilling and the waste stored there is itself eligible for oxidation reactions (Hagemann et al. 2006).

There are no safe models as to how much air would be available after completion of the operational phase, the complete backfilling of the cavities and after complete enclosure. Such models are location-dependent and depend on many factors (backfilling technology, type and time of inflow, presence of other oxidation processes, location and size of remaining cavities), which cannot be checked within the framework of this project. A sample calculation should illustrate the quantities of mercury which could react with 1 000 Nm^3 of air via a long-term reaction.

1 000 Nm^{3}of air contains 210 m^3 of oxygen, which corresponds to 8 600 mol O_2. This would be in a position in accordance with

$$2\,Hg(l) + O_2(aq) + 8\,Cl^- + 4H^+ = 2\,[HgCl_4]^{2-} + 2H_2O$$

to oxidise up to 17 200 mol or 3.4 tonnes of mercury. It depends on the available amount of solution and its composition as to whether this amount could be completely dissolved and which concentration could be achieved in the process.

4.3.4 Stability of mercury sulphide compared with saline solutions and atmospheric oxygen

Mercury sulphide is stable in a dry state. It reacts with atmospheric oxygen only above temperatures around 250°C (Wells et al. 1958). The situation is different in the case of contact with water. Mercury sulphide has only a relatively narrow range of stability in the pH/redox potential field. This is located at low redox potentials. In the presence of atmospheric oxygen, mercury sulphide is not thermodynamically stable and is oxidised to elemental mercury (or Hg^{2+}) and sulphate. Kinetic effects can lead to the non-occurrence of a direct reaction to sulphate and the occurrence of intermediates such as sulphite or thiosulphite instead (Brandon et al 2001, Fig. 3).

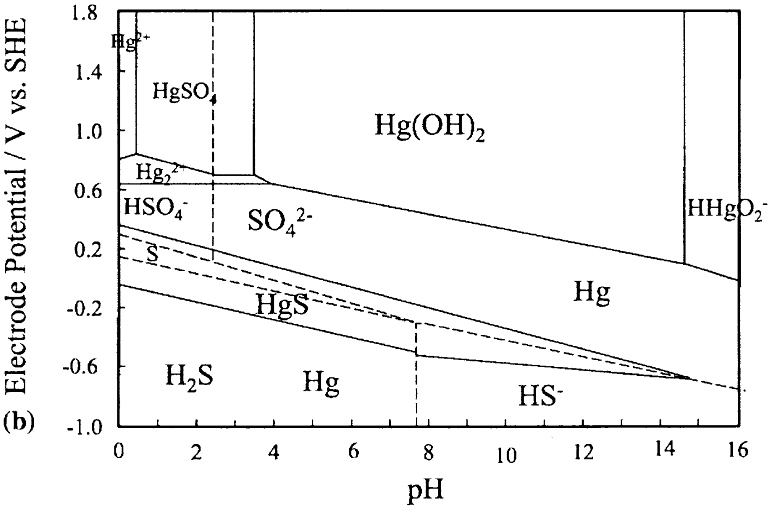

Fig. 3: Eh/pH diagram for the stable system Hg-S-H_2O at 25°C. Solution activity of Hg: 10^{-6}; S: 1 (Brandon et al. 2001)

However, this does not change the fundamental instability under atmospheric conditions. The oxidation reaction is slow and leads only to a partial release of Hg^{2+}because it is first sorbed by existing mercury sulphide (Burckstaller et al. 1975, Barnett et al 2001). Fe(III) can also act as an oxidising agent in addition to oxygen, at least in acidic solutions (around pH 2) (Burckstaller et al. 1975). Acid mine drainage can have such low pH values as a result of the oxidation of sulphides (Nordstrom et al. 2000). As already mentioned, they are unknown in salt mining. In the absence of oxygen and other oxidising agents, however, a massive phase of mercury sulphide is to be regarded as thermodynamically stable because it creates its own geochemical environment in which no other dissolving or recrystallising processes take place. This is also the case for saline solutions, even if "free" instead of dissolved Hg^{2+} chloro complexes such as $[HgCl_4]^{2-}$ are available (Fig. 4).

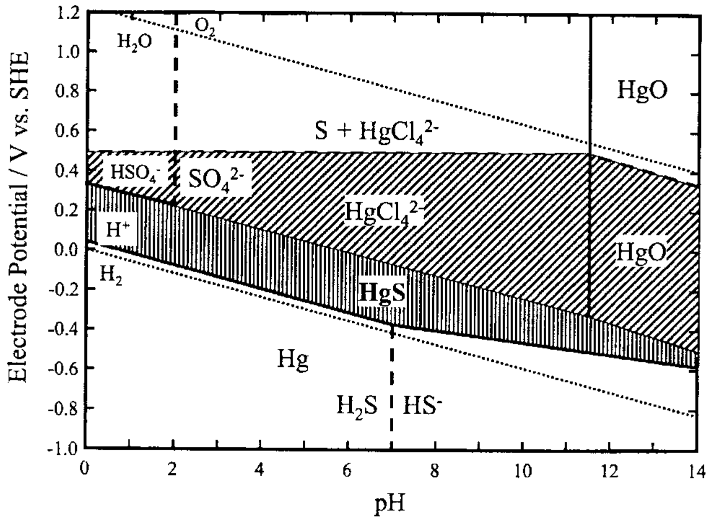

Fig. 4: Eh/pH diagram for the metastable system Hg-S-Cl-H_2O at 25°C. Solution activity of Hg: 10^{-6}, Cl: 1, S: 1 (Brandon et al. 2001)

4.3.5 Thermal stability of mercury sulphide

Mercury sulphide decomposes at higher temperatures and in the absence of oxygen in accordance with

$$HgS \rightarrow Hg(g) + ½\, S_2(g)$$

into elemental sulphur and mercury. At 585°C, the decomposition pressure equals 1 000 hPa, but already at a temperature of approx. 129°C, the calculated mercury decomposition pressure would be so high that it exceeded the occupational exposure limit for mercury (0.02 mg/m^3 equals $2.4 \cdot 10^{-4}$ hPa at 20°C][14]. In a closed system, only a relatively small amount of HgS would dissociate until the respective equilibrium is reached. In an open system in which gaseous mercury and sulphur are continuously dissipated, however, the decomposition process always continues. The decomposition rate depends on temperature. For example, only just over 1% of the mercury sulphide would be decomposed during a 60 minute heating to 260°C[15]. When heated to 310°C under experimental conditions (0.5 mg HgS in a quartz tube through which nitrogen flows), about 55% of the mercury sulphide was decomposed after 60 minutes (Fig. 5, Leckey and Nulf 1994). At 350°C, 10 minutes were sufficient in a large-scale experiment to remove 97% of the mercury sulphide from mercury waste.

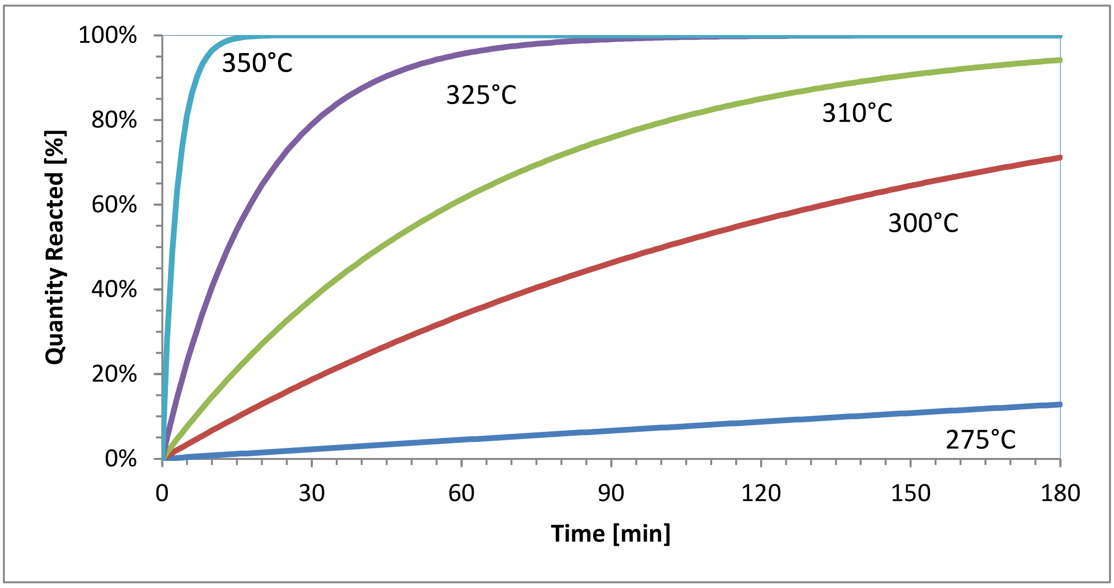

Fig. 5: Thermal decomposition of HgS at different temperatures according to Leckey and Nulf (1994)

With a sufficient supply of atmospheric oxygen, mercury sulphide is oxidised to sulphur dioxide and mercury from approximately 250-300°C (Wells et al. 1958, Habashi 1997)

$$HgS + O_2 \rightarrow Hg(l) + SO_2(g)$$

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[14] Own calculations based on the temperature function for the partial pressure of mercury using mercury sulphide pHg [atm]=1.26 e17.78-15098/T, which was specified in Leckey and Nulf (1994).

[15] Own calculations based on the rate constant from Leckey and Nulf (1994): k(T)=6.5·1018 e-27680/T . The relative proportion of the decomposed mercury sulphide is then calculated according to Q(t[min])=Q0(1-e-kt).

The standard enthalpy of combustion[16] (ΔH) is 243 kJ/mol or 1 046 kJ/kg HgS. If mercury is oxidised to mercury oxide at the same time in accordance with

$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2(g),$$

then the enthalpy of combustion is 668 kJ/mol or 1 436 kJ/kg. In both cases, the requirements of the Landfill Ordinance for a maximum calorific value (= standard enthalpy of combustion) of 6 000 kJ/kg were complied with.

4.4 Solubility of mercury and mercury compounds in saline solutions

4.4.1 Solubility of elemental mercury in water and saline solutions

There are numerous studies across a broad temperature range on the solubility of pure, elemental mercury (Hg^0) in pure water. They were compiled by Clever (1987) and analysed critically. According to the evaluation by Clever (1987), the solubility at 25°C is 3.01 (± 0.12) 10^{-7} mol/l or 0.06 mg/l. For comparison: The German Drinking Water Ordinance (TrinkwV) stipulates that the mercury level of drinking water may not exceed 0.001 mg/l.

There is very little data available on solubility in relevant saline solutions at 25°C (Clever 1987). Most of the literature values such as Sanemasa et al. (1981) are limited to weakly concentrated NaCl solutions up to about 1 mol/kg. Only Glew and Hames (1972) studied the solubility of mercury in saturated NaCl solution (6.1 mol/kg) and found a value of about $1.6 \cdot 10^{-7}$ mol/kg (0.025 mg/l). Thus solubility decreases with increasing salinity. In saturated NaCl solution, elemental mercury behaves similarly to neutral gases, which also dissolve in a molecular manner, that is, without dissociation, e.g. oxygen (Millero et al. 2002) or hydrogen sulphide (in acidic solutions: Moog and Hagemann 2004). Fig. 6 shows how the relative solubilities of these substances change with increasing sodium chloride concentration. Mercury behaves in saturated solutions similar to hydrogen sulphide as least at low concentrations and with some differences also. If one calculates the relative solubilities c_{rel} of Hg and H_2S with regard to the solubility in pure water $c_{I=0}$:

$$c_{H_2S,rel} = \frac{c_{H_2S,NaCl}}{c_{H_2S,I-0}}$$

it is easy to compare the development of the solubility depending on the salt concentration, even if the absolute solubilities are different. It is evident that the experimental data for the relative solubility of hydrogen sulphide (Moog and Hagemann 2004) in the lower concentration range is very consistent with the solubility studies of Sanemasa et al. (1981) for elemental mercury. In saturated NaCl solution, however, the relative solubilities for H_2S are approx. 30% lower than the measuring points of Glew and Hames (1972) for Hg(0) (Fig. 6).

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[16] Calculated on the basis of the standard enthalpies of formation of the reactants from Barin (1989)

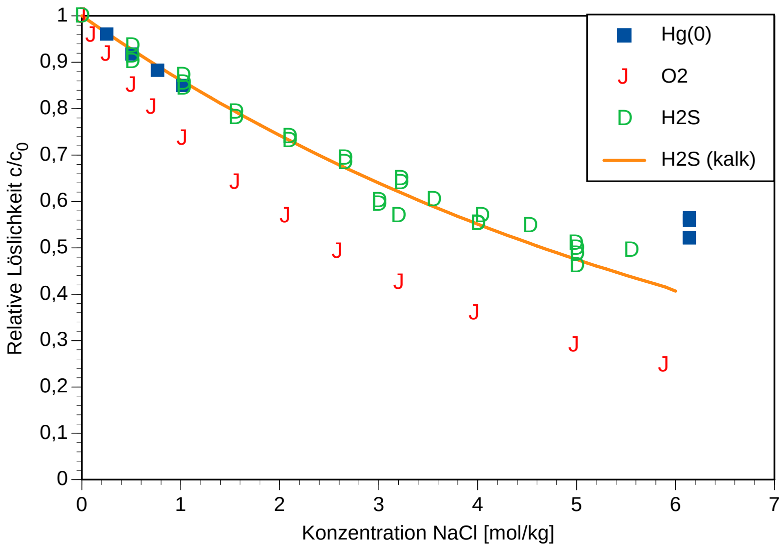

Fig. 6: **Comparison of the solubility of elemental mercury, oxygen and hydrogen sulphide in invariably concentrated sodium chloride solutions**

4.4.1.1 Experimental provisions

The solubility experiments were conducted over three months in total. In the measurements of the last five weeks, there were no significant changes in the observed concentrations. They amounted to the following for

NaCl solution:	0.5 ± 0.1 mg/l
IP9 solution:	0.7 ± 0.1 mg/l
Synthetic IP21 solution:	0.9 ± 0.2 mg/l

These values are well above the solubilities found in saturated NaCl solution (0.025 mg/l) by Glew and Hames (1972). It can be assumed that the ultra pure mercury that we use still contained traces of oxygen and oxidised mercury compounds which also cannot be reduced in the experiment by the addition of the reducing agent hydrazine. The measured values around 1 mg/l thus represent more practical solution concentrations, as they can arise during the reaction of solution and mercury in the relevant solution/mercury ratio, than thermodynamically substantiated solubilities. The elemental mercury waste intended for the underground storage is generally a used residual product of chlor-alkali electrolysis and should have nowhere near the purity of the tested Merck preparation. Thus rather more soluble contaminants are to be expected.

Much higher concentrations of mercury were found during the experiments under air inflow:

NaCl solution:	15 mg/l
IP9 solution:	49 mg/l
Synthetic IP21 solution:	64 mg/l

It was also observed that the mercury drops were covered with a grey coating with increasing duration of the experiments (Fig. 7). This was most evident in IP21 solution (less so in IP9, and least of all in NaCl solution). Here, dark grey shapeless lumps emerged in addition to matt mercury drops. The coatings as well as the lumps are probably calomel (Hg_2Cl_2). The dark colour is attributed in the literature to finely distributed mercury in the actually colourless to white calomel (Hollemann and Wiberg 1985). It arises during the photolytic decomposition of calomel into mercury and mercury(II) chloride in accordance with:

$$Hg_2Cl_2 \rightarrow Hg + HgCl_2$$

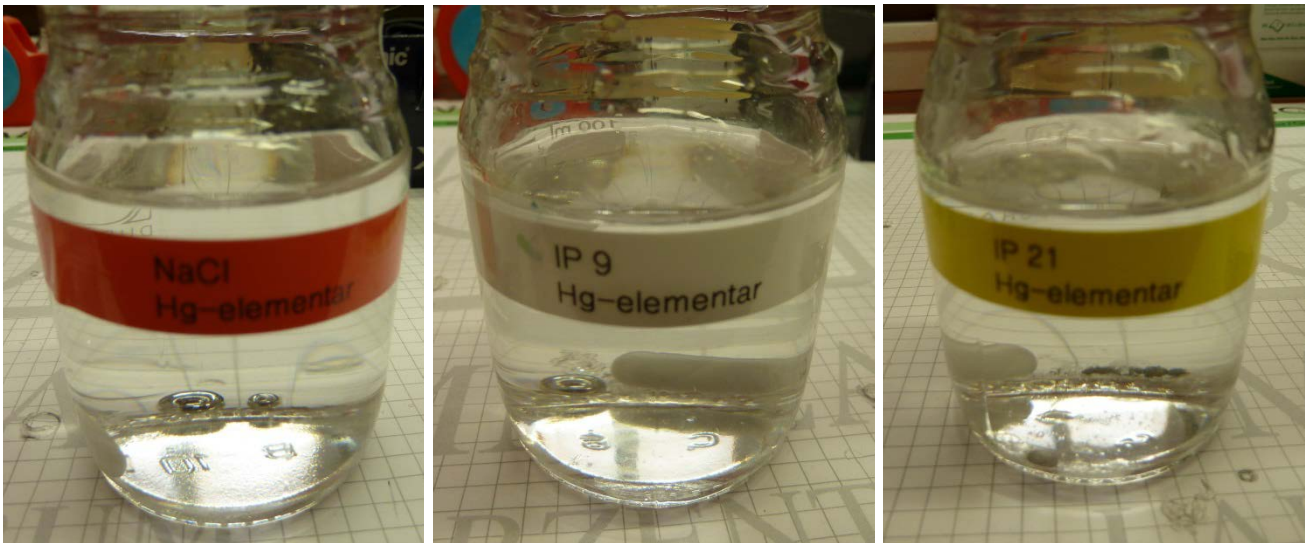

Fig. 7: Mercury drops at the end of the experiment in NaCl, IP9 and IP21 solution with air inflow

According to the calculations in section 4.3, the supply of atmospheric oxygen thus leads to a noticeable oxidation of mercury and to a significantly increased concentration of mercury in the solution.

4.4.2 Solubility of mercury oxide in saline solutions

Three modifications with different crystallographic structures are described in the literature for HgO:

- HgO, red (orthorhombic, montroydite)
- HgO, yellow (orthorhombic)
- HgO (hexagonal)

For the dissolution reaction

$$HgO + 2H^+ = Hg^{2+} + H_2O$$

the following solubility constants were found for 25°C in the course of the literature review by Powell et al. (2005):

HgO, red (orthorhombic):	log*Ks = 2.36 ± 0.08
HgO, yellow (orthorhombic):	log*Ks = 2.35 ± 0.08
HgO (hexagonal):	log*Ks = 2.39 ± 0.08

The solubility differences are obviously not significant and may be summarised as

HgO	log*Ks = 2.37 ± 0.08

To date, there was only the study by Herz and Hiebenthal (1929) on the solubility of mercury oxide in concentrated saline solutions. It shows that mercury oxide is only slightly soluble in diluted solutions, but its solubility increases strongly in sodium chloride solutions. The values of Herz and Hiebenthal (1929, 0.0089 mol/kg) and those found in this work (1 760-1 900 mg/l 0.01 mol/kg) are highly concordant for a saturated sodium chloride solution (Tab. 7; Tab. 19, Annex).

Tab. 7: Experiments with HgO: Hg concentration after 7.5 months

Solution type	Formulation (HgO/ solution) [g/ml]	Hg concentration [mg/l]
NaCl	0.067	1 760 to 1 900
Synthetic IP9	0.067	57 000 to 61 000
Synthetic IP21	0.067	61 000 to 64 000
MgCl2 "mixing solution"	0.67	63 000 to 64 000
IP21 solution (Asse CLV)	4.7	175 000 to 216 000

In IP9 and MgCl2 solutions, HgO was completely dissolved at an initial ratio of 0.067 g of HgO to 1 ml of solution (for formulations, see Tab. 19, Annex). Mercury concentrations of up to 59 ± 2g/l (IP9) or 62 ± 2g/l (synthetic IP21 solution) were found in the process. These solution concentrations are very high and indicate the presence of anionic chloro complexes (Hagemann et al. 2013).

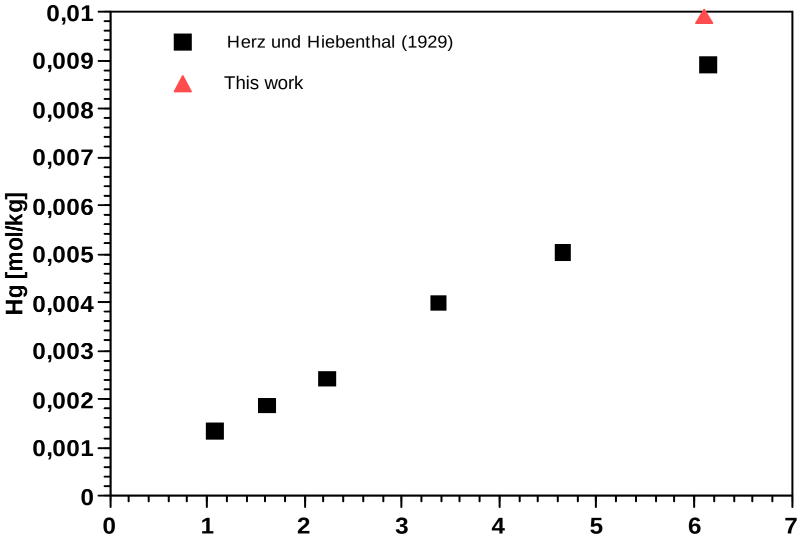

Fig. 8: Solubility of HgO in NaCl solutions

An increase in the solid/solution ratio to 0.67mg/l solution did not lead to any increase in concentration in MgCl2 mixing solution. A higher solid/solution ratio was used for an experiment with IP21 solution (Asse CLV). It leads to an increase in the concentration of mercury in the equilibrium solution to 175 - 216g/l. The final concentration in MgCl2 solutions is thus primarily determined by the solid/solution ratio. The dissolution of HgO in magnesium-containing solutions with precipitation of a white precipitate of magnesium hydroxide is illustrated in Fig. 9. In simplified form, the reaction is

$$HgO + Mg^{2+} + 4\,Cl^{-} + H_2O \rightarrow HgCl_4{}^{2-} + Mg(OH)_2$$

In conjunction with the solubility experiments with elemental mercury, it becomes clear that the existing readily soluble mercury compounds like mercury(II) oxide or mercury(II) chloride dissolve completely in the hypothetical case of a solution inflow to the underground storage. The resulting mercury concentration in the solution is then determined by these contaminants. The dissolution of pure elemental mercury only marginally increases the total mercury concentration. A sample calculation makes this even clearer: If a waste chamber with 100 tonnes of elemental mercury contains only 1 mg ($1 \cdot 10^{-9}$%) of soluble contaminants and a solution volume of 10 m^3, a mercury concentration of $1 \cdot 10^{-4}$mg/l results. However, the solubility of the elemental mercury is only $1.6 \cdot 10^{-7}$mg/l. Over 0.6 million m^3 of solution volume would be necessary to dissolve just 1 mg of elemental mercury out of 100 tonnes of metallic mercury present. However, 1 mg of soluble mercury compounds is sufficient to produce the same dissolved amount.

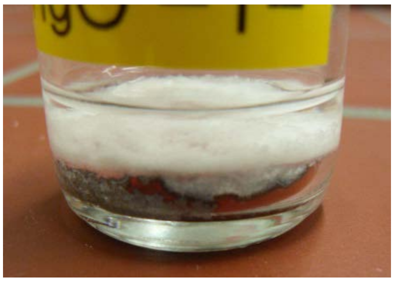

Fig. 9: Formation of a magnesium hydroxide precipitate upon contact of HgO with IP21 solution

4.4.3 Solubility of mercury sulphide in saline solutions

The dissolution of mercury sulphide can be described by the following equation:

$$HgS + H^{+} = Hg^{2+} + HS^{-}$$

The solubility constant for the reaction is specified as log K = -38.9 (Dyrssen and Wedborg 1991). However, it is not easy to derive a solution concentration for mercury from it. Depending on the sulphide concentration, mercury sulphide complexes are present, which can contribute to the total concentration in addition to Hg^{2+} (Paquette und Helz 1995). In this case, the observed solubility $c_{Hg,tot}$ of mercury sulphide is derived from the total of all concentrations c_i of the mercury species in equilibrium:

$$C_{Hg,tot} = v_{Hg,i} \sum_{i} c_i$$

ν_i Number of mercury atoms per species

Many different sulphide complexes are postulated in the literature, some of which were also able to be confirmed by spectroscopic measurements (Lennie et al. 2003). Without going into details of the various existing research studies, one can conclude that the solubility of mercury sulphide does not depend on the pH value in almost the entire range between pH 0 and pH 5.5, but is in fact constant (Schwarzenbach and Widmer 1963). The authors of this work found that the solubility of black HgS in 1 M KCl in the specified pH range is about 2.2 10^{-8} mol/l (0.0042 mg/l, log c = -7.7). They identified $[Hg(HS)_2]^0$ as a solubility-determining species, which cannot be differentiated from $[HgS]^0$ or $[HgOHSH]^0$, however, due to the experimental process.

At least in acidic solutions, the dissolution equilibrium for mercury sulphide could be described with the following equation:

$$HgS(s) = [HgS]^0$$

There are no direct experimental provisions for this reaction. Dyrssen and Wedborg (1991) estimated the equilibrium constant based on analogies with ZnS and CdS as

$$\log {}^\circ K = -10$$

This value marks the practical solubility of mercury sulphide. The mercury concentration can be higher in the presence of chelating agents. This may be the case in solutions containing chlorides. There, the dissolution reaction at least in acidic solutions can be described thus:

$$HgS(s) + 2H^+ + 4\,Cl^- = [HgCl_4]^{2-} + H_2S(aq)$$

This should also apply for neutral and possibly alkaline solutions because the formation of chloro complexes suppresses the formation of other complexes. In concentrated chloride-containing solutions, the equilibrium moves to the right with increasing proton concentration (decreasing pH) and the overall solubility increases.

Reliable data on the solubility of mercury sulphide in NaCl solutions was not available to date. A calculation of the solubility in 3 M NaCl by Nriagu and Anderson (1970) did not take any simple neutral complexes into account and predicted minimum solubility under 10^{-16} mol/l, which is contrary to the results of Schwarzenbach and Widmer (1963) in 1 M KCl (2.2 10^{-8} mol/l).

The results of our experimental studies are summarised in Tab. 8. It shows the mercury concentrations found after an experiment lasting 6.5 months (experimental formulations Tab. 20 and Tab. 21 in the Annex). The mercury concentrations found for all solutions are around the limit of quantification of the process (0.04 mg/l). For NaCl solutions, maximum values of up to about 0.3 mg/l were found, thus almost one hundred times higher than the values reported by Schwarzenbach and Widmer (1963) for 1 M KCl. This is a verifiable difference. On the one hand, the chloride concentration in the our experiments is much higher, thus the formation of chloro complexes is also much stronger, and on the other hand, it cannot be ruled out that the HgS preparations which were used by us contained small amounts of soluble mercury compounds (such as mercury oxide or mercury sulphate).

The solubility in various composite $MgCl_2$ solutions does not indicate any significant differences for black mercury sulphide as it is always around the limit of quantification of the analytical process (0.04 mg/l). With red mercury sulphide, however, the concentrations for $MgCl_2$mixing solution and IP21 solution (Asse) are around one order of magnitude higher and reach a maximum of 2.6 mg/l.

The concentration gradient over time is also interesting. The concentrations for the first measurement after the experimental formulation in black as well as red mercury sulphide were between 16 and 60 mg/l, but then fell in the second sampling (in the third sampling in one case) to the level indicated in Tab. 8 (Fig. 10).

Tab. 8: Mercury concentrations in solutions that are in equilibrium with mercury sulphide (limit of determination 0.04 mg/l)

Solution	HgS black [mg/l]	HgS red (DELA) [mg/l]
NaCl	<LOD to 0.045	<LOD to 0.30
IP9	<LOD to 0.26	<LOD
Synthetic IP21	<LOD to 0.045	<LOD
$MgCl_2$ mixing solution	< LOD	0.30 to 0.51
IP21 solution (Asse CLV)	<LOD to 0.13	2.6

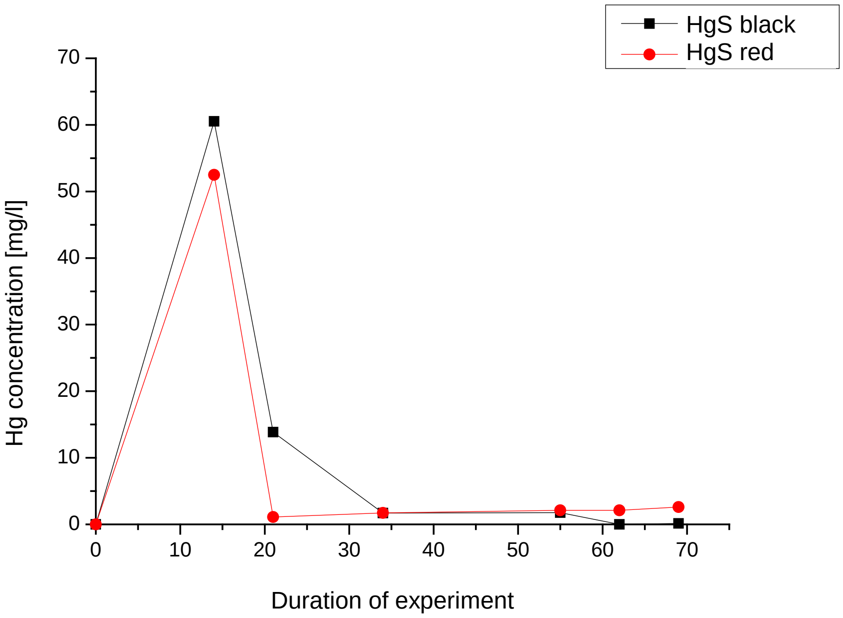

Fig. 10: Chronological gradient of mercury concentration for the reaction of mercury sulphides with IP21 solution (Asse)

Similar behaviour was also observed during the experiments with other saline solutions, even if it was not as pronounced. It can be assumed that existing dissolved mercury was first immobilesed to a large extent during the experiment by sorption or precipitation.

4.4.4 Mobilisation of mercury from mercury waste

Screenings of the GRS are available on the leaching behaviour of a large variety of mercury waste requiring special monitoring (Brasser 1991; Reichelt et al. 1995). They took place as batch or circulation column experiments. The waste contained up to 700 mg/kg of mercury, particularly the waste from combustion processes. The flue gas cleaning residues in particular indicated a measurable release of mercury in the leaching experiments. The concentrations here reached up to 8 mg/l in cap rock solution[17] and 2.8mg/l in Q solution (Tab. 9).

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[17] A cap rock solution is a solution which is saturated in gypsum (CaSO42H2O) and halite (NaCl).

Tab. 10 shows the mercury concentrations which have resulted during the experiments in our work. The tested mercurial sludge (CA 1005) led to a mercury concentration of up to 0.26mg/l upon contact with a NaCl or IP21 solution, however, this was below the limit of determination in some formulations.

The experiment with a mercury-contaminated catalyst (CA 1006) showed the highest release with up to 56 mg/l in an IP21 solution. The concentrations were 1.4 to 12 mg/l in NaCl and IP9 solutions. Similarly high concentrations (up to 49 mg/l) were achieved with the rubble (CA 554). They were somewhat lower (up to 7 mg/l) for the electrolysis residue (CA 545).

Tab. 9: Mercury concentrations when leaching waste (Brasser 1991)

No.	Waste description	Cascade experiments at 34.5°C: after 7th cascade		Circulation column experiments at 34.5°C after 90 days	
		With cap rock solution Hg [mg/l]	With Q solution Hg [mg/l]	With cap rock solution Hg [mg/l]	With Q solution Hg [mg/l]
CA 5	Flue gas cleaning residues	8.04	2.85	0.52	5.00
CA 8	Electrostatic precipitator dust (SAV)	< 0.01	< 0.01	(not determined)	0.024
CA 9	Slag (SAV)	-	-	0.002	-
CA 10	Silo dust (ESP dust/ slag/ ash) from SAV	-	-	0.02	0.01
CA 16	Sludge from flue gas scrubbing (HMV)	-	-	0.05	-
CA 17	Fly ash (SAV)	-	-	0.018	-
CA 19	Fly ash (HMV)	0.06	< 0.01	0.004	-
CA 22	Electrostatic precipitator dust (SAV)	0.06	0.04	0.004	0.85
CA 26	Flue gas cleaning residues (HMV)	0.01	< 0.01	0.004	0.028
CA 30	Flue dust (SAV)	0.01	0.49	-	0.183

(-): no experiment or not analysed for Hg

The highest mercury concentrations were found during the reaction of an activated carbon. They were between 520 mg/l (NaCl) and 960 mg/l (IP9). Mercury is present to an apparently considerable extent in easily soluble compounds in activated carbon. On the other hand, it must be assumed that mainly elemental mercury is present in the sludge as well as in the copper catalyst.

Of all waste, mobilisation was strongest in the IP21 solution and about 5 to 10 times higher than in the NaCl solution. This may be related to the higher chloride concentration in the IP21 solution, which promotes the chloro complex formation of mercury and thus its solubility. After higher values initially, the mercury concentrations of stabilised mercury waste from MAYASA were below the limit of determination of 0.04 mg/l. One exception was the experiment with

IP21 solution (Asse-CLV), where the concentration at the end of the experiment was 3.0 to 3.6 mg/l. A similar effect also occurred with red mercury sulphide (DELA). It must be assumed that the bromide content of the solution that was used (3 200 mg/l) also has a mobilising effect due to the formation of mercury bromide complexes to a lesser extent.

A comparison with the results from the solution experiments with mercury sulphide and elemental mercury show that Hg solution concentrations reach about the same order of magnitude in both cases. Pure mercury and pure mercury sulphide lead to much lower solution concentrations upon contact with a solution. Elemental mercury and mercury sulphide, even contaminated mercury, thus exhibit properties in terms of their dissolution behaviour which do not exceed the extent exhibited by underground storage-compatible mercury waste.

Tab. 10: Mercury concentrations during the reaction of waste with saline solutions (LOD= 0.04mg/l)

No.	Waste	Duration of experiment [months]	Saturated NaCl solution Hg [mg/l]	Synthetic IP9 solution Hg [mg/l]	Synthetic IP21 solution Hg [mg/l]	IP21 solution (Asse CLV) Hg [mg/l]
CA 545	Mercurial electrolysis residue (pace)	6.5	0.9 to 1.5	-	6.0 to 7.0	-
CA 554	Mercurial rubble and soil	5.5	30 to 35	-	41 to 49	-
CA 1005	Mercurial sludge	6.5	< LOD to 0.16	< LOD	0.09 to 0.26	-
CA 1006	Cu catalyst + Hg	6.5	1.4 to 4.7	6.7 to 12.3	37 to 56	-
CA 1007	Contaminated mercury	5.5	17	9.1	13	-
CA 1008	Mercurial activated carbon	6.5	520	960	590	-
CA 1009	Stabilised mercury waste from MAYASA	2	< LOD	< LOD	< LOD	3.0 to 3.7

(-): No experiment

4.4.5 Summary evaluation of the solubility experiments

In the hypothetical case of a solution inflow to stored waste consisting of elemental mercury, the resulting mercury concentration in the solution depends essentially on the amount of unavoidable, easily soluble mercury contaminants. The solubility of absolutely pure mercury is so low that no appreciable mobilisation can be anticipated. If, however, oxidising substances (atmospheric oxygen, certain types of waste) are available, oxidation and dissolution of mercury may occur. However, this is in competition with other oxidation reactions, e.g. the dissolution of metallic iron (from container materials).

The stabilisation of mercury to mercury sulphide leads to substances whose solubility is often so low that it cannot be measured by the processes which are used. In cases where a measurement was possible, the concentration which was found was in the same order of magnitude or lower than for mercury waste that was already stored in underground storage (Tab. 11).

In comparison to elemental mercury, the stabilised mercury waste (DELA and MAYASA) has lower solution concentrations in most experiments.

In relation to its mass, mercury waste can release significantly more mercury into the solution than elemental mercury or stabilised mercury waste (mercury sulphide). However, the absolute amount depends on the amount of stored waste. There is no exact information available concerning this, but it is known that mercury waste, e.g. from the dismantling of chlor-alkali facilities, is stored to a significant extent in underground storages. If the amounts (mercury waste, elemental / stabilised mercury) were in the same order of magnitude, more mobilised mercury could be expected from the already stored waste than from the newly added mercury in the hypothetical case of a solution inflow.

If the dissolution behaviour of stored waste mercury should be considered, it would be recommendable to avoid the occurrence of mercury oxide and other compounds that are easily soluble in saline solutions by increased purity standards for elemental and stabilised mercury.

Tab. 11: Mercury concentrations during the reaction of mercury, mercury oxide, mercury sulphide and mercury waste with saline solutions after the end of the experiment (2-6 months) (LoQ = 0.04mg/l)

Mercury containing substance	Saturated NaCl solution Hg [mg/l]	Synthetic IP9 solution Hg [mg/l]	Synthetic IP21 solution Hg [mg/l]	IP21 solution (Asse CLV) Hg [mg/l]
Elemental mercury (without air inflow)	0.5	0.7	0.9	
Elemental mercury (with air inflow)	15	49	64	
Mercury oxide	1 700 to 1 900	57 000 to 61 000	175 000 to 216 000	
Mercury sulphide (red/black)	<LoQD to 0.3	< LoQ to 0.26	<LoQ to 0.045	<LoQ to 2.6
Mercury wastes	< LoQ to 520	< LoQ to 960	<LoQ to 590	)*

)* Only one experiment with one waste type (stabilised waste from MAYASA): 3.0 to 3.7mg/l

4.5 Long-term behaviour of mercury sulphide in above-ground waste landfills

4.5.1 Legal basis for the disposal of mercury in landfills of classes 0-III

Hazardous waste, including that with a high heavy metal content, may be stored pursuant to §6 paragraph 2 DepV (German Landfill Ordinance) in above-ground landfills of class III if it meets all acceptance criteria of Annex 3 number 2 DepV. For mercury waste, this means that the mercury concentration in the leachate (leaching test according to DIN EN 12457-4) must not exceed 0.2 mg/l. Mercury sulphide also has the added distinctive feature that it is generally not classified as a hazardous substance or hazardous waste[18] because, according to the Commission decision 2000/532/EC (Waste Catalogue) and the German Waste Catalogue Ordinance (AVV), no hazardous properties (toxicity, carcinogenicity, among others) are assumed according to Annex III of the Waste Framework Directive 2008/98/EC. According to the Council Decision

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[18] See entry in GESTIS database of the Institute for Occupational Safety and Health of the German Social Accident Insurance (IfA) http://gestis.itrust.de/nxt/gateway.dll/gestis_de/004600.xml?f=templates$fn=default.htm$3.0

2003/33/EC (waste acceptance criteria) and the German Landfill Ordinance, it is currently possible to store mercury sulphide in landfills of all classes (including landfills for inert substances) provided the waste acceptance criteria are met. The mercury sulphide produced by DELA has a leachate concentration of less than 0.002 mg Hg/kg. According to the company's information the waste would theoretically be eligible for disposal in inert landfills according to the Council Decision 2003/33/EC (Kummel 2011). Although mercury sulphide shows a complete loss on ignition due to sublimation at 583°C (Lide 1991), this property would only lead to an exclusion for above-ground landfill classes 0 to III if it was attributable to organic components. No evidence exists, however, that mercury sulphide is currently being disposed of in above-ground landfills.

However, some European countries have stricter regulations. In Austria, Sweden, Belgium, Finland and the Netherlands, the depositing of mercury waste in above-ground landfills is not permitted if the total mercury level exceeds a certain threshold. Thus a maximum concentration of mercury in solid waste of 3 000 mg/kg applies in Austria, even for mercury waste stabilised as sulphide (Austrian Landfill Ordinance, Annex 2). Sweden and Austria stipulate that such waste is to be disposed of underground (BIOIS/GRS 2010). This raises the question of whether such restrictive requirements for the above-ground disposal of mercury sulphide are scientifically justified. This will be addressed below.

4.5.2 Thermodynamic stability

The chemical development of an above-ground landfill leads in the long term to a geochemical state similar to that of the environment. The surface sealing becomes porous and oxygenated rainwater and air penetrate the landfill body (Kranert and Kord-Landwehr 2010). Oxidising conditions are to be expected.

The thermodynamic stability of mercury sulphide in saline solutions was already dealt with above. They are not fundamentally different in dilute solutions that are to be expected near the surface. Mercury sulphide is stable only under reducing conditions. The inflow of oxygen leads to an oxidation of mercury sulphide to elemental mercury or mercury oxide (dissolved or solid) as well as sulphate (Fig. 11). Mercury can escape via the gas phase into the atmosphere (as indicated by the occurrence of mercury in the landfill gas of many sites (Lindberg et al. 2001, Lindberg et al. 2005, de la Rosa et al. 2006, Ilgen et al. 2007) or can be discharged in dissolved form into the groundwater. The solubility of mercury sulphide is significantly increased in the presence of humic substances (Reimers et al. 1974).

Under certain circumstances and geochemical conditions, mercury sulphide can also be formed in nature, e.g. in soils contaminated from elemental mercury, if reduced sulphur compounds are present (Barnett et al. 1997).

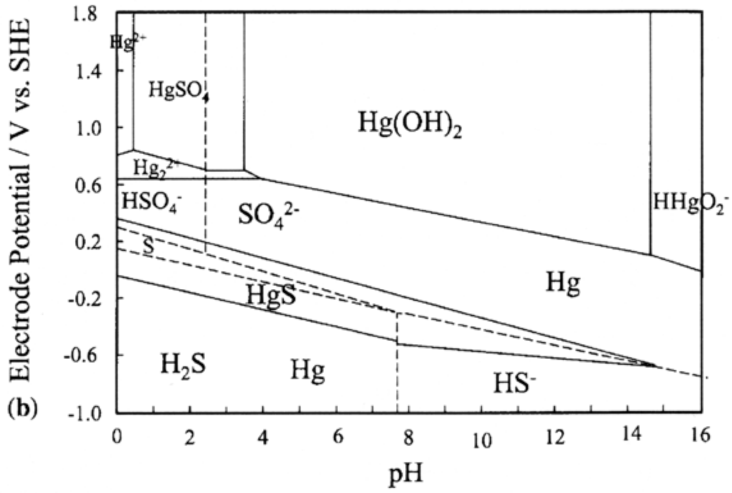

Fig. 11: Eh/pH stability fields for the system Hg-S-H_2O at 298 K (activities of Hg and S: 10^{-6} or 1) (Brandon et al. 2001)

4.5.3 Formation of methylmercury from mercury sulphide and other mercury compounds

Methylmercury, which can accumulate in the food chain as a lipophilic compound, is far more toxic than inorganic mercury compounds. It is produced as a by-product of the sulphate reduction under the reducing conditions of certain species of bacteria (Benoit et al. 2001; Boszke et al. 2003).

- If mercury waste is deposited in a landfill, methylmercury may be formed under suitable geochemical conditions. It can occur in landfill gas as a volatile organometallic substance and can be emitted into the atmosphere if there is an incomplete layout and retention (Lindberg et al. 2001, Lindberg et al. 2005, Ilgen et al. 2007).
- Mercury sulphide can also be used as a source for the formation of methylmercury. The neutral complex HgS^0, which is always in equilibrium with HgS, can be particularly well absorbed by certain strains of bacteria (Benoit et al. 1999; Benoit et al. 2001). The formation of methylmercury is correlated with the concentration of Hg(II), and especially with HgS^0(Hammerschmidt and Fitzgerald 2004).
- Methylation may also occur by abiotic means if suitable methylation reagents exist, which may have been created in turn by biotic means (Celo et al. 2006). An example of this is naturally-formed iodmethane in marine waters (Minganti et al. 2007).
- Akagi et al. (1977) described a photolytic reaction mechanism that leads to the direct formation of methylmercury from mercury sulphide and acetate.
- HgS can also be oxidised in acid mine drainage by Fe(III), even if a large part of the mercury is bound to other solid phases by subsequent reactions (Burkstaller et al. 1975).
- Optimum conditions for methylation in rivers and seas are high concentration of dissolved organic matter, sulphate (from surface water) and Hg(II), e.g. introduced by groundwater. The so-called hyporheic zones, where the groundwater enters the surface water, are of especially important. (Armstrong et al 2006).
- Methylation can occur both in the sediment as well as in the water columns of rivers, lakes and seas (Boszke et al. 2003).

- HgS dissolves in oxygenated water at an environmentally relevant rate, whereby sulphate is released. Some of the elemental mercury that is formed is emitted in the gas phase, while some is sorbed by the remaining mercury sulphide (Holley et al. 2007).
- Large amounts of soil were contaminated with mercury on the grounds of the Y-12 facility in Oak Ridge, Tennessee, USA. Most of this mercury is now present as mercury sulphide. It was possible to prove that this mercury sulphide has become a source of mobile and bioavailable mercury, especially after the growth of vegetation (Han et al. 2008).

The cited studies show that mercury stored near the surface can basically be mobilised by biotic and abiotic processes. On the one hand, mercury can be converted to inorganic species such as dissolved Hg^{2+}, gaseous mercury, but it can also be converted to methylmercury.

4.5.4 Transport paths

Elemental mercury can be transported in dissolved form or as a gas. Expansion via the gas path is significant insofar as landfills are a source of atmospheric emissions due to their mercury level. Basically, gaseous mercury can leave the landfill vertically (through the surface sealing or during the combustion of collected landfill gas), but also horizontally through the unsaturated zone (Walvoord et al. 2008). The release of gaseous methylmercury, which can result from the methylation of mercury and mercury compounds, is to be regarded as particularly critical (Lindberg et al. 2001, Lindberg et al. 2005).

The mercury concentrations in landfill gas can reach similar values to the exhaust air of coal-fired power plants. Since the absolute amount of landfill gas is much less than the exhaust air, however, the amount of mercury emitted is also relatively small. It can still contribute substantially to the mercury emissions at a local level. Methylmercury can also leave the landfill via the gas path. It is destroyed and converted to inorganic mercury (elemental or ionic) during combustion of the landfill gas (NEWMOA 2008).

In the case of municipal waste landfills, a stabilisation of the landfill body is generally expected within 50 to 100 years. After 20 to 30 years, the landfill gas formation already decreases so much due to the degradation of organic matter that a layout is often no longer provided (Weber 2002). However, it is doubtful that the oxidation of mercury sulphide and the formation of mercury gas have already been completed after this period. After the end of active monitoring, a landfill contaminated with mercury remains a source of emissions.

If the base sealing of the landfill is intact, leachate accumulates at the bottom of the landfill. A contamination of the leachate can be expected if mobile mercury species are present in the landfill body. Depending on treatment and recycling methods, some of the mercury contained there can be released (NEWMOA 2008) or it ends up in one of the many possible solid waste streams (filtrates, precipitates, sewage sludge, ash).

4.5.5 Kinetic behaviour

A near-surface landfill in which large amounts of mercury sulphide are stored can be compared with a cinnabar mercury deposit. The thermodynamic instability of mercury sulphide in contact with oxygenated solutions is clear. Whether a serious risk is posed by mercury sulphide in soil depends on its mobilisation and conversion rate.

The reaction of metacinnabar (β-HgS) with dissolved oxygen is slow in comparison to weathering reactions (e.g. dissolution of feldspars): $1.34 \cdot 10^{-2}$ to $5.87 \cdot 10^{-2}$ µmol/(g·d) at pH 4.7 (Barnett et al. 2001). The release rate is even lower because the largest part of the mobilised mercury is sorbed by the remaining HgS. Under natural conditions, it should be lower by about one to three orders of magnitude (Barnett et al. 2001). A projected stored amount of 100 tonnes of HgS would nevertheless result in a maximum of 1.2kg/day of dissolved mercury. There is a comparative experiment by Holley et al. (2007) in which oxidation in stirred and ventilated HgS sludge was studied. They found a significantly higher oxidation rate of 3.4 to 7.9µmol/(g·d). The release of mercury was significantly lower: about $8.3 \cdot 10^{-3}$µmol/(g·d). These figures can only be a benchmark because the reaction rate actually occurring in a landfill depends on a number of other factors such as availability of oxygen, compaction, pore size, organic matter, and so on. However, the previous findings suggest that the release of mercury from landfills with HgS could be significant.

To obtain reliable results for the release rate of mercury in a near-surface landfill, experiment studies as close as possible to reality would be required. Until such measurements exist, it can be assumed in accordance with the precautionary principle (see German Federal Emission Control Act - BImSchG §1 “Prevention of harmful effects on the environment”) that mercury sulphide stored close to the surface in the long run at least is an appreciable local source of mercury emissions, the formation of which should be avoided.

4.5.6 Summary evaluation

The reports make it clear that mercury sulphide can be converted to mobile mercury compounds, elemental mercury among others, by biological and abiotic processes, which can in turn react further under suitable conditions to particularly toxic methylmercury. Both elemental mercury as well as methylmercury are volatile and can leave the landfill via the landfill gas.

There is currently no evidence that mercury sulphide is stored in above-ground landfills. However, it is recommended to check whether mercury sulphide and other waste as of a certain mercury level should be excluded from above-ground storage in Germany, as is the case in other European countries.

5 Risks when dealing with metallic mercury during the operational phase and measures to avoid them

5.1 Introduction

For the safe permanent storage of metallic mercury in an underground storage in general, the protection of the employees and the surrounding area of the underground storage must be ensured during the operational phase by technical and organisational measures, whereby technical measures must be given priority.

First, an overview of the European and German legislation relevant to an underground disposal of mercury waste is presented below, and the requirements to be implemented specifically for handling metallic mercury are listed.

This is followed by an analysis of the specific risks which are posed by containers with elemental mercury in the course of normal handling and in the event of accidents. There are discussions on measures which are suitable for avoiding risks or for minimising mercury releases in the event of damage.

The considerations are supplemented by an in-depth consideration of possible container concepts and the problems of the verification procedure. Furthermore, possible measures for risk prevention on the basis of the usual workflows in an underground storage are presented.

This report is limited to a qualitative description of the effects of measures. For quantitative assessments, e.g. on the dispersal of mercury in the event of a fire, safety analyses would be needed that require site-specific data and a definition of the storage concept. These are not the subject matter of this project, no more than the consideration of economic aspects.

5.2 Rules and regulations

5.2.1 General requirements for the disposal of waste in underground storage

The disposal of waste is fundamentally regulated in the European Union in the Waste Framework Directive 2008/98/EC. It contains the key requirements for the national waste management systems and defines essential terms and concepts.

The disposal of waste in landfills is elaborated in the Landfill Directive 1999/31/EC. It defines different classes of landfill, formulates essential elements of the licensing and supervisory procedures, and defines the principles for a waste acceptance procedure. It is formulated as a fundamental objective that, during the entire existence of a landfill, negative effects on the environment - particularly the pollution of surface water, groundwater, soil and air - and on human health are to be avoided or reduced as far as possible. The directive excludes certain waste from disposal in certain types of landfill. For metallic mercury, Art. 5 para. 3 a) is relevant, which excludes the acceptance of liquid waste in landfills.

The reception procedure for the disposal of waste in landfills stipulates according to Art. 11(1b), inter alia, that the waste documentation must be checked by the landfill operators, a visual inspection of the waste must be performed at the entrance and conformity with the waste description must be verified if necessary. Representative sampling with appropriate laboratory tests may be required. The representative samples must be kept for at least one month. The testing of representative samples must be carried out by a competent laboratory (Art. 12). According to Art. 11(1d), the landfill operator must inform the competent authority immediately of any rejection of waste.

Annex I of the directive refers to general requirements for all classes of landfill. Thus section 5 stipulates that measures have to be taken to minimise annoyances and hazards arising from the landfill. This also refers to hazards that may be caused by fires and aerosols.

Annex II covers the waste acceptance criteria and the waste acceptance procedure. A three-level procedure is described regarding the testing of the waste to be stored.

- Level 1 covers the basic characterisation (leaching behaviour) of the waste to be disposed of using standardised methods of analysis. Level 1 tests are a prerequisite in order for a waste to be accepted on a reference list
- Level 2 refers to a compliance test, that is, a periodical testing with simple standardised analytical methods. Such testing is required for a specific waste type in order to remain on a site-specific reference list.
- In level 3, the investigation is conducted at the landfill. To this end, rapid check methods are used, which may also consist of only a visual inspection.

Annex III contains guidelines on control and monitoring procedures during the landfill operation. These are inherently relevant for above-ground landfills in particular.

The Council Decision 2003/33/EC continues the waste acceptance criteria and defines in detail the requirements wastes must meet in order to be accepted in a landfill of a certain class. In addition, the decision establishes how the safety assessment of an underground storage is to be conducted and which particular acceptance criteria apply for an underground storage. The following aspects are relevant for depositing metallic mercury:

- The deposited material must have the necessary stability, which is compatible with the geomechanical properties of the host rock. (Annex A 1.2.2. and 2.1 f).
  → It has to be checked whether the aggregate state of metallic mercury has an adverse effect on the stability of the cavities.
- For the operational phase, an analysis should demonstrate that there is no unacceptable risk of a pathway developing between the wastes and the biosphere; (Annex A 1.2.6. point 2).
  → It is necessary to check whether a risk of contact with the biosphere (which would not otherwise be feared) arises due to the specific chemical and physical properties of metallic mercury, i.e. whether the barrier properties of the salt rock and the technical structures could be impaired.
- For the operational phase, an analysis should demonstrate that there is no unacceptable risk affecting the operation of the facility (e.g. by systematic analysis of the operation of the facility, operational management and operating procedure) (Annex A 1.2.6. point 3). Contingency plans must be put in place.
  → It is necessary to check whether metallic mercury poses specific risks for the operational safety.
- Wastes and their containers, which can react with water or the host rock under landfill conditions and can endanger the operational safety or the integrity of the barriers are excluded (Annex A 2.1.b), third en dash).

→ It is necessary to check how metallic mercury reacts with salt rock or potentially occurring salt solutions.

- Wastes that can generate a gas-air mixture which is toxic or explosive are excluded. This particularly refers to wastes that cause toxic gas concentrations due to the partial pressures of their components (Annex A 2.1.e), first en dash).
  → It is necessary to check the conditions under which mercury can form toxic gas concentrations and how to prevent them.

In addition to these requirements, specific designs of sampling and test procedures are given in section 3 of the Annex of the German Landfill Ordinance, bearing in mind that the laboratories must have an appropriate quality assurance system. Sampling and testing can be conducted by independent qualified persons and institutions. It is described that the waste producers as well as the landfill operators may conduct the sampling.

The German Landfill Ordinance executes the German Waste Management Act (KrWG), transposes European waste regulations (inter alia, Landfill Directive 1999/31/EC and the Council Decision 2003/33/EC on waste acceptance) into German law, and specifies the requirements for the construction, operation, decommissioning and aftercare of landfills and long-term storage facilities. The following parts are particularly relevant in relation to the permanent storage of metallic mercury. §7 prescribes which waste is not approved for the individual landfill classes. The following list (Tab. 12) describes essential characteristics a waste must not have if it is to be deposited in a landfill of class IV (underground storage). It also identifies the technical questions that must be clarified with regard to permanent storage of mercury and mercury sulphide.

Tab. 12 Excluded waste according to the German Landfill Ordinance for landfills of class IV (Art. 7)

Property	Need for consideration
Liquid waste (clause 1 no. 1)	None, since EU Regulation 1102/2008 explicitly allows the permanent storage of liquid mercury in underground storage (disposal operation D12)
Waste with a calorific value of more than 6 000kJ per kg of dry matter, unless depositing in a landfill of class IV is the most environmentally friendly solution (clause 2 no. 3)	Calorific value of metallic mercury and mercury sulphide. Calorific value of Hg: 452kJ/kg (see 4.3.1) Calorific value of HgS: 1 046kJ/kg (see 4.3.5)
Waste which, by reacting among its various components or with the rock under deposit conditions, leads to volume increases, the formation of pyrophoric, toxic or explosive substances or gases (clause 2 no. 4)	Long-term behaviour of mercury in contact with salt rock: No reaction (see 4.3.2)
Waste which has insufficient stability under deposit conditions compared to the geomechanical conditions (clause 2 no. 5 c)	Evaluation of the long-term geomechanical behaviour of metallic mercury (see 5.3.10)
Infectious waste, unidentified or new waste, scrap tyres, waste which leads to offensive smells (clause 1 no. 3-6) Waste which, under deposit conditions, is explosive, extremely flammable or highly flammable or releases a pungent odour (clause 2 no. 5 a-b)	None, since metallic mercury and mercury sulphide do not exhibit these properties

The waste acceptance procedure is regulated in §8 of the Landfill Ordinance. It stipulates that the waste producer is to make a basic characterisation of the waste in terms of origin, mass, composition, compliance with classification criteria (only landfill classes 0-III) and hazardous properties, among other things. It is allowed to deviate from this acceptance procedure when the waste involved is asbestos-containing waste or waste about which all necessary information on leaching behaviour and composition is known and demonstrated to the authority (§8 subparagraph 2 Landfill Ordinance).

The landfill operator continues the acceptance inspection by checking, inter alia, whether the documentation for the delivered waste (basic characterisation) conforms with the waste. The check is carried out by a visual inspection before and after loading as well as a visual and sensory inspection (appearance, consistency, colour and smell).

The landfill operator must also perform regular control tests. These are due:

- From the first 50 or 500 tonnes of delivered waste to check compliance with the classification criteria. Since there are no such criteria for underground storage in Annex 3 of the Landfill Ordinance, this type of test is irrelevant.
- If there is evidence that the properties of the waste do not meet the requirements for the envisaged deposition.
- On a regular basis for each commenced 2 500 or 5 000 tonnes (non-hazardous or hazardous waste), but at least once a year.

In the event of a control test, the landfill operator must take a reference sample from the waste delivery and keep it for at least one month (§8 subparagraph 6 Landfill Ordinance). Furthermore, Annex 4 stipulates that the waste sampling shall be carried out by independent testing laboratories accredited according to DIN EN ISO/IEC 17025 or by a body licensed by the authority. In this context, it is necessary to examine how the obligation to perform acceptance inspection and control tests can be ensured while maintaining occupational safety.

According to §23 of the Landfill Ordinance, metallic mercury waste can be accepted in a long-term storage facility (facility for storing waste) if the long-term storage facility has the relevant approval and is equipped accordingly. The requirements for long-term storage facilities from European Directive 2011/97/EU are currently[19] transposed into the Landfill Ordinance.

Special requirements for underground storage in salt mines are listed in Annex 2 of the Landfill Ordinance. They refer almost exclusively to criteria independent of waste, such as the location and the proof of long-term safety.

As part of the proof of long-term safety necessary for the approval of an underground storage, the following points must be investigated:

- Geomechanical behaviour of the waste (Annex 2 2.1.2.4 point 3),
- Reaction behaviour of the waste in the event of inflow of water and saline solutions (solubility behaviour, gas formation, interaction with each other) (Annex 2 2.1.2.4 point 4).

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[19] As of: October 2012

Thus the geomechanical behaviour and reaction behaviour of metallic mercury and mercury sulphide must be evaluated with regard to long-term safety.

5.2.2 Specific requirements for the disposal of metallic mercury

According to Commission Decision 2000/532/EC and transposed by the German Waste Catalogue Ordinance (AVV), mercury waste is classified as hazardous waste (code number 06 04 04). The inclusion of a separate code number for metallic mercury is currently being discussed as part of the work on the revision of the European Waste Catalogue. As liquid hazardous waste, metallic mercury is excluded from disposal in above-ground landfills.

According to the ban on mercury Regulation 1102/2008, metallic mercury that is produced by certain sectors after March 15th, 2011, is classified as waste which must be disposed of in a way that is safe for human health and the environment (Art. 2). The final disposal provided in the regulation is disposal operation D12 (permanent storage, e.g. storage of containers in a mine, etc.) according to Directive 2006/12/EC (replaced in the meantime by the Waste Framework Directive 2008/98/EC) (Art. 4 subparagraph 3). The ban on the depositing of liquid waste has been lifted for metallic mercury.

However, special requirements must be met for this purpose. Art. 3 subparagraph 1 of Regulation 1102/2008 rules that the permanent disposal of metallic mercury may take place only in appropriate containment and only in the following facilities:

- in salt mines adapted for the disposal of metallic mercury
- or in deep underground, hard rock formations providing a level of safety and confinement equivalent to that of those salt mines.

On the one hand, the safety assessments according to Decision 2003/33/EC (waste acceptance criteria) shall ensure that the particular risks arising from the nature and long-term properties of the metallic mercury and its containment are covered (Art. 4 Abs. 1). On the other hand, the requirements for these facilities as well as acceptance criteria for metallic mercury according to Landfill Directive 1999/31/EC of the Council of the European Union shall be adopted on the basis of a proposal by the European Commission (Art. 4 para. 3). Two special requirements are mentioned explicitly in Regulation 1102/2008 (Art. 4 para. 2):

- regular visual inspections of the containers,
- installation of appropriate vapour detection equipment to detect any leak

The regulation gives rise to the following questions which must be clarified prior to permanent storage in salt mines:

- What are suitable containers?
- How are salt mines to be adapted for the disposal of liquid mercury? The question can be rephrased in terms of: Which specific risks arise in connection with permanent storage and must be taken into account in terms of the safety assessment (operational safety and long-term safety)?

To date, only the requirements for the temporary storage of liquid mercury (longer than one year) were submitted and approved by the European bodies (Council Directive 2011/97/EU). They are not applicable to permanent storage, but can be regarded as important criteria because salt mines are also considered as sites for temporary storage (Art. 3 para.1 a). Directive

2011/97/EU supplements Annexes I, II and III of Landfill Directive 1999/31/EC and regulates, inter alia,

- Requirements for the facilities (separate storage, base sealing, fire protection),
- Requirements for the mercury, the containers and the acceptance procedure (purity, container material, resistance of the containers, filling level, procedure during acceptance, labelling of the containers, certificates),
- Requirements in terms of monitoring, inspection, emergency measures and records (gas measuring system, visual inspection, contingency plans and safety devices, record-keeping).

5.2.3 Occupational and operational safety

The Dangerous Substances Directive 98/24/EC specifies minimum requirements for the protecttion of employees against risks to their heath due to handling chemical substances. Lists of limit values were agreed upon to meet these requirements. The third list laid down by the Commission (Commission Directive 2009/161/EU) set the limit value for elemental mercury and divalent mercury compounds at a guideline value of 0.02 mg/m³ air (8 hours[20]). A limit value for a temporary exceedance of the occupational exposure limit value was not laid down for mercury.

The directive is transposed into German law by the German Hazardous Substances Ordinance (GefStoffV). It generally regulates the measures which an employer must take to protect employees against the risks of hazardous substances. The German Technical Rule for Hazardous Substances TRGS 900 specifies the requirements for handling hazardous substances such as workplace conditions. Accordingly, the occupational exposure limit value (OEL) of 0.02 mg/m³ must be observed when handling metallic mercury. The occupational exposure limit value is defined as a time-weighted average with an imputed daily eight-hour exposure on five days a week. Compliance with this occupational exposure limit value is used to protect employees against a risk of inhalation of the relevant substance. Under certain conditions, temporary exceedance of the occupational exposure limit value can be permitted. The maximum exceedance factor is 8. No further exposure may occur in a shift beyond an 8-fold exceedance of the occupational exposure limit value for 15 minutes 4 times per shift because the product of shift length and occupational exposure limit value would be exceeded otherwise. According to §7 subparagraph 8 of the German Hazardous Substances Ordinance, the employer must ensure compliance with the occupational exposure limit values. He must check compliance by workplace measurements or by other appropriate methods for determining exposure.

According to the German Federal General Mining Ordinance (ABBergV), workplaces must be operated in such a manner that employees can perform the tasks assigned to them without endangering their own health and safety. Risks for life and health should not arise as far as possible in the process, and remaining risks must be assessed and reduced. Individual protecttive measures are considered only if sufficient preventive protection cannot be ensured. Thus breathing apparatuses and resuscitation equipment must be available for areas in which

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[20] Time-weighted average, measured or calculated for a reference period of eight hours

employees may be exposed to hazardous substances or harmful gases in the atmosphere. Insofar as toxic gases can be present in a hazardous concentration in the atmosphere, the operator must draw up a plan in which the preventive measures and the required protective equipment must be specified in detail (gas protection plan).

According to Annex 1 Federal General Mining Ordinance and in accordance with a risk assessment, monitoring equipment for automatic and continuous measurement of gas concentrations at certain points, automatic alarm systems and equipment for automatic disconnection of electrical equipment and combustion engines must be installed and operated. In cases in which measurements are performed automatically, the operator must record the measurement results and retain them for a reasonable period.

5.2.3.1 Fire protection

At European level, Directive 92/104/EEC defines minimum requirements for improving the safety and health protection of employees in surface and underground mineral-extracting industries. According to this directive, the employer must take measures to prevent, detect and combat the outbreak and spreading of fires and explosions.

The directive is transposed by the Federal General Mining Ordinance (ABBergV). This stipulates that the operator must provide escape routes and emergency exits as well as escape and rescue facilities and maintain means of communication and a contingency plan. He must take appropriate measures in order to be able to assess whether potentially explosive or hazardous substances are present in the atmosphere. Moreover, he must take appropriate safety precautions to prevent the outbreak and spreading of fires. Fast and effective fire-fighting must be ensured in the event of a fire. The workplaces must be equipped with fire-fighting equipment. The operator must put in place a fire protection plan using the measures and facilities for fire protecttion.

Further details can be found in the mining ordinances of the federal states. Thus the General Mining Ordinance for the Federal State of Hesse stipulates that accumulations of highly flammable substances are to be avoided, but may only occur in particularly suitable locations if unavoidable. In the event of fire, the staff in the danger zone threatened by fire or combustion gases must be withdrawn immediately. The regulation also sets minimum requirements for the mine rescue team. The intention in salt mining is that each person has a self-contained breathing apparatus for a service life corresponding to the longest possible escape route in the presence of dangerous gases. Further requirements for the mine rescue team are defined in the guidelines of the professional associations (e.g. Bergbau-Berufsgenossenschaft 2006).

5.2.3.2 Occupational accidents

Since the operation of a underground storage is also subject to mining legislation, inter alia, the Federal Mining Act (BBergG) and the Federal General Mining Ordinance - ABBergV), the mining regulations on avoiding occupational accidents must be observed in addition to the waste disposal requirements. The general rule is that the safety of the underground storage and the employees must be ensured. A management plan is approved only if the necessary precautions against the risks to life, health and for the protection of material goods, employees and third parties have been demonstrated (§55(1) Federal Mining Act - BBergG). In this respect, measures should exist for the implementation of the generally accepted rules of safety technology including the relevant health and safety regulations.

The waste-specific requirements must be taken into account in addition to the mining legislation. According to § 4 of the German Landfill Ordinance (DepV), the operator must operate the landfill in such a way that accidents are avoided and possible consequences of an accident are limited. According to § 13 and Annex 5, the operator must compile an operations manual which must contain, inter alia, statements on the necessary measures in the event of malfunctions. It is thus necessary to examine which unplanned incidents can lead to a release of mercury, how such incidents are to be avoided or how the release is to be prevented or at least minimised in the event of an incident.

5.2.4 Environmental protection

Direct emissions into the environment are to be expected only via the exhaust air during the operational phase of an underground storage. Effects on the soil or water are only indirectly conceivable after emission into the air followed by absorption or precipitation. A direct release from the landfill area into the groundwater implies a failure of the geological and technical barriers in the decommissioning or post-operational phase and, even then, would require centuries or millennia depending on the migration speed. For this reason, further concern with protection objectives in the area of soil and water is ruled out.

Mandatory requirements for air emissions from facilities subject to licensing are contained in the first general administrative regulation for the German Federal Emission Control Act (Technical Instructions on Air Quality Control – TA Luft). Emissions in terms of this administrative regulation are the air contaminants originating from a facility.

According to this administrative regulation, any adverse environmental impact which cannot be avoided by applying state of the art techniques must be kept to a minimum. For exhaust gases from industrial plants, a mass flow of 0.25 g/h or 0.05 mg/m^3 may not be exceeded for mercury (as a pulverised inorganic substance).

Continuous monitoring of the exhaust gases is required if it cannot be reliably demonstrated that this limit value can assume only a maximum of 0.01 mg/m^3 . Thus it is necessary to check whether this value is likely to be exceeded in normal operation.

5.2.5 Public transport

According to the Waste Framework Directive 2008/98/EC, the member states must take necessary measures to ensure that hazardous waste is properly packed and labelled for transport in accordance with the applicable international and Community standards (Art. 19). Directive 2008/68/EC on the transportation of dangerous goods as well as the International Carriage of Dangerous Goods by Road (ADR) and by Rail (RID) are decisive. The regulations are transposed into German law by the:

- Law on the Transportation of Dangerous Goods (German Carriage of Dangerous Goods Act - GGBefG),
- German Ordinance on the Carriage of Dangerous Goods by Road, Rail and Inland Waterways – GGVSEB and
- Guidelines for Implementation of German Ordinance on the Carriage of Dangerous Goods by Road, Rail and Inland Waterways (GGVSEB) (implementation guidelines for dangerous goods).

Metallic mercury (UN No. 2809) is assigned to class 8 (corrosive substances) in accordance with Annex A of the ADR agreement. It is necessary to proceed according to Packing Instruction P800 for the packaging to be used for public transport. This means that either pressure receptacles, pistons or steel bottles with screw caps with a maximum content of 3 l or inner packagings with a maximum net weight of 15kg must be used.

Only pressure receptacles are possible for transporting larger amounts of mercury. They are subject to the requirements according to section 6.2 in the ADR. "Pressure receptacles and their closures shall be designed, manufactured, tested and equipped in such a way as to withstand all conditions, including fatigue, to which they will be subjected during normal conditions of carriage and use."". Approval is granted by a national authority (Bundesanstalt für Materialforschung und -prüfung in Germany[21]) on the basis of a prototype test by an accredited laboratory. It investigates whether the sample meets the relevant standards and performs tests to determine compliance with the standards. The container requirements refer to transport under normal conditions. Accident conditions are not considered.

The storage containers intended for the permanent storage of metallic mercury must be approved by the authority responsible for the storage according to Regulation (EC) No. 1102/2008. In the case of underground storage, the relevant regional mining authority is responsible.

5.3 Specific risks when handling liquid mercury in an underground storage during the operational phase

5.3.1 Overview

There are currently no rules and regulations for a systematic analysis of potential accidents in an underground storage. This is also true for the thematically related underground disposal of radioactive waste. However, consideration was given to possible accidents in the course of the plan approval procedure for the Konrad mine final repository (Gründler et al. 1986, NMU 2002), the Morsleben final repository for radioactive waste (ERAM) (ISTEC 2006, BfS 2009) and the comparison of options for retrieving radioactive waste from the Asse final repository (DMT and TÜV Nord Systec 2009). They are based on a technical analysis of all handling operations from the entrance gate to the storage location. They base their procedure on the procedure of other nuclear facilities. This approach corresponds to the procedure in the Incident Guidelines (BMI 1983)[22]. A distinction is made between internal events, which are caused by the operation of the facility itself, and external events such as earthquakes, weather, and actions of third parties, which affect the operation. Such events which have an impact due to technical failure, human error or geomechanical processes and can lead to a release of radioactive substances into the environment are of interest.

All incidences are divided into two classes:

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[21] BAM, Federal Institute for Materials Research and Testing

[22] German: "Störfallleitlinien". Now merged into the "Safety Requirements for Nuclear Power Plants" (Sicherheitsanforderungen für Kernkraftwerke) (BMU 2012)

a) Class 1: Accidents whose occurrence cannot be avoided. The effects of the accident must be limited in such a manner by the design of the facility or the waste packages that the requirements of § 49 subparagraph 1, no. 1 and 2 of the German Radiation Protection Ordinance (Strahlenschutzverordnung, StrlSchV) are complied with reliably.

b) Class 2: Accidents whose occurrence is reliably avoided by the design of the facility or the waste packages. These are assigned to residual risk, thus are regarded as so improbable that further measures are no longer required[23].

The subsequent safety analysis aims to prevent the exceedance of a certain radiation exposure in the workplace or in the environment by technical and organisational measures. To this end, incidents and countermeasures are analysed and modelled in terms of their quantitative effect on the possible radiation dose.

Since the accident analysis relates to radioactive waste and radiation exposures, a direct transfer to underground storage of hazardous waste is not possible. However, the system of analysis can be applied analogously. Analogous to the radiological objective of the Radiation Protection Ordinance "During the planning of structural or other technical protective measures against accidents in or at a nuclear power plant [...], an effective dose of 50 millisievert [...] can be taken as a basis in the worst accident involving the release of radioactive substances into the environment", it can be formulated that a release of mercury into the environment in the worst accident must not lead to

- a permanent exceedance of the occupational exposure limit values in the active operational parts of the underground storage or
- to an authorised release into the environment of the facility.
- Temporary exceedances can be countered by personal protective measures.

The findings in the area of the final disposal of radioactive waste are used to assess the specific risks involved in handling elemental mercury as well as stabilised mercury in an underground storage. The following assumptions and procedures apply here:

- Apart from specific measures for radiation protection, the operational processes in an underground storage and a final repository are regarded as comparable.
- The incidents identified for the final repositories for radioactive waste Konrad, ERAM and Asse are used as a basis for further studies.
- More detailed consideration is given only to such incidents which involve specific risks for the storage of approved waste types compared to others, and which are based on the characteristics of elemental or stabilised mercury.
- A specific assessment in terms of the possibility of the release of mercury and the likely consequences for operational safety is carried out for each of these incidents.
- External events are not considered in more detail because they basically involve all types of waste and are not specific to mercury.

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[23] Residual risk is a risk that is regarded as so insignificant when falling short that no further measures to reduce the risk seem necessary, e.g. a risk that is so low that it can be ignored (Risikokommission, German Risk Commission 2003). This includes, e.g. the crashing of transport and storage tanks during shaft transportation. Such an incident is regarded as technically simply avoidable (TÜV Nord, Ercosplan 2009).

- A quantitative analysis of mercury releases in internal and external incidences does not take place. This would be a task of a separate safety analysis.

The following table (Tab. 13) lists internal incidences of facilities, which were considered during the risk analyses for the final repositories for radioactive waste Konrad, ERAM and Asse. In addition, the following potential incidents are relevant for underground storage operation:

- Leakage or gaseous leakage of mercury from open transport containers during sampling for the incoming inspection,
- Corrosion of mercury containers from the inside (by mercury or contaminants).

Tab. 13: Consideration of internal incidences of facilities during the accident analyses of the final repositories of Konrad, Morsleben and Asse

Incident	Description/Examples	Final repository (K= Konrad; E= ERAM, A= Asse)
Above-ground mechanical impact	Damage to transport units with waste packages due to mechanical stress during: a crash of transport units, a crash of heavy loads on waste packages and a collision of vehicles.	K, A
Above-ground fire	Above-ground fire involving vehicles, technical equipment and buildings	K, A
Underground mechanical impact	Crash of transport units Crash of heavy loads on waste packages Rockfall Collision of vehicles Drilling operations	K, E, A
Geomechanical effects on stored waste	Mechanical effect due to convergence or rock fall from the roof	E
Underground fire	Fire involving vehicles or technical equipment (e.g. workshops, storage)	K, E, A
Internal fire or smouldering fire involving stored waste	Spontaneous combustion of stored waste in storage chambers or functional areas	E
Instantaneous release of mine air	Sudden expulsion of possibly contaminated air from non-backfilled or incompletely backfilled storage chambers with sudden loss of integrity of a retention barrier	E
Deflagration of flammable gas mixtures	For example, ignition of hydrogen/air mixtures from the corrosion of metals	E
Leakage of liquids	Leakage of waste containers at the storage location (due to long storage periods, mechanical effect, corrosion)	A
Remote effects on storage building	Remote effects on storage building, e.g. due to incidents in oil, material and explosives storage, explosive locations	E

5.3.2 Normal operation

Depending on the location, waste can be delivered to the underground storage by truck or rail. The waste containers must meet the requirements of the ADR (road transport) or RID (rail) as well as the underground storage. Generally, delivery on pallets is required. Certain forms of waste (produced in large quantities) can also be delivered in silo trucks. They are then placed in big bags at the underground storage site. These measures ensure that there is no release of hazardous substances during normal handling. The containers are unloaded and undergo the acceptance inspection in the underground storage. Damaged containers are not accepted and must be taken back by the waste producers.

For substance inspections, the containers must be opened randomly and examined visually and sensorially. Random samples are taken and examined chemically. After the control test is completed, reference samples are stored for at least one month in the underground storage. After having passed the acceptance inspection, the delivered waste is allocated to the shaft transport (and placed in a transport container for internal transport if necessary). The containers are then brought underground in the mine cage and are loaded on to transport vehicles there. The vehicles go to the intended storage section (or storage area), where the waste is unloaded and, as a rule, stacked. If a storage section is filled, it is backfilled and walled off.

If metallic mercury or mercury sulphide is delivered in sealed, undamaged containers, a release of elemental mercury or mercury compounds is not to be feared in normal operation until after the placing of the containers in the storage area. It is to be expected that the occupational exposure limit value (0.02mg/m^3) is observed and that the emissions via the exhaust air of the facility meet the requirements of the Technical Instructions on Air Quality Control – TA Luft (0.05mg/m^3 or threshold value for continuous measurements 0.01mg/m^3). Thus negative effects on occupational health and safety and the environment are not expected when handling containers with mercury in normal operation.

5.3.3 Above-ground mechanical impact

Damage to waste packages due to mechanical stress can occur during (NMU 2002):

- a crash of transport units, e.g. during unloading or transhipment;
- a crash of heavy loads on waste packages (e.g. after a collision with facility parts or crash of one waste package into another one);
- a collision of vehicles.

A crash of the waste package from a height of 3 m is classified as a design basis accident in the Konrad mine final repository.

Mechanical damage in the area of the shaft, e.g.

- crash of the waste package when loading the mine cage,
- crash of waste packages when being conveyed underground,
- crash of heavy loads on waste packages in the mine cage,

- carrying the mine cage too far[24]

can be avoided by designing the system so that it is no longer to be regarded as a residual risk.

5.3.3.1 Possible consequences

In the event of mechanical damage to waste packages, a leakage of liquid mercury can occur. In the event of adverse damage, the entire contents of the container may leak, e.g. 80 l from a 1 tonne container. Breathing apparatus and personal protective equipment must be worn when performing the necessary work to recover the leaked and dispersed mercury due to the high toxicity of mercury.

5.3.3.2 Preventive measures

The following measures are appropriate for avoiding vehicle collisions and load crashes (NMU 2002)

- Limiting the driving speed on the site to 10 km/h,
- One-way system and barriers to avoid encountering several transport vehicles,
- Design and protection of parts of the building so that no heavy loads can fall on the waste packages in a collision,
- Technical limitation of the speed of forklift trucks so there is no fear of damage to transport units.

In order to limit the consequences of leaking mercury, the areas in which waste packages are unloaded, reloaded or stored temporarily should be designed so that mercury cannot seep into the ground, but accumulates in one spot due to a slight slope, where it can then be absorbed. Sufficient cleaning agents and binders[25] as well as consolidated containers should be provided in order to be able to absorb the mercury as well as the used binders and cleaning agents. Moreover, mercury waste should be handled separately from other waste types to avoid contamination of other waste packages. Devices for monitoring the occupational exposure levels should also be provided.

Additional safety can be achieved if the waste package is designed so that it can withstand a crash or also a crash with another waste package or is constructed in such a manner that there is no fear of mercury leaking even in the event of damage.

5.3.4 Underground mechanical impact

Damage to transport units with waste packages due to underground mechanical stress can occur during (Gründler et al. 1986, NMU 2002):

- a crash of transport units (during loading and unloading),

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[24] "Overdoing it" describes the incident where the mine cage, on being driven out of the shaft, is drawn beyond the actual intended end stop to the top of the winding tower. This may cause severe damage to the mine cage or the wire rope hoist.

[25] For example, Mercurisorb (cf. Professional Association of Raw Materials and Chemical Industry - Berufsgenossenschaft Rohstoffe und Chemische Industrie 2012)

- a crash of heavy loads on waste packages,
- rock fall (e.g. loosening of salt rock from the roof),
- a collision of vehicles.

The design fault, that is, the maximum height of the fall of the waste package depends on the storage concept, particularly the maximum stacking height of the waste packages in the storage chamber. In the Konrad final repository, 5m is assumed to be the maximum fall height for handling operations in the unloading or storage chamber. These values may be higher or lower in underground storage depending on the storage concept. The crash of waste packages during loading and transport operations is documented for the former underground storage Stocamine (COPIL 2011). No relevant information is available for German underground storages.

The potential damage in a collision results from the maximum permissible speed of the transport vehicles and the transport concept. If the waste containers are reloaded directly on to the transport vehicle, the potential damage is higher than if a roll container[26] is used, which is loaded above ground and only unloaded in the storage chamber.

5.3.4.1 Possible consequences

In the event of mechanical damage, there may be a leakage of liquid mercury and a contamination of the mine air. In the event of adverse damage, the entire contents of the container may leak, e.g. 80 l with a 1 tonne container. Breathing apparatus and personal protective equipment must be worn when performing the necessary cleaning due to the high toxicity of mercury. Due to its high surface tension, mercury forms very small, heavy beads to some extent, which easily penetrate the smallest pores and cracks. Mercury must not be left there because it represents an ongoing source of contamination and thus a health risk. Superficial cleaning is thus insufficient on porous surfaces, but in fact a surveying of the floor would be necessary to a depth in which no more traces of mercury are found. All technical equipment which may have had contact with liquid mercury must also be removed. This work may cause a resuspension of mercury-contaminated dust, which can in turn result in secondary contamination.

5.3.4.2 Preventive measures

As for above-ground transport movements, underground preventive traffic measures which minimise the likelihood of vehicle collisions are recommended. These include

- Limiting vehicle speed (Konrad mine: 10km/h),
- Avoiding oncoming traffic and overtaking

The design of underground routes and chambers in a manner that released metallic mercury can be safely collected and absorbed is not feasible technically or at least not viable economically. It should thus be ensured that liquid mercury does not leak even if one of the four specified incidents occurs.

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[26] Roll containers are used in Zielitz (K+S, undated)

As a general rule, internal transport and storage processes should be carried out as quickly as technically and organisationally possible. It is recommended that the storage is performed in stages so that mercury-laden transport and storage containers are transported separately from other waste containers.

5.3.5 Above-ground fire

Fire loads are also present above ground. This concerns, inter alia, vehicles, installations, workshops and storage facilities. It is assumed that any fires will remain confined to the incipient stage because they can be fought quickly due to the easily visibility and availability of extinguishing agents and personnel (NMU 2002). If there are areas with higher fire loads (warehouses, administrative buildings) at a distance from the areas in which waste is handled, there is no fear of fires spreading to the waste.

5.3.6 Underground fire (fire technical equipment, machines and vehicles)

5.3.6.1 Description

In an underground landfill, larger fire loads can occur in the area of workshops, fuel depots and explosives magazines. The vehicles and machines with combustion engines including the waste transport vehicles used underground are also important fire loads. Other smaller fire loads (e.g. cables, electrical equipment) are distributed throughout the whole mine. They are to be classified as less critical than a vehicle fire. Flammable materials include oil and fuels, explosives, wood, plastic, paper and textiles (DBE 2006). Part of the stored waste can also be flammable or release flammable gases (Hagemann et al. 2006).

Vehicles and conveyors are a common cause of fires in mines (COPIL 2011). Fires on a loaded waste transport vehicle are of particular importance. Fires in underground routes and chambers are particularly problematic because, as with tunnel fires, high temperatures may occur due to the spatial restrictions and the limited possibilities for heat dissipation. In the course of the accident analysis for the Konrad mine, it was assumed as a design basis accident that a complete burning (fully developed fire) of a vehicle can occur, which is characterised by a fire load of 700 l of fuel and oils as well as 1700 kg of solids (types, cables, paints). A temperature curve was derived, which illustrates the course of the fire and temperature (NMU 2002):

- for the time t = 0 mins to t = 5 mins: linear increase in temperature from 30°C to 800°C,
- for the time t = 5 mins to t = 65 mins: constant temperature from 800°C,
- for the time t = 65 mins: Temperature drop to 30°C,
- from t = 65 mins: constant temperature from 30°C.

5.3.6.2 Release of mercury

In the event of a fire, waste packages in the vicinity can heat up, they may, for example, be located on the loading area of the transport trolley. The heating can lead to changes in the state of the waste and to the loss of integrity of the container (NMU 2002). At temperatures above the boiling point of metallic mercury (357°C), it must be assumed that mercury builds up a significant vapour pressure in a closed container for which the container or the closure of the container may not be designed. At 800°C, the vapour pressure is approx. 10 bar (Huber et al.

2006). The container may then rupture and an explosive leakage of mercury vapour may occur. The mercury vapour can then continue to spread with the combustion gases and mine air.

The release of relatively small amounts of mercury can cause significant exceedance of limit values. The international standard “flasks” contain, for example, 2.5l or 34.5kg of mercury. For assumed complete evaporation, this amount is enough to contaminate 1.73 billion m^3 of air to the extent that the occupational exposure limit value of 0.02 mg/m^3 is exceeded[27].

5.3.6.3 Adverse effect on the immediate environment

Released mercury can contaminate the immediate environment. All contaminated materials (vehicle, container, technical installations and in-situ salt rock) must be either cleaned or disposed of as waste. Similarly, part of the roof and walls affected by the fire in the Stocamine underground storage became waste or will become waste if it comes into contact with already contaminated materials in the course of the clean-up operation (COPIL 2011). Whether the heat generation of a vehicle is enough to cause mechanical damage to roof and walls, as is documented for a fire in a waste warehouse in Stocamine (COPIL 2011), cannot be assessed here. The 10-day duration of the fire in Stocamine was much longer than is assumed for a vehicle fire (one hour - design fault in Konrad mine, NMU 2002), so that a direct comparison is not permitted.

5.3.6.4 Contamination of further mine areas and the above-ground environment as well as decontamination

Combustion products and volatile waste components are transported away from the location of the fire by the mine air ventilation as well as by the independent dispersal of hot combustion gases. Depending on the geometry of the mine and the mine air ventilation, there may be a transfer of pollutants to more distant parts of the mine and deterioration of air quality. During the underground waste storage fire in Stocamine, thick sulphur dioxide-containing smoke even appeared in the isolated potash mine which - among other reasons - necessitated an initial temporary interruption, but then the final termination of the operation (Caffet and Sauvalle 2010).

It can be assumed that gaseous mercury would spread in the same manner with the combustion gases if the containers were leaking. When cooling mercury containing combustion gases, e.g. on the cooler surfaces of the roof to under 357 °C, there is increasing condensation of mercury and contamination of surfaces along the mine air ventilation. Transport to the surface is possible if the mine air ventilation is not disrupted.

Condensed mercury forms fine droplets which penetrate pores, cracks and crevices due to their high specific weight. All around the cavities created by mining methods in a salt mine, there is an excavation damaged zone which has a higher porosity and cracking compared to the unaffected salt rock (Wieczorek and Zimmer 1998). If there is widespread contamination, there is a fear of an exceedance of the occupational exposure limit values in parts of the underground

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[27] Calculation: mass of Hg (34.6 kg = 34.6·106 mg) divided by OEL (0.02 mg/m3). For comparison: the Asse mine had a cavity volume of approximately 4.3 million m3 after the end of the salt mining. (GSF 2006) .

landfill even after successful fire fighting. These parts could then no longer be entered without donning personal protective equipment (including breathing apparatus).

If mercury penetrates these excavation damaged zones, it must be assumed that decontamination is possible only by a complete removal of all affected surfaces and excavation damaged zones. As a consequence of this activity, mercury containing material could be released in liquid (Hg droplets), solid (in salt rock and dust) and gaseous form (Hg gas). It can be assumed that decontamination work must be performed at least with breathing apparatuses, but also with full protective suits depending on the pollution. At the same time, it must be ensured that there is no secondary contamination of other parts of the mine due to the releases during the decontamination measures and the ventilation. Overall, it may be assumed that the time and organisational effort for the necessary clearing up and cleaning would be considerable.

Ventilating permanently is insufficient for the evaporation of the smallest drops. Experiments showed that the evaporation of the smallest drops proceeds very slowly, probably due to the formation of a fine oxide layer on the surface of the mercury (Stock 1934).

5.3.6.5 Preventive measures

The basic requirements for the operation of mining facilities include the planning and implementation of fire protection measures. Apart from radiation protection regulations, the legal basis with regard to fire protection for a final repository and underground storage is regarded as comparable. It results, inter alia, from the Federal General Mining Ordinance, more extensive mining ordinances of the federal states and the Guidelines of the Central Mine Rescue Service (Bergbau-Berufsgenossenschaft 2006, section 5.3.2). They are sufficient in principle as a basis for developing fire protection concepts. A good example of this is the fire protection planning for the ERAM final repository (DBE 2006). It includes, inter alia, the following measures:

- Avoidance of ignition sources: smoking ban and ban on the use of propane and butane gas. In mining areas with increased fire loads, possible ignition sources are removed and equipment for extinguishing incipient fires is installed.
- Reduction of fire loads: storage of flammable materials only in suitable containers, no storage of combustible equipment or flammable substances within a 20 m radius of the shaft, removal of unnecessary or replaceable fire loads (cables, wooden fixtures), additional protection of tank spaces and warehouses for flammable substances.
- Fire detection: installation of systems for early fire detection (gas sensors for carbon monoxide and temperature measurement) at selected locations, installation of fire alarm systems in places with high fire loads.
- Fire-fighting: mining areas with unavoidable fire loads must be equipped with sufficient fire extinguishers. Mobile fire dams can be used for the containment of fires.
- Containing conflagration gases: ventilation doors for separating incoming and outgoing mine air must be manufactured from non-flammable material. Conflagration gases are prevented from spreading by ventilation structures, which divide the mine into various ventilation sections, and by switching off fans.
- Personal protection: anyone entering the mine is equipped with an oxygen self-rescuer, which will enable the wearer to reach unpolluted areas in the event of a fire.

Due to the particularly serious risk as a result of the release of mercury, the precautions, which are required by the German Federal General Mining Ordinance (ABBergV) and implemented in the underground storage for avoiding the outbreak of fires when handling other waste, should be expanded. The following observations focus primarily on further preventive measures to avoid the outbreak of vehicle fires and the release of mercury.

Technical defects are a major cause of incipient fires in vehicles (DBE 2006). They can be reduced by regular maintenance and inspections, but cannot be excluded. Other possible causes of an incipient fire are collisions of the transport vehicle with another vehicle. Such collisions can be avoided by traffic management measures, whereby no crossing over or two-way traffic is permitted during the waste transport. Stationary vehicles and technical equipment should only be passed by at a reduced speed. A collision with parts of the mine can also be avoided by driving slowly or at least its effect is thus reduced. Also limiting the fire loads in the vicinity of reloading processes and during storage or in the course of transportation (e.g. limiting the number of towing vehicles near the containers) seems advantageous.

Since incipient fires on transport vehicles cannot be avoided, the containers should withstand an underground fire without allowing a relevant mercury release. To avoid a release, the use of accident-proof transport and storage containers with several barriers is suggested, which guarantee that no mercury escapes even under design fault conditions. A more detailed description of the requirements and possible implementation can be found in section 5.4.3.

Basically, emissions cannot be excluded either for other waste disposed of underground in the event of a thermal load. In contrast to probably most other waste types, relevant for underground storage[28], metallic mercury consists almost completely of a slightly volatile, highly toxic and also liquid substance, which is highly mobile if the container fails. An extensive contamination of the mine may be the consequence. Special safety regulations thus appear justified for reasons of occupational and operational safety.

By storing mercury waste in campaigns and subsequently backfilling and walling up storage sections, already deposited waste can be protected against future fire incidents.

5.3.6.6 Fire-fighting measures

It can be assumed that an incipient fire in the vehicle cannot always be fought by the operating personnel with the immediately available fire-fighting equipment, but may require the services of the mine rescue team. However, consideration must be given as to whether the transportation of containers with liquid mercury should involve vehicles with self-extinguishing systems. In such vehicles, by means of special fine spray nozzles, the extinguishing agent envelops the engine or other vehicle parts with a fine spray mist and prevents a larger fire, further heating and also a re-ignition of the fire (Fetting et al. 2010). Vehicles equipped in such a manner are already in use in German coal and salt mining.

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[28] A test as to whether there are other waste types which pose a comparably high risk in the event of a fire was not the object of this study.

If the incipient fire cannot be extinguished immediately, there may be a spreading of the fire and the formation of toxic combustion gases as well as a possible escape of mercury from the thermally loaded container before the mine rescue team arrives.

If the mine air ventilation is interrupted in the event of a fire and the fire area is limited by closing doors and ventilation flaps or by using mobile fire section dams, the contamination is confined to the thus created fire section. This can prevent a leakage of conflagration gases and thus possibly of mercury from the mine.

5.3.7 Internal fire or smouldering fire involving stored waste/ Deflagration of flammable gas mixtures

5.3.7.1 Description

Due to incomplete oxidation reactions, waste may heat up, start to smoulder or self-ignite under certain circumstances. Thus the storage of self-ignitable waste led to fires in 2002 in the French underground landfill Stocamine (Caffet and Sauvalle 2010) as well as in the backfilling mine Teutschenthal (Mitteldeutsche Zeitung 2002). The fire in Stocamine involved waste with a high organic content which, probably due to bacterial degradation reactions, first heated up and later ignited. In Teutschenthal, pyrolysis coke from a recycling plant ignited, which exhibited a high percentage of carbon and aluminium metal (Südkurier 2002). The possibility of smouldering fires is considered in principle for ERAM (BfS 2009).

Hagemann et al (2006) were also able to show that different types of waste stored in underground storages exhibit high potential for release of hydrogen gas, which still persists even after conditioning. In extreme cases, this can result in the formation of ignitable mixtures.

5.3.7.2 Effect and consequences

A spreading of fires to mercury waste can cause a failure of the container and a gaseous release of mercury.

5.3.7.3 Preventive measures

A spreading of fires to waste packages with elemental or stabilised mercury can be avoided by storing potentially gas-forming waste solely in structurally separate and geographically remote storage sections. In addition, waste with elemental or stabilised mercury should be brought into the underground storage separately from other waste types to exclude incidents during transportation.

5.3.8 Corrosion of container materials

5.3.8.1 Description

Metallic transport containers are subject in principle to corrosion. Depending on the material, however, the corrosion may be so slow that it does not lead to any material impairment within the operating life of an underground storage. A review of some up to 30-year-old mercury containers (“flasks”) owned by the Spanish company MAYASA showed in fact corrosion for some containers. However, this was very minor and did not endanger the tightness of the containers.

A study by Oak Ridge National Laboratories also determined that the welds were the weak point of the container (BiPRO 2010).

5.3.8.2 Effect and consequences

Mercury can be released from corroded containers and contaminate transport vehicles and routes. This can lead to an environmental and health hazard.

5.3.8.3 Preventive measures

Elemental mercury corrodes many other metals. Therefore, mercury may only be transported and temporarily stored in special containers. According to Council Directive 2011/97/EU, the containers for temporary storage are to be manufactured from carbon steel or stainless steel and welds are to be avoided. Their outside must be resistant against storage conditions. The mercury itself must have a purity better than 99.9% by weight and also may not contain any contaminants which can corrode carbon steel or stainless steel (nitric acid solution or chloride salt solutions).

It may be assumed that containers which are approved for temporary storage of more than one year[29] are also corrosion-resistant under underground conditions for a sufficient period – i.e. the time between first delivery to and closure of a storage chamber. The conditions underground are rather more favourable due to the absence of meteorological influences and lower humidity. If storage occurs in dry conditions and the storage chamber is closed within five years, there is no cause for concern in relation to failure of the container due to corrosion.

If the period between filling, transport to the underground storage, storage and closure of a storage section could be limited to well under five years by organisational measures, it would be likely that the requirements in terms of the purity of mercury would be lower. However, there is a lack of sufficient information to be able to determine which combination of purity and container requirements provide adequate safety. Therefore, it is conservatively assumed that the purity requirements for permanent storage should correspond to those of long-term storage. However, the requirement of Directive 2011/97/EU regarding the absence of corrosive contaminants

“no contaminants which can corrode carbon steel or stainless steel (e.g. nitrate solution [actually nitric acid solution] or chloride salt solution)”

cannot be implemented technically because complete absence cannot be achieved. The maximum concentration of individual substances under which an absence can be assumed is not defined either. Furthermore, the corrosive substances which should be tested are also not defined.

It would be better to replace this requirement with a requirement for the absence of an aqueous phase. Corrosive substances, especially salts and acids, have to be expected solely in an aqueous phase because they are not soluble in mercury. As the aqueous phase generally has a lower density (about 1 g/cm^3) than mercury (13 g/cm^3), it must float on the mercury. This can

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[29] In the reasons for Directive 2011/97/EU, it is stated that the regulations are regarded as the best available techniques for storage of up to five years. However, this period is not to be found in the actual text of the directive.

be tested by simple qualitative analysis, e.g. by a visual inspection and the use of test strips to detect water[30]. A visual inspection should also show that no oily or solid phases are floating on the mercury, thus a bright, mirror-like surface is to be seen, which does not form any film upon contact with air[31].

In terms of long-term corrosive processes, no further requirements are necessary for permanent storage if the storage sections are backfilled and closed immediately after storage. If, at a later stage, a perforation corrosion of the container occurs, the contamination is limited to the backfilled storage chamber. Gas emissions into adjacent open drifts would likely be very small. It can be assumed that the gas flow between the walled off storage chamber and the open drift is low and that the mine air will rapidly dilute the mercury down to concentrations which are no more relevant for occupational safety ($<0.02 mg/m^3$)[32]. However, a quantitative assessment would be possible only by means of a numerical modelling. The safety analysis for normal operation in ERAM may serve as a comparative case (Müller et al. 2006). In this study it was investigated whether gaseous ^{14}C, which enters the active mine areas from walled up storage areas[33], can contribute to a significant increase in dosage. Based on a numerical modelling this hypothesis could be negated.

Regardless of the requirements for the purity of the mercury, an external visual inspection should be carried out upon reception of the container. Containers with obvious defects should not be handled any further, but should be returned to the waste producers in an outer packaging in accordance with the transport regulations.

5.3.9 Leakage of mercury from leaking containers

5.3.9.1 Description

Containers that are not sealed properly can emit mercury in liquid or gaseous form into the environment. The transport of mercury containers that were leaking or starting to leak led to contamination of a road of over 40 km in length in Peru in 2000 (ICMM 2011).

5.3.9.2 Effect and consequences

Leaking mercury can contaminate the work environment, vehicles and transport routes.

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[30] There is no standardised method for detecting water on mercury. However, there are test strips available on the market for the qualitative detection of water in heating oil tanks, which discolour upon contact with water (e. g. Aquatec test sticks from Macherey-Nagel, Düren).

[31] A relevant test is described in the standard DIN EN ISO 24234 (Dentistry - Mercury and alloys for dental amalgam). It is provided here that mercury does not form any film after 20 minutes of contact with air.

[32] For a litre of mercury-saturated air with 20mg/m3, a cubic metre of air would be necessary to achieve a permissible gas concentration of 0.02mg/m3.

[33] In the following section, a distinction is made between storage areas (areas of the mine which are used for storing waste) and storage sections (parts of a former excavation chamber or a cavity which is suitable for storing waste).

5.3.9.3 Preventive measures

The incoming containers should be checked visually for leaks. Mercury beads on the closures and the outer shell indicate leaks. Such containers should not be handled any further, but be returned to the waste producers in an outer packaging.

5.3.10 Geomechanical effects on stored waste

5.3.10.1 Description

After storing the waste packages, geomechanical processes may cause salt rock to fall from the roof or side walls and thus damage the containers. Another possible process is the building up of pressure all around by convergence. The rate of convergence depends on the site and can also vary between storage areas in one mine. It may be in the region of several centimetres per year for non-backfilled cavities (e.g. Asse, Heydorn et al. 2005). In backfilled cavities, the convergence remains the same for a long time and only decreases if the remaining residual cavity is so small that the backfill develops a supporting effect (DBE 2001). Depending on the compressive strength of the container, the gradually developing mechanical load can damage the container and lead to a release of liquid mercury.

5.3.10.2 Consequences

The convergence is a relatively slow process so that, between the start of storing mercury in a section and backfilling and closing this section within weeks or months, a mechanical pressure on the containers is not likely to occur. The long-term development must be assessed somewhat differently. If the operational phase of the underground storage is to continue for decades, it cannot be excluded - depending on the local convergence rate - that the pressure on the waste container will become so high that a failure of the container occurs. It is not possible to determine the earliest time to expect a failure without detailed experimental studies and numerical modelling. The worst case would be a failure of the container at a time in which the residual porosity of the backfill would still be so high that the mercury could spread in the backfill. This is not relevant for the overall safety because the contamination would be limited to an area of the mine that separated from active areas by a wall.. For longer periods, however, it could not be excluded that, depending on the local conditions, mercury could reach this wall. It may pass through the masonry if the pressure is sufficient and the wall possibly be already damaged and thus leave the storage section.

5.3.10.3 Preventive measures

The extent of the mechanical damage to the container depends essentially on the height from which the rock falls. Thus either the waste containers should be stacked up to the roof in the storage sections or the remaining cavity should be backfilled immediately with salt grit. This is already common practice in underground storages. Additional protection is ensured by double-walled waste containers. In addition, it is recommended that storage sections are completely backfilled and walled off immediately after the end of a storage campaign. To exclude adverse effects of damage to the containers after closure of a storage section, the operator should demonstrate that a pressure effect exceeding its design is not to be expected on the container during the remaining operating period of the underground storage due to the low rates of convergence in the storage area. Otherwise, the storage area should be designed so that, even in the event of a failure of containers, there is no fear of liquid mercury leaking from the storage area (e.g. by designing the storage section as a lowered cavity or by installing a gas and liquid-tight enclosing dam at the end).

5.3.11 External events

In addition to the aforementioned incidents arising from the operation of the final repository, external events which can occur without human intervention are also considered during accident analyses for final repositories. These include (Gründler et al. 1986, ISTEC 2006):

- Inflow of shaft waters and saline solutions in the mine workings,
- Earthquakes,
- Floods,
- Weather events: storms, ice and snow, lightning,
- Impact due to blast waves of explosions,
- Plane crash,
- Effects of fire from the outside,
- Absorption of explosive and toxic gases,
- Actions of third parties.

These events principally can also occur in an underground storage. They have an unspecific effect on all waste types stored and handled in the facility. If there were a disturbance of operational safety or even of long-term safety, all deposited or still openly stored wastes in the underground storage would be affected. Thus the events would (if at all) cause a release/mobilisation of a wide range of pollutants and not only of mercury. A detailed analysis of the probability of occurrence and the possible extent of harmful effects can usually only be conducted on the basis of site-specific data, in particular on the spatial situation in relation to potential sources of danger Only then, for example, is would be possible to carry out an assessment of flood risk and an assessment of the risk of a blast wave of an explosion due to transports of dangerous goods on adjacent routes.

However, evaluations can be summarised from the accident analyses for the Konrad mine (Gründler et al. 1986) and the Morsleben final repository (ISTEC 2006):

- For earthquakes, it is assumed that the effects on underground facilities are of minor importance.
- Meteorological events (storms, ice, snow, lightning) have no effect on waste stored underground and will not be dealt with any further.
- An absorption of explosive and toxic gases is likely if large amounts of a flammable gas (e.g. natural gas) leak from a nearby defective pipeline system. Even then, underground ignitable mixtures are not expected to be achieved due to the dilution which occurs immediately (ISTEC 2006).
- Plane crashes are not regarded as a design basis accident. Like blast waves of explosions, damage is considered only for above-ground facilities. No catastrophic impact is to be expected even there. It was calculated for the Konrad final repository that the

conventional risk of a plane crash was higher than the radiological risk of a crash on the above-ground mines.

- The inflow of shaft waters and saline solutions in the mine workings is an event to be considered. Limited amounts of solution without hydraulic contact with the overburden can occur in salt deposits and are activated by subsidence movements or mining activeties. The quantities to be expected depend on the respective repository. A maximum amount of some 1 000m^3 is assumed for ERAM. These amounts are not regarded as endangering safety. Inflows from the shaft are collected, used, stored or channelled into lower situated mine areas during the operational phase.

It was derived for the Morsleben final repository that there is no fear of a release of radionuclides in the vicinity of the facility due to external events (ISTEC 2006). A general derivation for German underground storages is not possible without site-specific data. Based on these analyses for the final repositories Konrad and ERAM, there are only two events possible which could have a direct effect on deposited waste: the water inflow from limited deposits of solution or via the shaft. In both cases, manageable amounts of solution occur, which can be collected and diverted without causing a release of mercury.

5.4 Specific technical and organisational requirements for the underground deposition of elemental mercury during the operational phase

5.4.1 Objectives and basic principles

To supplement the analysis of potential accidents, preventive measures across the processes of the underground storage operation as well as some preliminary processes will be identified and explained in detail. Fig. 12 gives an overview of the essential operations ranging from the acceptance inspection via internal transport to the prepared storage chamber and its closure. An advanced acceptance control, which takes place at the place of the waste producer, has been added.

In terms of occupational safety, the protection objectives result from the German Hazardous Substances Ordinance and the Federal General Mining Ordinance. Workplaces must be operated in such a manner that employees can perform the tasks assigned to them without endangering their own health and safety. Measures need to be taken to protect employees for this purpose. Preventive measures are intended to ensure that risks do not arise at all.

Thus consideration is to be given not only to the regular operation, but also to occupational accidents, insofar as they are not assigned to the residual risk. The development of requirements for permanent underground storage of metallic mercury is based on the approved procedures of underground disposal, such as the storage of the container, to achieve an integrated procedure for the safe permanent storage of metallic mercury. This also includes the integration of processes which precede storage in the landfill area, such as:

- production of containers to be stored permanently and
- transportation of the containers to be stored.

Other preliminary processes, such as the delivery of metallic mercury or mercury waste to be treated or the treatment process by the waste producer himself, are not part of the report.

The proposals for preventive measures for safe permanent underground storage of metallic mercury are based for the operational phase on

- compliance with German and European legislation for occupational and operational safety (see section 5.2),
- the approved conditions for operating underground storages,
- the operational experience gained in conjunction with the interim storage and final disposal of radioactive waste,
- the requirements resulting from the properties of metallic mercury.

In the development of process-specific requirements, the following objectives were pursued:

- Open handling of metallic mercury should be avoided, e.g. the opening of containers,
- A release of liquid metallic mercury or of mercury via the gas phase should be excluded to a large extent by technical and organisational measures,
- In case of a mercury release the consequences for environmental and occupational safety should be limited.

With respect to the storage of metallic mercury the requirements for mining safety and technical equipment do not exceed the provisions in the German Federal General Mining Ordinance.

General rules for the acceptance, handling and permanent storage of hazardous waste, which are also applicable for metallic mercury, are assumed as a given and are not included in the assessment. These include, e.g.:

- Permit procedure for a certain type of waste also taking into account conditions relating to water legislation
- Application procedure for acceptance of waste,
- Compliance with the requirements for public transport by road and rail,
- Labelling of waste containers,
- Existence of management system for the landfill operator,
- Existence of clear rules about the responsibility of the landfill operator.

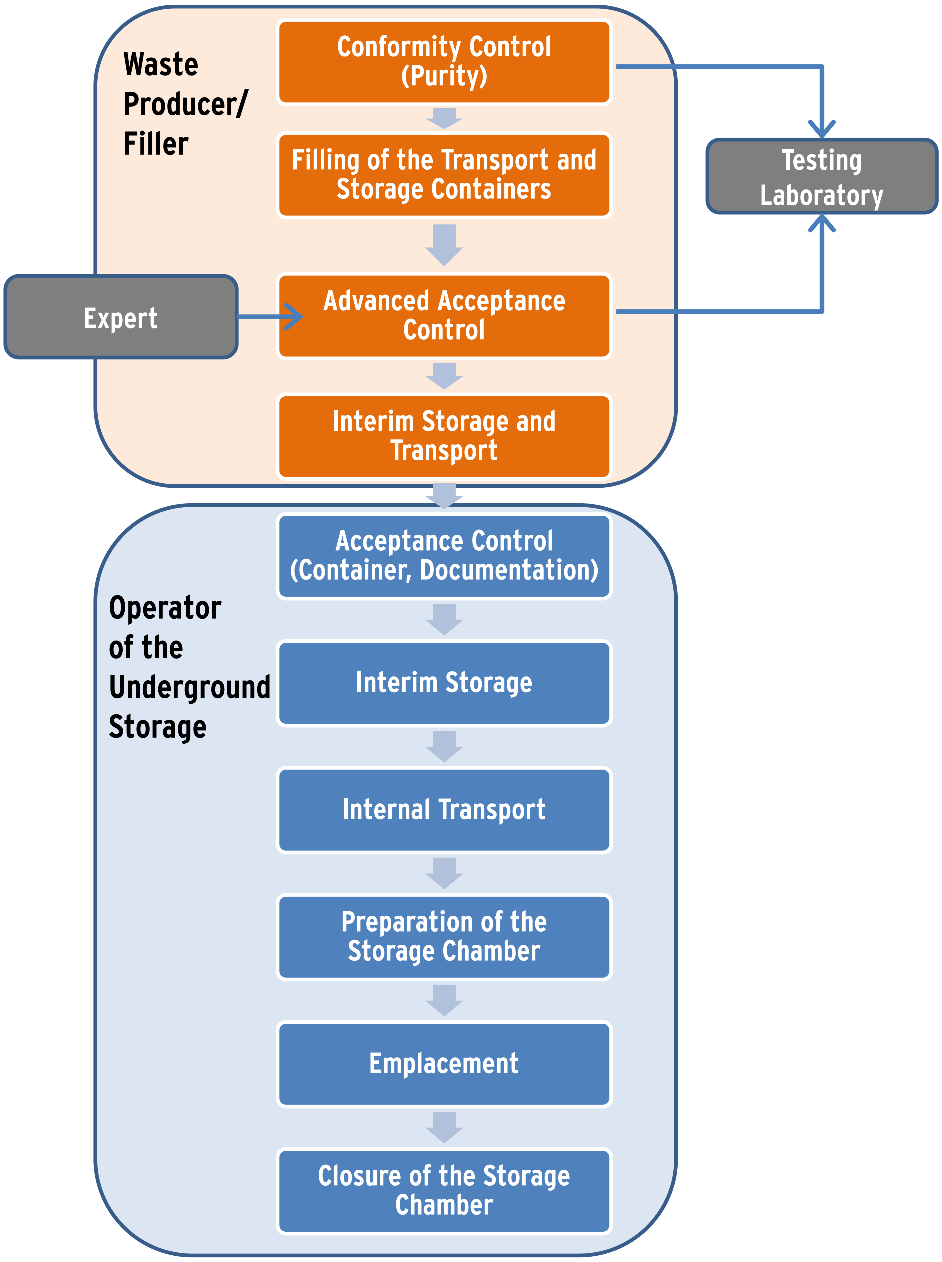

Fig. 12: Procedure for permanent storage of metallic mercury in an underground storage with details of those responsible

5.4.2 Conformity inspection

As was shown above, mercury should have a high purity to ensure that interior container corrosion does not have to be expected during the manipulation and open storage period (see section 5.3.8). In the hypothetical case of a solution inflow, it also more favourable if mercury is in its elemental form and contains as few easily soluble components as possible (see section 4.4.2).

Because of this it is recommended that specific requirements for the purity of the mercury and for the properties of the transport and storage containers are formulated for permanent storage as well.

The purity control should be carried out in two stages. A conformity control is intended to ensure that only mercury of a sufficient purity is filled in the transport and storage containers. In doing so transport and storage containers are prevented from being irreversibly damaged by contaminated mercury. The control must therefore be carried out before the transport and storage containers are filled. The second control should be carried out before delivery of the mercury to the underground storage. It ensures that the delivered mercury, which is already in the transport and storage containers, meets the purity requirements. This second check is described in section 5.4.4 ("Advanced acceptance control").

The waste producer must provide proof of purity. The purity analysis should be carried out by a qualified testing laboratory accredited according to the standard DIN EN ISO/IEC 17025 in accordance with Annex 4 of the German Landfill Ordinance. To this end, a test procedure corresponding to the testing of other waste properties is to be defined in Annex 4 of the Landfill Ordinance[34].

The methods already defined in the Landfill Ordinance (Annex 4 no. 3) are insufficient for this purpose. They refer to mercury in aqueous solutions.

5.4.3 Transport and storage containers for liquid mercury

5.4.3.1 Objective of the requirements

The observations in sections 5.3.4 and 5.3.6 have shown that the release of mercury from a container damaged by an accident poses a serious safety risk, which should be counteracted by preventive measures. The containers that are used should thus be designed both for internal transport as well as for permanent storage as accident-proof, non-reusable transport and storage containers (combination packaging, composite packaging). In addition to the requirements for public transport by road or rail, they should also fulfil the requirements for safe handling during the operational phase in an underground storage. Overall, it is necessary to demonstrate that no impermissible emissions emanate from the transport and storage containers for metallic mercury during normal operation and assumed incidents.

5.4.3.2 Technical requirements for the container

Essential technical requirements already result from the application of the conventions on the transportation of dangerous goods (ADR, RID, ADN). The objective of these requirements is that the pressure receptacles and their closures are designed, manufactured, tested and equipped so that they can withstand all stresses, including fatigue, to which they are exposed under normal conditions of carriage and use.

It must also be ensured that they are adapted to the underground storage conditions. Directive 2011/97/EU on the (temporary) storage of mercury has defined technical requirements for the properties of containers, which can be used as the starting point for requirements for permanent storage. It includes the issues of choice of materials, corrosion resistance, leakproofness, maximum filling ratio, type and labelling. The following table (Tab. 14) indicates the extent to

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[34] The definition of an analytical method is already foreseen in the current amendment of the Landfill Ordinance.

which the requirements defined in the Directive can be transferred to permanent storage, or when different criteria are to be recommended.

The requirements for corrosion resistance from Directive 2011/97/EU can be applied to permanent storage even if the minimum integrity to be achieved for the container would be lower due to the only short open storage in dry storage chambers in the salt rock. It was not possible to clarify within this project the corrosion protection measures which were thus dispensable. For this reason, it is recommended to proceed conservatively and to apply the requirement for corrosion protection from the directive for temporary storage.

Detailed specifications of the container material and the requirement to avoid welds can be waived if the basic requirements are met in accordance with approval for public transport, protection against corrosion and resistance to design basis accident conditions. It may be left to the container manufacturers as to how and with which materials they are to meet the objecttives, as long as the applicable standards and regulation are complied with.

Additional criteria should be met for the safety of the internal transport. These are discussed in the following sections.

5.4.3.3 Labelling

Clear labelling of the container is important. Directive 2011/97/EU has changed the Landfill Directive in Annex II sections 6 C-D and formulated requirements for the labelling of containers for the storage of mercury which is classified as waste:

- Each container has a permanent engraved stamp which contains the identification number, the construction material, the empty weight, the reference to the manufacturer and the date of manufacture.
- A plaque with the identification number of the certificate must be attached to each container.

A certificate is issued for each container, without which acceptance for storage is not possible. It contains information on

- name and address of the waste producer,
- name and address of the responsible for the filling,
- place and date of filling,
- quantity of the mercury,
- the purity of the mercury and, if relevant, a description of the impurities, including the analytical report,
- confirmation that the containers have been used exclusively for the transport/storage of mercury,
- the identification numbers of the containers,
- any specific comments.

Tab. 14: Requirements for the container for temporary storage compared to the requirements for permanent storage

Property	Requirements for the (temporary) storage of metallic mercury according to Directive 2011/97/EU	Recommended requirement for the permanent storage of metallic mercury
Maximum open-ended storage period	Five years are stated in the reasons, but are not defined in Directive 2011/97/EU. Pressure containers for mercury (80 l, maximum 10 bar) must undergo an internal check in accordance with the Ordinance on Industrial Safety and Health (BetrSichV) at least every five years and thus cannot be used any longer without a check.	Not defined, but the operating life should be as short as possible. Open storage in the storage section of an underground storage should take no more than several days or weeks during a deposition campaign.
Corrosion protection	The containers used for the permanent storage of metallic mercury must be corrosion-resistant and shock-proof. Welds should thus be avoided.	The containers used for the permanent storage of metallic mercury should be corrosion-resistant and shock-proof with respect to the storage conditions. The reference to welds can be omitted if the other requirements are met.
	The outside of the container must be resistant to the storage conditions.	Repeated previous requirement and is dispensable.
Container material	Container material: carbon steel (at least ASTM A36) or stainless steel (AISI 304, AISI 316L).	A detailed definition can be omitted if the technical requirements for corrosion resistance and the approval for public transport are met.
Tightness	The containers must be impermeable to gases and liquids.	The requirement for leakproofness arises from the regulations for the public transport of hazardous substances (ADR/RID) and is dispensable.
Type	The type of container must pass the drop test and the leak test in accordance with sections 6.1.5.3 or 6.1.5.4 of the manual for tests and criteria of the UN recommendations for the transport of dangerous goods (UN 2011).	Not applicable for 80l Hg containers as pressure vessel (section 6.1 of the UN recommendations) applies only to packages with a net weight of up to 400 kg. Section 6.2 of the ADR Convention applies for the public transport of pressure vessels. Higher requirements are necessary for internal transport underground: Only such containers should be allowed for permanent storage that are capable of preventing leakage or degassing or of keeping it so low that there is no endangerment of occupational safety due to the released mercury ,even when assuming accidents (e.g. collision, crash, vehicle fire) with mechanical and temporary thermal load that cannot be excluded.
Filling level	The maximum filling ratio of the container shall be 80 % by volume to ensure that sufficient ullage is available and neither leakage nor permanent distortion of the container can occur as a result of an expansion of the liquid due to high temperature.	The safety requirements for internal transport are higher and are oriented to a safety objective, thus a requirement for the filling level may be omitted.

These requirements can be applied to the transport and storage containers for permanent storage. When using a container-in-container concept, however, it is advisable to label both the inner and outer container.

5.4.3.4 Specific requirements for underground storage

A potential additional requirement arises for the practice in underground storage: Transport and storage containers should be designed as stackable packaging in such a manner that the underground storage chambers can be optimally filled. However, the dimensions of the containers may have to adjusted to the geometry of the storage chambers and routes and can thus be site-specific. The container types required by the operators of the underground storages in Germany (especially big bags, steel boxes, barrels) (e.g. K+S 2011) usually have this property, but stackability is not a legal requirement.

5.4.3.5 Accident-proof design

As was shown above, a leakage of mercury from the containers during the underground transport must be avoided. In the event of an accident with a mechanical or temporary thermal impact, the container should thus be able to prevent a leakage or degassing.

It must be noted, however, that section 6.1 of the UN Directive applies only to packages with a net weight of up to 400 kg. Mercury containers in the standard net quantity of 80 l / 1 000 kg are designed as pressure vessels and are subject to the specifications in accordance with ADR section 6.2.

Accidents are neither assumed for the requirements for public transport (ADR) nor for the safety assessment of the underground transport in underground landfills. In particular, no additional requirements for waste containers were previously derived from the possibility of a vehicle fire and the resulting thermal load.

Such requirements are made, however, for the design approval of containers which are to be used for the final disposal of radioactive waste in the Konrad mine (Federal Office for Radiation Protection (BfS) 2010 c, d). Waste product groups with different backgrounds in each case and maximum radioactive inventory are defined, which are assigned to one of two classes of waste containers. Waste container of class II may contain a higher inventory. Additional accident-proof containers of both packaging classes are defined. If a container meets some additional requirements for mechanical fixation, impact stability and thermal resistance, higher inventtories are possible (Tab. 15). The containers can consist of a packaging (container, barrel) and an inner container.

For testing the mechanical and thermal resistance of final repository containers for storage in the Konrad mine (drop test, impact test, and fire test), the Federal Institute for Materials Research and Testing (BAM) has experience and experimental methods. These methods may be used as a basis for testing methods for transport and storage containers for mercury. The requirements for the mechanical and thermal type testing were last defined in the Federal Office for Radiation Protection - BfS (2010d). The tests can be done both experimentally as well as mathematically.

Tab. 15: Design requirements for containers for radioactive waste in the final repository Konrad mine (selection)

Characteristic	Waste container class I	Waste container class II

Characteristic	Waste container class I	Waste container class II
Mechanical impact and fire	After collision (speed 4m/s) and subsequent hostile fire (800°C, 1 h), the oxygen inflow is so limited that flammable waste products only pyrolysis at a melting point above 300 °C, and do not burn with a naked flame.	After a fall from a height of 5m, total leakage rate ✥ $1 \cdot 10^{-4}$ $Pa \cdot m^3/s$ Total leakage rate for a hostile fire (800°C, 1 hr) before the fire < $1 \cdot 10^{-5}$ $Pa \cdot m^3/s$ and during the fire (including 24 hour cooling phase) quantity of the substance of the released gas from the packaging ✥ 1 Mol
Additional requirement for accident-proof packaging	Waste is fixated or inner container moulded so that they are dimensionally stable. An inactive layer with thermal resistance$\geq$ 0.1 $m^2 \cdot K/W$ envelops the waste product, which remains intact up to an impact speed of 4 m/s For a fall from a height of 5 m, fixation of the waste and the integrity of the inner container remain intact	For a fall from a height of 5 m, total leakage rate ✥ $1 \cdot 10^{-4}$ $Pa \cdot m^3/s$ For a fall from a height of 5 m, fixation of the waste and the integrity of the inner container remain intact (only for fixed dimensionally stable waste which is packed in inner containers) Wall of the packaging has a thermal resistance of at least 0.1 m^2 K/W, which remains intact up to an impact speed of 4m/s, or proof that with a hostile fire (800 °C, 1 hour) and cooling phase within 24 hours, no radiologically relevant release of radioactive substances occurs

For various reasons, the quantitative requirements cannot be transferred directly to the permanent storage of mercury, inter alia, because

- The protection objective when designing containers for radioactive waste results from the Radiation Protection Ordinance. The protection objective for mercury should be defined differently (no release of mercury, or at least no exceedance of the occupational exposure limit value in the event of damage).
- Only solids are allowed in the final disposal of radioactive waste. Parts of these are volatile. These substances can leave the container only via the gas phase. However, mercury can also leak in liquid form from storage containers.
- The test for fire is carried out using the parameters of leakage rate or amount of substance (total amount of escaping gases per unit of time). During the thermal test of final repository containers, the amount of the substance of released gas may not exceed one mole within a fire and cooling phase of 24 hours. In the case of mercury, 1 mole would be the equivalent of 200 g of mercury vapour, which would probably be far too much in terms of compliance with the protection objectives.

It will thus be necessary to adapt the essential requirements to the test methods and the test objectives. In this case, the mining authorities would be responsible (those who would have to approve the containers for use in underground landfills). Investigating bodies can assume individual responsibility for the detailed definition of the test methods. The mining authorities should then check whether the selected methods comply with the basic requirements and allow reliable statements about meeting the test objectives.

Based on health and safety regulations and the assumptions for the underground mechanical and thermal load (Konrad mine), the following basic requirements may be formulated:

- Only such containers should be allowed for permanent storage that are able to prevent leakage or degassing or to keep it so low that there is no concern about an endangerment of occupational safety due to the released mercury, even when assuming occupational accidents (e.g. collision, crash, vehicle fire) with mechanical and temporary thermal load that cannot be excluded.

Similar to the requirements for the final repository containers, it could be defined:

- The waste containers should ensure that a leakage of liquid mercury does not occur if there is a fall from a height of 5 m on to an unyielding surface. The fall height to be examined can be reduced to the maximum lifting height for loading and stacking processes if it is proved that greater lifting heights do not occur in an underground storage.
- The waste containers should also ensure that there is no release of mercury or mercury compounds with an impact at a speed of 4 m/s and subsequent thermal stress (800°C, one hour duration), or the released amount of mercury or mercury compounds is so small that there is no concern of an exceedance of the workplace concentration of $0.02 mg/m^3$ at the location of the fire or in another part of the landfill. The impact speed to be examined can be reduced if the operating concept provides for lower speeds of transport vehicles.

The definition of a maximum release amount similar to the Konrad requirements would be useful for the specific application of the test according to the second bullet point. However, this would require a more extensive numerical analysis of dispersion processes and maximum attainable concentrations, which cannot be performed within the course of this project. Alternatively, the test could be conducted in such a manner that it is proved that the mercury container remains intact even after the combined mechanical and thermal load, and that there is no indication of the release of mercury (e.g. by concentration measurements during the tests).

5.4.3.6 Possible realisation of the container concept

Transport on public roads is sufficiently regulated by the conventions of ARD, RID and ADN. However, the above formulated requirements for avoiding mercury releases during an internal mechanical and thermal impact go beyond these requirements. It is not expected that thin-walled container types such as barrels have a sufficient resistance, particularly with regard to thermal loads. Such properties are also not known for the mercury containers (3l or 80l) currently on the market.

It would thus be a task for the container manufacturers to develop new types of containers that meet these requirements, or to prove compliance with the requirements for existing containers.

One way of increasing mechanical and thermal resistance is to use a container-in-container concept. The aim of this is that, in the event of damage to the container due to external (fire, accident) or internal events (corrosion, fatigue), there is always a second barrier, which prevents leakage of mercury and slows the heating of mercury at the same time so that no beyond-design-basis pressures arise.

When constructing the transport and storage container, one can look to the accident-proof steel containers for transporting and storing (final disposal) radioactive waste which are used in practice and approved by the BAM. They were developed in accordance with the final disposal conditions for the Konrad mine (latest version: Federal Office for Radiation Protection - BfS 2010c, d).

They are designed as a multi-barrier system, so that they can resist a thermal load of 800 °C for one hour without releasing a prohibited amount of radioactive substances (class 7 according to ADR). They consist of a steel sheet container with a concrete casing surrounding the waste with a minimum value for the integral thermal resistance, which is calculated from the product of thermal resistance and material thickness.

A similarly constructed storage container for liquid mercury would consist accordingly of the three elements inner container, insulation layer and outer container (Fig. 16). It should be examined whether container types that are already approved for transport and storage of hazardous wastes, could be used for this purpose.

5.4.3.7 Inner container

80 l containers (Fig. 13) and 2.5l steel cylinders (Fig. 14) are widely introduced and approved for road transport. They may also serve as inner containers. There is at least one manufacturer who has 80 l containers in his product range, which have unlimited BAM approval. They are made of stainless steel and have a payload of 1 000 kg (80 l) of metallic mercury. Inside, the containers are lined with a thin layer of plastic to prevent direct contact between the mercury and the metal. The dimensions of the container including the frame are approximately 0.8 x 0.8 x 0.8m. This transport container represents a pressure vessel. Before initial use and then at regular intervals of 5 years, this transport container is to be tested according to the BAM approval at a pressure of at least 0.6 MPa (6 bar). A leak test must also be performed after filling the container. If the testing of the transport container is not performed every 5 years this automatically means that this transport container is no longer approved for public transport.

Fig. 13: Example of an 80l / 1 tonne mercury container (© UTM GmbH[35])

Currently, steel cylinders made of carbon steel are also used for road and sea transport of mercury. 34.5 kg of metallic mercury (approximately 2.5 l) can be transported in a steel cylinder (Fig. 14). No approval is required in accordance with the ADR regulations for these containers. Only general requirements for public transport because a capacity of 3 l is not exceeded. Due to properties of the carbon steel used, external corrosion may occur if the

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[35] Reproduction with permission from UTM GmbH, Lübeck, Germany, http:://www.utmluebeck.de

cylinders are exposed over time to damp conditions. A failure of the container can be avoided if sufficient quality management is pursued during its manufacture and the cylinders are coated from the outside and stored in a dry location (Pawel 2009).

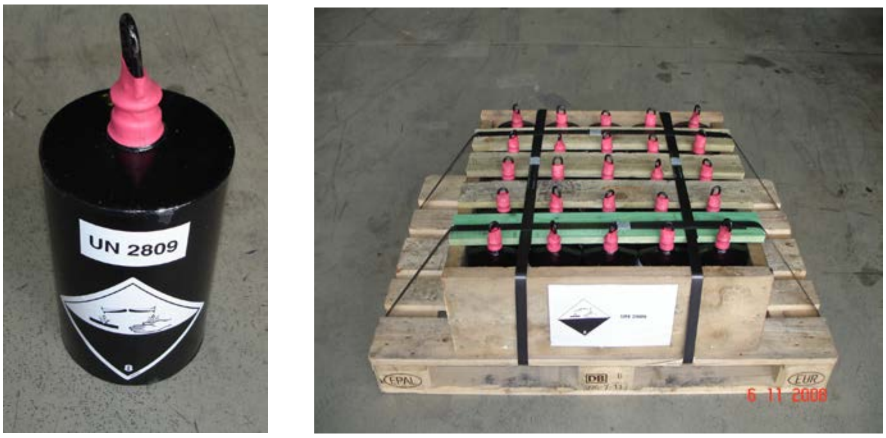

Fig. 14: Mercury steel cylinders (flasks): single flask and flasks on a pallet (© DELA GmbH[36])

5.4.3.8 Insulation layer

An insulation layer (e.g. concrete) surrounding the inner container slows down any possible heating. The material thickness could, for example, be designed in a way that in the event of a one-hour fire the container remained leak-proof: the

metallic mercury in the inner container would not be heated to temperatures above the boiling temperature (356°C) or at least the mercury vapour pressure would not lead to an exceeding of the design inner pressure of the container.. The requirements for Konrad containers (thermal resistance$\geq$ 0.1m^2 K/W) are met, for example, by a 0.16m thick layer of normal concrete (ρ=2 200 kg/m^3, thermal conductivity 1.6 W/(m K). Thinner layers are possible when using materials with lower thermal conductivity. The use of concrete increases the geomechanical stability of the containers at the same time.

5.4.3.9 Outer container

The steel boxes (Intermediate Bulk Container IBC), for example, which are already in use in underground landfills in various formats may serve as outer containers (Fig. 15).

The dimensions of the inner and outer containers that are used should be adapted to each other in such a manner that the container-in-container concept can be realised. The outside dimensions as well as the total weight must comply with the specific conditions of acceptance (dimensions and weight) of the respective underground landfill[37]. Further protection of the outer and inner container against corrosion is achieved by a protective coating (paint/plastic coating) applied all around them.

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[36] Reproduction with permission from DELA GmbH, Dorsten, Germany, http://www.dela-gmbh.de

[37] Maximum weight between 1.5 tonnes and 3 tonnes depending on the specific underground storage. Maximum dimensions (LxWxH) around 1x1.2x1 m to 2x1.2x1.2 m.

Fig. 15: Steel containers for the transportation and disposal of waste in underground landfills (© mh Verpackungsservice38)

Fig. 16 illustrates a possible version of the design of a transport and storage container for metallic mercury consisting of

- a standard 1 tonne mercury container (0.8 x 0.8 x 0.8m),
- a thermal insulation made of normal concrete ($\rho = 2\ 200\ kg/m^3$) in the form of a surrounding inner lining (wall thickness: 0.15m),
- a steel box (IBC) (1.1 x 1.2 x 1.1m) that is approved for underground storage,

In this case, the total weight of a container was about 2.6 tonnes (steel box: 300 kg, concrete: 1100 kg, mercury including container: 1200 kg).

The mercury container should be fixed in a suitable manner in the steel box to prevent slipping during transport. Mechanical fixation can be omitted if the inner container is pre-cast with concrete.

The container concept described above represents only one conceivable example. Before approval of transport and storage containers for transporting (BAM) and permanent storage (responsible mining authority in each case), it would be necessary to check via testing or modelling whether a certain transport and storage container meets the requirements, inter alia, with regard to mechanical and thermal resistance.

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38 Reproduction with permission from mh Verpackungsservice, Porta Westfalica, German, http://www.mh-verpackungsservice.de

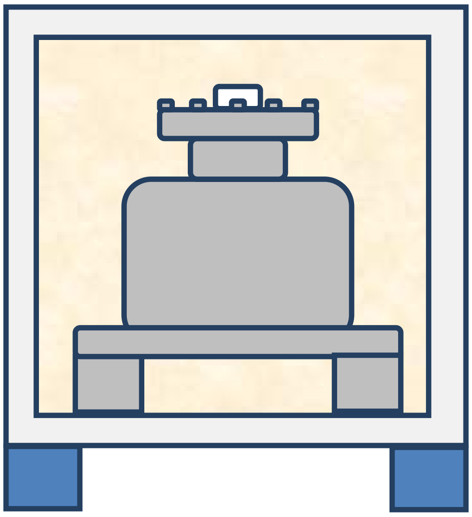

Fig. 16: Exemplary scheme of a transport and storage container for metallic mercury (1 tonne mercury container in steel box with insulating material on underground storage pallet or on feet from profiled wood or profile steel

5.4.3.10 Retrievability

The retrievability of stored waste containers during the period of operation of an underground storage is not an approval criterion of underground storage operation or of the transport container. However, some examples are known where waste has been retrieved from an underground storage (e.g. selenium-containing waste and transformers, Öko-Institut 2009, Hessischer Landtag 2010). This was done solely for economic reasons because the stored waste had reached such a high market value that the complex retrieval was worthwhile. A retrieval of stored liquid mercury and also stabilised mercury from an underground storage would be contrary to the intention of the mercury export ban regulation of 2008, namely to prevent mercury from specific sources from coming on the market. Retrievability due to a possible future commercial exploitation is thus not foreseen for mercury.

The subject of retrieval was included in the current safety requirements for the underground disposal of heat-generating radioactive waste. Thus the "Safety requirements for the final disposal of heat-generating radioactive waste" (BMU 2010) stipulate that the waste containers can be retrieved as an emergency measure during the period of operation of the final repository and can be secured after the end of the period of operation for a period of 500 years. There is currently no retrievability requirement for negligible heat-generating radioactive waste.

The examples of ASSE II and Stocamine show that in the event of an emergency - or if other safety reasons exist (for example, waste which is incorrectly declared and unfit for underground storage) - retrieval should be possible. The waste packages should thus be designed so that they can be retrieved during the anticipated remaining operating period of the underground storage (e.g. 40 years), without concerns about endangering operational safety. This requirement is clearly already met for containers with solid waste, as was demonstrated by the retrieval of waste during operation (Öko-Institut 2009). Even if the containers are damaged, only minor and small-scale leakage of solids is expected. The situation must be assessed differently for containers with liquid waste. If these are no longer leak-proof, the liquid could leak completely and spread. Retrieval may still be possible but only with a great and possibly no longer justified effort with regard to occupational safety. The requirements for containers with liquid waste must thus be set higher. For underground landfills in salt rock, the containers should be stored in a way that the convergence within the anticipated remaining operating time does not lead to a beyond-design-basis mechanical load of the containers in the storage chambers. Retrievability is increased if the containers are designed so that they have sufficient geomechanical stability, e.g. by using concrete components.

The containers should also be sufficiently corrosion-resistant for the anticipated remaining operating time and the geochemical conditions in the storage chamber so that a leakage is not expected.

Retrieval is to be regarded as an emergency measure. It is assumed that it comprises only the transportation of the container back to above ground. Whether and how the containers are transported above ground is outside the scope of this study. It is assumed that above-ground measures are taken, which enable further transport (e.g. transfer or secondary packaging).

The possibility of a recovery even centuries after closure of the underground storage is not taken into consideration. An underground storage is not designed to be accessible for such long periods of time. In fact, it aims to ensure a rapid and complete isolation of waste through geological and technical barriers.

5.4.3.11 Container inspection by the waste producer

The waste producer should satisfy himself of the compliance with the technical requirements before using a transport and storage container.

5.4.4 Advanced acceptance control for liquid mercury

5.4.4.1 Objective of the requirements

The open handling of metallic mercury poses significant risks for the health of employees due to the vapour pressure which far exceeds the occupational exposure limit value (see sections 3.1 and 5.2.3). Such open handling is essential during the acceptance control according to the German Landfill Ordinance to satisfy oneself of the consistency of the waste with the accompanying documents and of conformity with the material requirements. It is thus necessary to consider how the acceptance control for the special case of metallic mercury can be organized differently to avoid its open handling at the site of the underground storage according to the precautionary principle in the German Hazardous Substances Ordinance (GefStoffV) and the German Federal General Mining Ordinance (ABBergV).

Liquid mercury which is to be disposed of in an underground storage should be subject to a number of controls to ensure that it can be safely stored. These controls are intended to ensure that

- the liquid mercury to be disposed of has the envisaged minimum properties, thus meets the purity requirements and does not contain minor constituents or only within the permitted concentration limits. This also covers the control tests envisaged in §8 subparagraph 5 of the Landfill Ordinance (at least once a year in the case of waste exceeding 50 tonnes or for each commenced 2500 tonnes),

- the delivered waste is consistent with the accompanying documents. §8 subparagraph 4 point 5 of the Landfill Ordinance envisages an inspection of appearance, consistency, colour and odour. An odour inspection is to be omitted for mercury.
- the containers used for transport and permanent storage meet the requirements with regard to suitability and labelling and exhibit no defects,
- the content of accompanying documents is consistent with the delivered waste and containers.

The legally prescribed inspection of appearance, consistency, colour and odour as well as the random chemical control tests should not take place in the underground storage for health and safety reasons. In addition, opening the especially designed and sealed transport and storage containers and then closing them should be avoided. On the other hand, however, an acceptance control may be not waived because the underground storage operator must, for reasons of operational safety and to comply with the statutory provisions, satisfy himself that the delivered waste complies with the requirements and the declaration. The waiver of an acceptance control in Stocamine caused that non-compliant waste was stored, which led later to the fire and the closure of the underground storage (COPIL 2011).

To avoid open handling of mercury in an underground storage, there is a proposal to bring forward the waste control and have them already performed by the waste producer. This procedure is similar to the exemption for asbestos-containing waste described in §8 subparagraph 5 of the Landfill Ordinance, for which a control test by the landfill operator is omitted. Due to the high toxicity of mercury and the special requirements for the purity of mercury, however, it is recommended not to waive the control test, but to expand the inspections by the waste producer.

A similar procedure with preliminary characterisation of waste and waste packages by independent experts is approved in Germany as a control concept for the final disposal of radioactive waste. Checking compliance with the requirements of final disposal is carried out by independent experts as part of the so-called product control at the place of the waste producer or conditioner - even before the waste is transported to the final repository. These product control measures may cover individual waste packages including the radioactive waste or the waste product, charges of waste but also specific conditioning processes (BfS 2010d, BfS 2010e).

5.4.4.2 Advanced acceptance control

If open handling of mercury in the underground storage is to be avoided, all material tests which would accrue for the acceptance of waste in the UTD should be performed in advance by the waste producer. As the underground storage operator is still responsible for the safe operation of the underground storage, there is a need for control and safety mechanisms which allow a verification of compliance with the requirements of the Landfill Directive, regardless of the interests of the waste producer. This should start with the filling of the transport and storage containers and extend to the delivery at the underground storage. All measures from container inspection and sampling via filling and sealing should be checked by an independent expert and carried out in his presence to some extent:

- Before filling the containers, a check should be carried out on the basis of the supplied documents and a visual inspection as to whether the containers comply with the requirements for transport and permanent storage.

- The waste producer should perform the filling operation of transport and storage containers on the basis of the requirements laid down in the approval or in the underground storage authorisation of the transport and storage containers. Technical equipment should ensure that the filling level of the inner container can be inspected and that no exceedance of the maximum filling quantity occurs. This can, for example, be done by means of weighing or volume measurement. The expert should check compliance with the statutory requirements and the accuracy of the labels on the container based on the documents and a visual inspection.
- After filling, a sample should be taken from each container in the presence of the expert. This should ensure that the laboratory sample is clearly related to the contents of the container. He should also make sure that the filling ratio of the containers meets the requirements. In addition to the test sample for the testing laboratory, a reference sample should be taken in each case for the waste producers and the landfill operators. After sampling, the expert should seal the cap of the filled transport and storage container.
- The sealed reference sample from the waste producer should be kept in the area of responsibility of the waste producer at least until the storage is completed in the underground storage without objection. The reference sample can be disposed of by the waste producers after relevant information is provided by the landfill operators and consultation with the responsible authority. The second sealed reference sample should be provided to the landfill operator with the delivery, which he must keep in accordance with the guidelines according to §8 subparagraph 6 of the Landfill Ordinance (DepV). An unbreakable and shock-proof container which is impervious to gas and liquids should be used for the reference sample in order to prevent contamination of the sample storage. It is worth considering whether to store reference samples of liquid mercury solely above ground, for example, in suitable hazardous substance cabinets, in order to avoid the use of small containers underground. The leakage of small amounts of mercury from damaged small containers can also lead to considerable contamination underground. The reference sample can be disposed of by the underground storage operator after the end of the prescribed retention period, but at the earliest after closure of the relevant storage section. The same regulations should apply to the mercury from the reference samples, as for the sampled mercury itself.
- Several samples should be analysed per delivery to record any possible heterogeneity of the mercury, for example, per commenced 10 tonnes. The analysis report is made available to the landfill operator, the independent experts and the waste producer. A delivery to the underground storage should occur only if the test results of the laboratory on the purity of the mercury are available. If at least one sample shows non-compliance with the requirements, all other samples of the relevant delivery should be investigated in order to identify those containers that do not comply with the requirements. If non-compliance is confirmed by a repeat measurement, permanent storage may be allowed only after further purification and positive conformity analysis of the mercury.

Basically, it is irrelevant how many waste producers deliver metallic mercury to an underground storage for disposal. With regard to verification of the required waste characteristics, however, it is more efficient if the delivery is made by only a few waste producers in the course of a so-called collective disposal. This procedure is covered by the Landfill Ordinance. This would have the advantage that the quality assurance measures could also be performed centrally by only a few waste producers and independent experts who are familiar with the special requirements for the disposal of mercury.

5.4.5 Disposal of metallic mercury from abroad

The proposed concept for acceptance controls can be applied also to the disposal of metallic mercury from abroad. Three procedures are conceivable in principle:

- The transport and storage containers are loaded at the waste producer's site and sampled in the presence of an independent expert. After verification of compliance with the purity requirements, the advanced acceptance control is carried out. If this is positive, the transportation to the underground storage takes place in accordance with the international requirements for the transport of dangerous goods, for example, ADR.
- The mercury is filled into a transport container at the site of the waste producer or the filler after a successful conformity inspection and is sampled in the presence of an independent expert. The transport container is transported to Germany and is then combined into a transport and storage container (if such a concept is technically feasible and approved), and then transported to the underground storage.
- The metallic mercury to be disposed of is first delivered in a standard transport containner to a German waste disposal company (for example, a mercury recycler) and is then filled into an approved transport and storage container. The advanced acceptance control is carried out in Germany.

A transfer should be avoided where possible, however, it may be necessary if the technical requirements for the transport and storage containers (see section 5.4.3) could not be met by the waste producers from abroad.

Regardless of the procedure, Regulation (EC) 1013/2006 on shipments of waste must be considered when importing waste to Germany. The waste producer has to notify the responsible national authority in his own country of the shipment of mercury waste (and other types of waste). A shipment is permitted only after obtaining the consent of the responsible authorities of the export and destination countries, and of transit countries if necessary. The waste producer has to provide basic information on the waste, in particular about the origin and the composition of the waste. The measures to be taken to ensure transport safety must also be specified. The responsible authorities may also impose conditions in respect of the transport.

A special procedure is required for mercury which has to be transported by sea (if no land route is available or if it is too expensive). Currently, carriage by sea takes place only in containners with a maximum volume of 3 l (flasks)[39]. Larger transport and storage containers intended for permanent storage can only be filled on the mainland. It would also be useful to consider whether the storage containers could be made with pallets of 3 l flasks, instead of only allowing one or a few 1 tonne containers. However, the advanced acceptance control would be more complex in this case. To obtain a representative overview of the purity of mercury, more sampling would be needed because the mercury is distributed over 300 flasks with a shipment of 10 tonnes.

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[39] In accordance with the requirements of the International Maritime Dangerous Goods Code (IMDG Code)

5.4.6 Interim storage and transport

5.4.6.1 Interim storage

It can be assumed that not all loaded transport and storage containers can be transported promptly by the waste producer to the underground storage. Interim storage must take place in this case. As long as the storage does not exceed one year, the main waste producers (e.g. chlor-alkali plants) or recyclers should already have approved storage capacities. The additional requirements of Council Directive 2011/97/EU take effect only for storage longer than one year. These include, inter alia,

- Metallic mercury shall be stored separately from other waste.
- Containers shall be stored in collecting basins suitably coated so as to be free of cracks and gaps and impervious to metallic mercury with a containment volume adequate for the quantity of mercury stored.
- The storage site shall be provided with engineered or natural barriers that are adequate to protect the environment against mercury emissions and a containment volume adequate for the total quantity of mercury stored.
- The storage site floors shall be covered with mercury-resistant sealants. A slope with a collection sump shall be provided.
- The storage site shall be equipped with a fire protection system.

Storage shall be arranged in a way to ensure that all containers are easily retrievable. The following requirements must also be observed:

- A continuous mercury vapour monitoring system with a sensitivity of at least 0,02 mg mercury/m^3 shall be installed in the storage site. Sensors shall be positioned at ground level and head level. This shall include a visual and acoustic alert system. The system shall be maintained annually The storage site and containers shall be visually inspected by an authorised person at least once a month. Where leaks are detected, the operator shall immediately take all necessary action to avoid any emission of mercury to the environment and restore the safety of the storage of the mercury. Any leaks shall be considered to have significant adverse environmental effects as referred to in Article 12(b) of Directive 1999/31/EC.

5.4.6.2 Emergency plans and adequate protective equipment suitable for handling metallic mercury shall be available on site. Transport

The transport of containers to the UTD is carried out within the area of responsibility of the waste producer. It is performed according to the regulations for dangerous goods on road, rail and inland waterway transport after successful final inspection by the waste producer or by a suitable transport company commissioned by him. Delivery to the underground storage should take place in campaigns in order to allow for optimizing operational procedures in the underground storage.

5.4.7 Acceptance control in the underground storage

If the substance-based acceptance control within the meaning of §8 subparagraph 4 of the Landfill Ordinance (acceptance inspection) and paragraph 5 (control tests) are is brought forward to the waste producer, the acceptance control at the underground storage site can be limited to external checks of containers and accompanying documents (§8 subparagraph 4 no. 1 to 4 Landfill Ordinance):

1. Check as to whether the basic characterisation for the waste is available.
2. Determination of the mass, the waste code and the waste designation in accordance with the Annex to the German Waste Catalogue Ordinance.
3. Control of documents pursuant to paragraph 3 clause 5 of the Landfill Ordinance whether they correspond with the information on the basic characterisation (analysis report from the advanced acceptance control).
4. Visual inspection of the containers before and after unloading.

A visual inspection would include a visual inspection of the transport and storage containers and a check of the labelling of the container and the seals. In addition, there would be a check as to whether the investigation report of the independent expert is available and if compliance with the requirements for the purity of mercury was confirmed.

After a positive acceptance control, the waste as well as the transport and storage containers becomes property of the landfill operator.

Upon detecting deviations, i. e. if the transport and storage containers do not meet the requirements, the relevant transport and storage containers should be stored separately from the other waste containers. The responsible supervisory authority must be informed in accordance with §8 subparagraph 10 of the Landfill Ordinance (DepV). A proposal for the further course of action should be submitted to the responsible supervisory authority, for example, outer packaging for a return to the waste producer in accordance with the transport regulations.

5.4.8 Above-ground interim storage in the underground storage

To reduce the potential risk of accidents involving transport and storage containers, interim storage should either be avoided or restricted to the shortest period possible. Even if this period of time is very limited, the design of the storage area should be based on the requirements for the storage of metallic mercury. The entry of liquid mercury into soil and/or groundwater should be safely ruled out. The requirements correspond to the points listed under sections 5.3.3 (Above-ground mechanical impact) and 5.3.5 (Above-ground fire).

5.4.9 Internal transport underground to the storage area

To avoid mechanical and thermal loads for waste containers set aside, the internal transport of containers between the waste acceptance area and the underground storage chamber should take place immediately and without interruption. Underground interim storage should be avoided. The internal transport lots should consist solely of the transport and storage containers with metallic mercury to avoid mixing waste in the hypothetical case of a vehicle accident.

5.4.10 Storage area

The leakage of metallic or gaseous mercury in the open storage area can lead to a contamination of the area which is difficult to clean and to an exceedance of occupational exposure limit values (see sections 5.3.4 and 5.3.9). Thus measures should be taken to avoid events which can lead to a leakage of mercury in the storage area. In addition, it is recommended to choose and equip the storage area and the storage sections so that any possible contamination is as limited as possible and the operations of the remaining underground storage areas are as unaffected as possible.

The storage area to be used should be a separate mine area away from other chambers, routes and possibly other cavities. It may be used only for the permanent storage of metallic mercury. Simultaneous storage of other types of waste should be excluded. In addition, it is recommended to select the storage area so that it is possible, in the event of an accident, to direct the ventilation in a way[40] so that an airborne contamination can be limited to as small a mine area as possible.

The ground level of the storage section should be set slightly lower than the level of the access route to be able to capture potentially released metallic mercury in this area without it being able to reach the access route.

Even if technical measures (double container concept) to prevent a release of mercury are paramount, careful monitoring of the storage section is essential to detect a leakage of mercury in good time and to initiate countermeasures. Regulation 1102/2008 stipulates regular visual inspections and the installation of vapour detectors for this purpose.

There is no substantial difference between open permanent storage and open long-term storage. If it is planned to keep a storage section open for longer than one year from the time of the first storage, the measures provided for long-term storage[41] in accordance with Directive 2011/97/EU and the Landfill Ordinance (DepV) should also be applied.

Then, additional measures would have to be taken, such as installing a fire protection system, covering the floor with a material resistant to mercury, setting up the mercury containers in collecting basins.

It is recommended to store mercury in campaigns. After completion of a campaign, the respecttive storage section should be backfilled and sealed with a wall. Processes that subsequently lead to the release of mercury from the containers would have only little or no relevance for the operation of the underground storage. As additional protection, however, it is proposed to prevent potential consequences of geomechanical influences. This can be done either by showing that the development of a beyond-design-basis pressure on the containers is unlikely to occur until the end of the decommissioning of the mine or by measures which prevent a leakage of liquid mercury from the storage section (cavities and enclosing dams, see section 5.3.10). Sufficient ventilation must be ensured during the work in an open storage section.

Whether there is a need for an automatic and continuous measurement of the mercury concentration in the air pursuant to Annex 1, 1.1.2 of the German Federal General Mining Ordinance (ABBergV) should be decided on the basis of a risk assessment according to §3 subparagraph 1 clause 5 No. 1 ABBergV. In view of the recommendation to store metallic mercury solely in accident-proof transport and storage containers, a release of mercury in

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[40] The system for the even supply of fresh air to the mines and for discharging used air is known as the ventilation system. By installing ventilation structures (e.g. locks and doors), there can be a better or worse flow of air in certain parts of the mine.

[41] To be transposed into German law by March 15th, 2013

normal operation seems to be very unlikely. If it is also planned to keep the storage section open for only a few days in the course of the storage stage, a similar protective effect can be achieved if the concentration is measured with location-independent devices. However, the measurements should then be taken several times a day: before, during and immediately after completion of the daily work in the area of the open storage section. The measurements should be taken at ground level as well as at head height in the immediate vicinity of the waste containners. The measurement results must be recorded and retained for a reasonable period. In addition, a regular visual inspection of the open storage section should be carried out daily if work is planned for there, otherwise at least once a month.

Upon exceeding the occupational exposure limit value of 0.02 mg/m^3 (unique daily measurement or as an 8 hour average for continuous measurement by stationary measuring instruments), measures must be taken to prevent further exposure of workers (e.g. access restrictions, personal protective equipment, modified ventilation system). It is recommended to define a lower concentration (e.g. 0.005 mg/m^3) as the alert threshold as of which a close immediate examination of the chamber and the deposited container must take place in order to determine the source of mercury pollution in the air and intercept it. A concentration of mercury in the air which is significantly above the background level is an indication of a mercury release from the containers.

The recommended measures are summarised in Tab. 16 and are compared with the requirements for temporary storage in accordance with EU Directive 2011/97/EU.

5.4.11 Occupational and operational safety / emergency plan

When operating an underground storage, the avoidance of risks by preventive measures is paramount. The measures to be taken (including explosion protection, fire protection, and escape routes) are described in §8 and Annex 1 of the German Federal General Mining Ordinance and are part of the practice of any mining operation (see section 5.2.3). For an underground storage that handles containers containing mercury, the German Federal General Mining Ordinance stipulates the following specific requirements:

- Waste containers which contain mercury should be handled only by specially trained personnel who are informed about the specific risks, the required special processes, and the planned emergency measures.
- Employees must also be able to take appropriate measures themselves to avert danger and limit damage for their own safety or the safety of other persons, even if the responsible person cannot be reached.
- In addition, employees must cease working if there is significant imminent danger and be able to escape to safety by leaving their workplaces immediately.
- Equipment should be available to measure the concentration of mercury in the atmosphere.
- Automatic and continuous measuring systems and alarm devices should be set up in accordance with a risk assessment.
- Employees must have access to suitable breathing apparatuses and resuscitation equipment. In the event of mercury vapours, the breathing apparatus would have a special filter Hg-P3 (red and white) (VBG 2012).

Tab. 16: Requirements for the storage area within the course of temporary storage compared to permanent storage

Property	Requirements for the (temporary) storage of metallic mercury according to Directive 2011/97/EU	Recommended requirements for the permanent storage of metallic mercury
Separation from other waste	Metallic mercury shall be stored separately from other waste.	Same requirement
Preventive measures to contain leaked mercury and to prevent emissions	Containers shall be stored in collecting basins […].	By storage in campaigns and subsequent closure, the containers are stored in the open for only a short time. A failure of containers is very unlikely at this time. Collective basins and drains are unnecessary. The failure of containers is no longer relevant to safety after closure of the storage section.
	The storage site floors shall be covered with mercury-resistant sealants. A slope with a collection sump shall be provided	
Barriers	The storage site shall be provided with engineered or natural barriers that are adequate to protect the environment against mercury emissions and a containment volume adequate for the total quantity of mercury stored	The presence of a permanent geological barrier is a basic prerequisite for the approval of an underground storage. To prevent leakage from the final repository area during the operating phase, the level of the storage sections should be set slightly lower.
Fire protection	The storage site shall be equipped with a fire protection system.	Minimisation of fire loads and ignition sources. An incipient fire is only of concern if a transport vehicle is located in the storage section. Fire protection is ensured by the accident-proof containers.
Retrievability	Storage shall be arranged in a way to ensure that all containers are easily retrievable	Retrieval is not intended for final disposal by means of permanent storage.
Inspections and monitoring	A continuous mercury vapour monitoring system with a sensitivity of at least 0,02 mg mercury/m 3 shall be installed in the storage site. Sensors shall be positioned at ground level and head level. This shall include a visual and acoustic alert system. The system shall be maintained annually.	By depositing the waste in campaigns and subsequent closure of the storage sections, the containers are stored in the open for only a short time. For this reason, it is considered sufficient to take the measurements several times a day with location-independent devices before, during, and after completion of the daily work in the storage area. If thresholds are exceeded, measures must be taken according to prepared action plans.
	The storage site and containers shall be visually inspected by an authorised person at least once a month. […].	The storage sections should be kept open only for as short a time as possible. If they are open longer than one month, a visual inspection should take place at least once a month and a measurement of the mercury concentration should be taken at the same time.-

- Preventive measures and the required protective equipment must be thoroughly defined in a gas protection plan and continuously updated.

Measures and procedures should be defined in the emergency plan, which must be performed in the event of a foreseeable major incident in connection with the handling of mercury (for example, vehicle fire). This aims to curb the spread of mercury and to minimise the risk to humans and the environment.

Such measures can, for example, include a modified ventilation system or instructions on how to handle damaged transport and storage containers. If special technical means are required for this purpose, they must be maintained ready for use. This may involve the holding of reserve containers including the required handling technology. In addition, measures should be defined as to how to deal with secondary waste that may arise. Furthermore, a catalogue of measures should be created in the event of an exceedance of the limit and threshold values. Possible actions may include retrieval of the waste containers, continued monitoring of the measuring point or an immediate closure of the storage chamber or a second closure of the storage chamber.

Monitoring of the mercury concentration in the mine air should not only be carried out in open storage sections, but also regularly in other places where mercury containers are handled. The occupational exposure limit value of 0.02 mg/m^3 in the 8 hour average must not be exceeded either. It is recommended to set a lower alert threshold as of which measures must be taken to identify and contain releases. In addition, regular or continuous measurement of the mercury concentration in the exhaust air at the entrance to the shaft is also recommended. Routine monitoring measures should also include regular visual inspections of the interim storage, where available.

5.5 Overview of possible additional costs

Compared to the current practice, the implementation of the previously discussed safety measures requires additional organizational and technical effort and thus also financial costs. The additional costs are to be borne completely by the polluter (the waste producer), or are passed on to him by the landfill operator.

5.5.1.1 One-off costs

- Development and approval/authorisation of a transport and storage container,
- Accreditation of at least one testing laboratory that undertakes the analysis of metallic mercury,
- Approval for the interim storage and erection of interim storage capacity for filled transport and storage containers (if necessary and if unavailable at the waste producer’s site),
- Adjustment of the underground storage design with respect to the deposition of metallic mercury: e g. preparation of storage chambers, acquisition and use of devices for monitoring the air concentration, training of staff, provision of specific protective equipment, reserve containers, acquisition/upgrading of transport vehicles with self-extinguishing equipment, measures for ventilation system,
- Underground storage occupational and operational safety: revision of emergency plans, gas protection plan,
- Procedure for the extension of the operating licence for storage of metallic mercury.

5.5.1.2 Running costs

- Manufacture and provision of transport and storage containers,
- Filling of transport and storage containers at the waste producer's site including the final inspection,
- Laboratory analyses of metallic mercury,
- Testing/monitoring activities of independent experts,
- Interim storage of loaded transport and storage containers,
- Additional expenditure at the underground storage operation due to additional safety requirements (modified transport concept, storage in campaigns, air monitoring, repeat training), disposal of reference samples.

5.6 Aspects of practical implementation

Overall, a volume of approximately 11 000 tonnes of mercury is expected in the EU over the next 40 years, which must be disposed of in accordance with the mercury ban regulation 1102/2008. Additional quantities may be pending disposal if there is no longer a market for mercury from the treatment of mercury waste due to lower demand within the EU (see section 2.1). The majority of the expected waste mercury, approximately 8 400 tonnes, will accrue between 2011 and 2020, thus averaging 840 tonnes per year.

If it is assumed as an example that a transport and storage container has a net weight of 1 tonne of metallic mercury and a gross weight of 2.6 tonnes, this corresponds to 840 transport and storage containers annually. An assumed amount of 20.8 tonnes per truck load (with 8 containers each) would give rise annually to 102 transports by road (significantly less in the event of the possibility of rail transport). The shaft transport is the capacity-limiting factor for internal underground storage transport. Assuming a capacity of 10 tonnes[42] and a permissible payload of 7.5 tonnes, two containers could be transported per trip. A maximum daily cycle of 50 rides, each with 2 containers, would require 8.4 days of a continuous stage to store the annual amount of 840 tonnes of mercury.

This is just a sample calculation. It is also conceivable to perform several campaigns per year, each with a smaller number of containers. In any case, the delivery should be such that direct transport to the storage chamber is possible without interim storage.

5.7 Options for legal implementation

The handling of liquid mercury in an underground landfill poses additional health and environmental risks which must be addressed by organisational and technical measures. First and foremost, situations must be avoided which can lead to an opening or damage to the transport and storage containers and thus to a release of mercury. Additional technical measures are necessary to prevent the release of mercury in the event of an accident also. The proposed measures require a legal definition. This applies to both national and European law.

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[42] Example from Zielitz (Dartsch and Schaub 2003). Herfa-Neurode has a cage capacity of 7 tonnes (Ganesh and Baumert, 2003).

5.7.1.1 Purity standards for metallic mercury

- A new section should be inserted in the Landfill Directive 1999/31/EC Annex II which would contain the purity requirement for metallic mercury that is to be stored permanently (more than 99.9% by weight), a similar addition would be required for Annex 3 of the German Landfill Ordinance for landfills of class IV.
- In the German Landfill Ordinance (DepV), a test method for the characterisation of metallic mercury should be defined[43], which would be applied in the conformity inspection and the advanced acceptance control.
- In the same place (EU Landfill Directive and German Landfill Ordinance), it should be specified that mercury should be free of aqueous, oily, or solid phases. This should be checked by visual inspections and application of a qualitative analysis of water.

5.7.1.2 Transport and storage containers and conformity inspection

- Requirements for transport and storage containers should be defined in Annex II of the Landfill Directive (similar to the new section 6 on storage in Annex II). The requirements should include corrosion resistance, choice of materials, labelling and filling level and accompanying documents, similar to the requirements for temporary storage in Directive 2011/97/EU or Directive 1999/31/EC (Annex II, section 6 B and C).
- However, requirements in terms of resistance to design basis accident conditions can also be recommended for the Landfill Directive: Only such containers should be allowed for permanent storage that as are able to prevent leakage or degassing or to keep it so low that there is no fear of an endangerment of occupational safety due to the released mercury, even when assuming occupational accidents (e.g. collision, crash, vehicle fire) with mechanical and temporary thermal load that cannot be excluded. The precise determination of design basis accidents (e.g. underground vehicle fire after impact, underground container crash during loading, transferring and unloading processes) can already be carried out in the EU Landfill Directive or left to the German Landfill Ordinance. The parameters (impact speed, fall height, fire duration, temperature curve (e.g. similar to the Konrad mine) could be defined within guidelines by the Working Group of the Federal States on Waste (LAGA). They must be determined by the facility operator in consultation with the approving authority in every individual case as part of the licensing procedure for a specific facility.
- The approval of the transport and storage container for public transport can occur according to regulations (ADR, etc.).
- Additional requirements for the transport and storage containers may arise from the operational features (e.g. cage dimensioning, individual facilities (e.g. dimensions, weight and labelling of containers). They are defined by the underground storage operators.
- It should be specified in the Landfill Ordinance (e.g. §6 or in a new annex) that the transport and storage containers may be filled solely with metallic mercury of the required purity. This should be documented by a previously conducted conformity inspection.

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[43] Already provided by new Annex 6 (as of: October 2012)

5.7.1.3 Advanced acceptance control

- The acceptance procedure should be described in Annex II of the Landfill Directive (similar to the new section 6 part C for temporary storage). The equivalent is located in §8 of the Landfill Ordinance (e.g. in a similar manner to the special handling of asbestos-containing waste). The regulation should explain that an acceptance inspection according to §8 subparagraph 4 clause 1 point 5 and regular checks according to §8 subparagraph 5 may be waived by the landfill operator if there has been a prior inspection of mercury as to identity and purity at the waste producer's site or at the place where the transport and storage containers were filled.
- The advanced control should be carried out in the presence of an independent and competent expert and include sampling, labelling of the containers and samples and the sealing of the waste containers. Permanent storage should only occur if the purity was confirmed by an accredited testing laboratory and the test report is enclosed with the delivery to the landfill.

5.7.1.4 Acceptance inspection in the underground storage

- The requirements for the acceptance inspection for the permanent storage of mercury in Annex II paragraph 6 C and the certificate in Annex II, section 6 C and D of the Landfill Directive (purity requirement, container inspection, engraved stamp, plaque) can also be transferred to permanent storage. The certificate should also include the test results of the testing laboratory on the purity of the mercury and the report of the independent expert on sampling and sealing.

5.7.1.5 Operational health and safety

Requirements for operational safety already arise from the application of the German Federal General Mining Ordinance (ABBergV) but, similar to the requirements for the long-term storage of mercury, they should be anchored in a new section in Annex III of the Landfill Directive. They should include the following points:

- Requirements for monitoring, inspection and emergency measures (according to the Landfill Directive Annex III, section 6 A). It should be specified that as long as filled mercury containers are handled at specific locations, measurements must be taken of the concentration of mercury in the air before, during and after completion of the work. Open storage sections should be visually inspected at least once a month and, if there is evidence that mercury has leaked, measures must be to taken to prevent further release and to clean contaminated areas (e.g. to anchor in Annex 5, 3.2 of the Landfill Ordinance (DepV) measurement and inspection programme).
- Existing emergency plans should be supplemented with regard to potential accidents with mercury releases and measures for the protection of employees should be prepared (e.g. in Annex 5 subparagraph 5 of the Landfill Ordinance (DepV)). Precautions should be taken so that, in the event of a mercury release, measures can be taken to limit the spread quickly and effectively and to collect leaked mercury again.
- Requirements for internal transport and fire protection. The Landfill Directive should specify in Annex 1 no. 5 (transposition in Annex 5, paragraph 5 of the Landfill Ordinance - DepV) that waste consisting of liquid mercury must be handled and stored in such a manner that no emissions emanate from it. At this point, reference could be made to measures which contribute to achieving this objective (e.g. use of special trans-

port and storage containers, measures to increase safety during internal transport (one-way system, maximum speed), self-extinguishing systems, specially prepared storage chambers, storage of mercury in stages with subsequent backfilling and walling up of storage sections).

- It should also be specified that fire loads should be minimised and potential ignition sources should be removed as far as possible from the vicinity of open storage sections. It should also be possible to prevent the spread of potentially arising conflagration gases by installing appropriate ventilation structures.

  Additional requirements arise from other legal instruments such as the Federal General Mining Ordinance and the Hazardous Substances Ordinance and the corresponding Technical Rules for Hazardous Substances (TRGS 900) as well as the Workplaces Ordinance. It is the task of the responsible supervisory authorities to monitor compliance with these regulations also with regard to handling metallic mercury and to order an improvement in occupational health and safety if necessary.

5.7.1.6 Requirements for the storage area

- It is recommended to specify that waste which consists of metallic mercury must be stored in a separate storage area. Mercury should be stored in campaigns. The storage sections should be backfilled and closed as quickly as possible after the end of a stage. The sections should be created in a way that liquid mercury cannot flow out from the storage chamber in the event of damage to containers.

6 Risks when dealing with stabilised mercury during the operational phase and measures to avoid them

6.1 Possible waste emplacement concepts

Mercury sulphide is already deposited in underground storages and stowage mines as solid waste according to valid legislation. As far as is known, the storage currently takes place in mainly dry conditions (in barrels or big bags). Two other storage techniques are also possible, which are used in underground landfills or backfilling mines: hydraulic backfilling and pump stowing.

6.2 Dry storage

Mercury sulphide can be accepted and stored as a powdery solid (DELA) or as a monolithic product (MAYASA) according to the existing approval situation in each container approved for the respective underground landfill.

When handling mercury sulphide, various accidents are conceivable that can lead to a release of mercury sulphide or elemental mercury, in particular:

- above-ground mechanical impact,
- underground mechanical impact,
- above-ground thermal impact,
- underground thermal impact.

If the waste containers are damaged above ground or underground, a leakage of powdery mercury sulphide can occur. As a heavy powder, however, it remains in the place where it leaks and can be picked up there by simple means (shovel, sheets). Donning of personal protective equipment (protective clothing, filter mask) is advisable to avoid inhaling dust. Additional risks do not emanate from mercury sulphide because it has no gaseous emissions. If the container was damaged slightly, monolithic stabilised mercury waste would not leak due to its high stability, unless the damage was so severe that the monolith itself was damaged and broken down. In this case, possibly released quantities of waste could be collected easily.

If a transport vehicle fire occurs underground, a thermal load of the waste packages cannot be excluded, regardless of the type of waste. Standard waste containers (barrels, bags, containers) would offer little protection in this case. The thickness of plastic bags (big bags) as well as barrels is so minor that a significant delay in heating up is unlikely to occur.

As was shown above, mercury sulphide partially decomposes to the elements at increased temperatures or is oxidised to mercury and sulphur dioxide by oxygen.

Heating and decomposition of a compact waste body will likely be slower than in a laboratory experiment with small amounts. Nevertheless, it can be assumed that a one-hour thermal impact at 800°C leads to extensive or complete destruction of the container and extensive decomposition of mercury sulphide. The mercury concentration which arises due to a thermal impact on a potentially mechanically damaged, open container depends on the fire duration, the temperature, the total amount of mercury, the influenced cavity volume and the type of damage to the container. The following example calculation may serve as a guide:

During a transport of 4 tonnes of mercury sulphide, and assuming an unimpeded air supply to the waste, an influenced cavity volume of 25 000 m^3 and a 60-minute heating up to 165°C, $1.4 \cdot 10^{-5}$%[44] of the mercury would be decomposed. This is equivalent to a mass of 571 mg and is sufficient to raise the concentration of mercury in the air to 0.023 mg/m^3. If the containers remain tight on the other hand, the mass of decomposed mercury is minimal and of no relevance because no mercury is released.

In the presence of atmospheric oxygen, mercury sulphide is oxidised from approximately 250-300 °C to sulphur dioxide and mercury (see section 3.3). The result of decomposition as well as an oxidation would be, similar to the behaviour of elemental mercury, extensive contamination of the mine.

Mercury sulphide is a special case in comparison to other types of waste, because it completely or, in the case of a mixed stabilised product (e.g. from MAYASA), largely consists of a thermally decomposable substance. Typical mercury wastes such as contaminated soil, sludge, gas cleaning residues, or rubble contain, contain mainly siliceous materials or other inorganic substances which are stable at 800°C. Much of the thermal energy is then consumed without consequence for heating of the inert components. Mercury compounds in wastes are equally subject to decomposition as pure mercury sulphide. How high mercury releases would be in individual cases depends very much on the waste and cannot be predicted without in-depth, experimental studies. The same applies to emissions from other wastes which contain substances that can decompose at fire temperatures.

If the discussed fire scenario is taken as a basis, the currently used waste containers (big bags, drums) are insufficient. It would be advisable to use a multiple-barrier system in which the actual waste containers are placed in thermally insulating outer packaging. It would be necessary to check whether a sufficient reduction in mercury releases could be achieved by cementing the mercury sulphide. For low level radioactive waste, cementing is considered sufficient to achieve less than the emergency plan values even with a design-basis fire (Morsleben final repository, ISTEC 2006). It would also be necessary to check whether the use of closed transport containers for internal transport, as they are, for example, used in the Zielitz underground storage, already provides sufficient thermal insulation.

Alternatively, the use of transport vehicles with self-extinguishing systems should be considered. These should be able to fight incipient fires automatically or at least cool the containers in the event of fire to such an extent that the mercury sulphide cannot decompose to any signifycant extent (<129°C), until the vehicle fire itself can be extinguished by emergency forces (also see section 5.3.6 Underground fire).

6.3 Hydraulic backfilling

In hydraulic backfilling, waste is mixed with concentrated saline solutions (so-called residual brines) and is flushed in specially prepared chambers where it precipitates. The supernatant solution is drained and is used for further backfilling in the cycle. This technique is used in

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[44] Own calculations based on the rate constant from Leckey and Nulf (1994)

backfilling mines, e.g. Bleicherode. Currently, nothing is known of an application with mercury sulphide.

The reaction of mercury sulphide with atmospheric oxygen in the sludge can cause the formation of elemental mercury, which dissolves in the brine on the one hand, and is emitted into the air on the other hand. If the concentrated brine that is used for flushing is used in the cycle, it may lead to the accumulation of mercury in the brine. It should be noted that mercury is sorbed on many surfaces, surface and can lead to a contamination of equipment. The actual concentration of mercury to be feared in the recirculated residual solution or in the gas compartment currently cannot be estimated.

6.4 Pump stowing

In pump stowing, waste is mixed with saline solutions and aggregates which are capable of setting (e.g. mortar) and is pumped into chambers where it solidifies. It should be noted that mercury sulphide is unstable in very alkaline systems, except under highly reducing conditions, and is easily oxidised to elemental mercury and hydrogen sulphide. There may then be a release of elemental mercury into the displaced mine air. The pump stowing concept is applied e.g. in the Sondershausen underground storage. Currently, nothing is known of an application with mercury sulphide.

6.5 Conclusion

Solid mercury sulphide is now already disposed of underground. Its handling involves only a few additional risks when compared to other types of solid waste. Since it has no significant vapour pressure under normal ambient conditions and is solid, only minor and spatially confined mercury releases can be expected even in the event of an accident with purely mechanical impact. However, additional risks occur in the event of a fire if the containers are damaged at the same time. A thermal decomposition of mercury sulphide is likely to occur as well as oxidation if there is an air inflow. Gaseous mercury is released in both cases.

For this reason, it is proposed to use double-walled transport and storage containers, as for metallic mercury also, which are able to prevent the release of mercury sulphide in the event of a thermal impact. Alternatively, the effect of prior solidification with cement or the use of self-extinguishing systems should be examined.

For pump stowing and hydraulic backfilling, it is currently not possible to estimate where and in which amounts mercury could be released. Basically, the wet backfilling is to be regarded as problematic since mercury sulphide is unstable during the mixing with saline solution, and a release of elemental mercury may occur. This potential source of risk can be avoided by dry emplacement.

7 Long-term behaviour of stored mercury after decommissioning and closure of the underground landfill

7.1 Scenarios for long-term development

7.1.1 Planned development - dry complete enclosure

According to the German Landfill Ordinance, proof of complete enclosure must be furnished prior to obtaining an operating licence for underground storages in salt. This means it must be shown that, based on geotechnical considerations, the deposited wastes are isolated from the biosphere permanently and without the need for after-care after the decommissioning of the underground landfill. Permanent enclosure is achieved when the geological and technical barriers permanently prevent the penetration of solutions from the overburden into the deposit area or a leakage of pollutants from the underground storage. If no solution comes in contact with the waste, a mobilisation of pollutants cannot occur via the solution phase. If the geological and technical barriers are leak-proof, they are usually also gas-tight. There are only a few exceptions to technical barriers that are designed in a way that they are initially permeable to gases and only become gas-tight and leak-proof by convergence of salt or (hypothetical) inflowing solutions (e.g. the “Self-healing salt backfilling”, Herbert et al. 2005). However, these are always used in combination with gas-tight barriers. For this reason, the propagation of pollutants via the gas path in the event of complete enclosure must also be excluded.

The waste which is brought into the underground landfill has itself the task of having a long-term stabilising effect on the stability of cavities (Annex 2, 2.1.4 clause 1 point 3 of the Landfill Ordinance). Exposed metallic mercury has no mechanical stability as a liquid, and thus does not develop any supporting effect and does not contribute to the stabilisation of cavities. Since the storage should always take place in rigid containers, an analysis of geomechanical stability should be conducted for the system containers/mercury/backfilling. The system can be referred to as a solid mixture with islands of fluids after backfilling has taken place. If the previously proposed transport and storage containers are used, the required long-term geomechanical stability can be ensured by the waste containers enclosed in backfilling. However, a separate proof is still needed for each selected container concept.

Another long-term process is the release of gas due to the corrosion of metallic container materials. A solution inflow to the deposited waste does not occur for planned development, thus corrosion occurs only to a very limited extent by consumption of atmospheric oxygen and any existing residual moisture. The gas release is negligible in this case.

7.1.2 Disturbed development - solution inflow from limited fluid deposits

When excavating cavities in salt rocks, limited solution deposits are occasionally found (“brine bags”), which have originated from the time of the salt formation and are not in contact with the overburden (Keller 2007). In the long-term development of a decommissioned and closed underground storage, it cannot be ruled out that previously undiscovered solution deposits can be activated by settling movements and can flow into several storage areas. The size of potentially existing solution deposits depends on location and formation. For the Gorleben scenario analysis, for example, several hypothetical brine bags were assumed, which were each the size of 100 m^3 (Buhmann et al. 2008a). As long as it does not simultaneously or subsequently lead to a combined failure of route and shaft caps, mercury can be mobilised, but it remains spatially confined to the storage area. Long-term safety then continues to be ensured.

The effect of the inflowing solution on the metallic container materials has to be seen differently. The materials are not stable with respect to saline solutions and corrode under hydrogen formation to metal oxides and metal hydroxides. However, this process does not depend on the contents of the container, and thus does not depend on the mercury either. In fact, much of the waste stored in underground landfills is packed in steel barrels or in steel boxes. With overall capacities of a few hundred thousand to millions of m^3 per underground storage site, the amounts of metals brought in by mercury containers (maximum 11 000 t Hg in 40 years) play a minor role. A significant additional risk does not arise due to the mercury containers.

7.1.3 Disturbed development – failure of technical barriers and solution inflow from the overburden

Experience of the past years on various occasions have shown that unscheduled event sequences may occur even after prior assumption of a safe operation and complete enclosure. For example, increased solution inflows have been observed since the late 1980s in the Asse II mine, a final repository for radioactive waste. , In the years before, the stability of the mine and its isolation against the overburden have been repeatedly confirmed (e.g. Dohnanyi 1972[45]). In the final repository for radioactive waste Morsleben (ERAM), which was still classified in 1997 as risk-free (BMU 1997), a partial collapse of chambers occurred in subsequent years, whereupon the Federal Office for Radiation Protection irrevocably renounced the storage in 2001 because "the continued storage of radioactive waste was untenable from a safety perspective" (BfS 2010a).

The host rock salt in the Asse mine and in Morsleben occurs in the form of so-called salt domes. Their overall geological situation is hardly comparable with existing underground storages, e.g. Herfa-Neurode. At this site the salt deposits are still present in their original, flat stratification (Baumert und Glienke 2003). Potash mining has always taken place at great depth and the potash seams are overlaid by mighty strata of rock salt over 100 m thick. The salt deposits of Asse (BfS 2010b) and of ERAM (BfS 2000), however, occur in steep or folded stratification. In the mining past of both sites, this has led to the fact that potash mining was performed extensively and sometimes up to the edge of the salt deposits. The remaining residual thickness of the salt rock amount to just a few metres and is not very stable under the influence of convergence and subsidence movements in the salt dome. This led to acute solution inflows in the Asse (GRS and Colenco 2006).

The case of the Stocamine underground storage must be discussed separately (Wittelsheim, France). The facility was built in part of an Alsatian potash mine and commissioned in 1999. However, Stocamine had to be closed a few years later (2002) as a result of a fire in a waste chamber (spontaneous combustion of waste), and was closed after months of fire fighting

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[45] "The penetration of water can be excluded with a probability bordering on certainty"; Klaus von Dohnanyi was Parliamentary Secretary of State in the Federal Ministry of Science in 1972.

(Caffet und Sauvalle 2010, COPIL 2011). The still active potash mine that was connected with the storage facility underground, had to shut down its operations at the same time. How the mine and wastes are to be dealt with has been examined ever since. In the course of a re-evaluation of the geological situation of Stocamine, it became clear that an inflow of groundwater in the facility cannot be prevented, contrary to previous assumptions. Even the installation of technical barriers was regarded as insufficient to prevent the leakage of hazardous substances from the underground storage area into the groundwater over time. Mercury wastes were identified as particularly critical. These wastes, which contain approximately 50 tonnes of mercury, would lead to a mercury concentration of up to 7 g/l in the saline solution after complete flooding of the mine according to the calculations of an expert committee. Contamination of the groundwater with mercury could not be ruled out. The expert committee thus recommended in July 2011 to retrieve at least the mercury wastes, and then to seal the underground storage and the potash mine (COPIL 2011, Nückles 2011).

This study does not attempt to assess the likelihood of similar events in German underground storages. The differences in the geological stratification conditions and in the overall geological situation give rise to the assumption that the risk of a solution inflow from the overburden is much smaller or even negligible for German underground storage sites. However, such an accident, if only hypothetical, is discussed in this project for the purpose of safety considerations.

7.2 Potential propagation mechanisms

7.2.1 Preliminary remark

After the end of the operational phase and complete enclosure of waste in the salt rock, the waste and thus also the mercury are isolated from the biosphere. They remain isolated over the long term if the complete isolation is maintained permanently. The geological evolution of an underground storage in the post-operational phase can theoretically let the initially complete enclosure become incomplete at an indefinite point in time. Such a case can occur, for example, by movement of the waste in the salt rock (subsidence) or if newly developing pathways occur in the area of technical and geological obstacles, which lead to contact of a solution with the waste.

So far, very few scientifically sound deliberations were conducted on the long-term behaviour of mercury after the end of the operational phase. In a Swedish study, for example, it was stated that salt rock was not suited to the permanent storage of mercury because it could subside due to the large density difference or could be extruded as a result of convergence (Statens Offentliga Utredningar 2008, in BiPRO, 2010). Since there is a lack of practical experience with the permanent storage of mercury, the assessment of conceivable processes in the post-operational phase is carried out on the basis of investigations on the final disposal of radioactive waste in salt mines.

7.2.2 Failure of geological and technical barriers and extrusion of fluids from an underground storage

After the complete enclosure the deposited waste in an underground storage is surrounded on all sides by salt rock and technical barriers. Even in this condition, the convergence of the salt rock and backfilling material continues until the pore space in the storage area is almost completely gone (Tix and Hirsekorn 1996). The convergence acts from all directions on the waste packages and stabilises them in the storage location. This is only the case if the salt rock surrounding the waste has the same mechanical properties. Powerful anhydrite strata can lead to uneven convergence, for example. This shows that the geological constraints can affect long-term safety. Extrusion cannot be assumed for an underground storage which was properly sealed and is developing in an undisturbed manner.

Extrusion of fluids is of concern only if the enclosure is not yet completed, for example because drifts and shafts are still open or technical barriers do not perform as intended. It is also possible if the geological barrier was damaged or incomplete from the outset or started to leak in the course of the operation. This can eventually cause solutions from the overburden to advance to the wastes and mobilize the pollutants from the waste. The convergence of existing cavities can then cause solutions from the storage areas to be pressed into drifts and shafts, and ultimately into the overburden. Such a scenario is thought to be possible for the Asse final repository. Solution inflows occurred here repeatedly during the original mining operation in the 1930s. Since the 1980s, a solution inflow has been observed, which turned out to be an overburden solution and cannot be prevented by technical measures. There is a concern that, in the course of further convergence of the salt body, solution can flow into the mine via the existing access, react with the waste and leave the mine again in contaminated form (GRS and Colenco 2006).

A similar development is also assumed for the long-term development of the French underground landfill Stocamine. There is already a slow inflow of solution today. It is expected that it will lead over the course of several hundred to 1 000 years, in combination with the convergence of the salt rock, to a complete flooding of the remaining cavities. If the routes are sealed, this process will be delayed by up to 10 000 years. Although it is assumed that the convergence will ultimately lead to a complete enclosure of waste, there is doubt as to when this enclosure will be completed. In the long term (some ten thousand years) and with progressive convergence, it is not excluded that the solution in the remaining cavities will be extruded from the mine by the surrounding rock pressure. The originally proposed closure method (introduction of salt grit) would lead to an increase in contaminated solution up to the groundwater level in a few centuries. If the pessimistic assumptions about the solubility of mercury apply, it would lead to an exceedance of the drinking water limit values in the affected groundwater within a radius of a few kilometres. This predicted development was deemed to be unacceptable. Other pollutants could also reach excessive levels, but more calculations would be required for this assessment. Several alternative action concepts were considered. A selective retrieval and recycling of mercury wastes were regarded as the best compromise between feasibility and safety. These should be followed by a closure of open drifts and a permanent monitoring of the shafts (COPIL 2011).

The projected developments in Asse and Stocamine cannot be transferred to the underground storage operation practised so far in Germany. The long-term safety case required in the Landfill Ordinance requires, inter alia, an assessment of events and processes if they can jeopardise the complete enclosure of waste and can cause pollutant mobilisation. These include:

- Leakages due to exploration drilling,
- Water penetration during the deposit and decommissioning phase,
  for example, via the shafts,

- Lye or gas inflow during the deposit and decommissioning phase,
- Failure of the shaft sealing.

The long-term safety case is possible only if it is proven that such events are unlikely to occur. Before decommissioning, it must also be proven that the planned final measures remove the deposited waste from the biosphere. A failure of the geological and technical barriers during the operational phase or after the decommissioning is excluded by the design of the plant. Facilities such as the Asse or Stocamine mines, in which water inflows obviously exist, could not have been approved as underground storages in Germany. It is unknown, however, whether the underground storages, which were licensed before the Landfill Ordinance or the Technical Instructions on Waste came into force, already fully provided a long-term safety case in accordance with the Landfill Ordinance. This would have to be checked by the licensing authorities and requested if necessary.

7.2.3 Extrusion of liquid mercury

It is questionable whether an extrusion of liquid mercury is possible. The mobility of mercury in porous media is much lower than that of aqueous solutions because mercury has a very high surface tension (Hg: 480 mN/m, saturated NaCl solution: 83 mN/m, Lide 1991). It does not wet most mineral surfaces. Mercury is thus not drawn by the capillary effect into porous mineral media as it is the case with water or aqueous solutions. It has to be forced into the pores by applying pressure. The measurement method of the mercury porosimetry is based on this principle.

Technical barriers that have become permeable with respect to aqueous solutions, contrary to their design, can still have a locking effect with respect to mercury even in the event of a pressure gradient. For example, a pressure of 20 MPa (typical order of magnitude for the rock pressure) is required in the case of rock salt to press mercury into pores of 0.1 µm (Elliger 2005). In the context of the present study, it was not possible to determine the pressures that would be required to make other types of barriers permeable for mercury.

Since the storage areas of underground landfills lie far below groundwater levels that are worth protecting, mercury would have to be pressed upwards against gravity to reach this groundwater. This is possible in principle, but mercury is always in “competition” with lighter fluids, which are also located in the underground storage: gases and possibly aqueous solutions. In a vertical, porous column (as represented by, for example, the sealing of a shaft), mercury can reach a usable groundwater level only if all lighter fluids were already completely displaced. Such a case is unlikely as compacted backfilling and filling materials still have a significant residual porosity. The currently favoured concept for sealing the shaft of an underground storage provides for the use of a several hundred metre high stable stone column with large porosity, which is closed at the upper end by a combination of sealing elements (Wilsnack et al. 2008).

7.2.4 Propagation of gaseous mercury

At temperatures of around 25°C, elemental mercury has a slight gas pressure (20.6 mg/m^3 Clever 1987). If a gas phase exists in the underground storage (enclosed mine air or newly formed gases (e.g. hydrogen from waste or the corrosion of containers), mercury can become saturated in this gas phase. This remains meaningless in terms of safety as long as the complete enclosure remains effective. If there is a failure of technical or geological barriers, a leakage of gases from the underground landfill is possible under certain circumstances, as was also discussed for the final repository (Reactor Safety Commission 2005).

A pollutant transport in the gas phase is being investigated internationally in connection with the final disposal of radioactive waste. The process is identified in Buhmann et al. (2008b) as a process with a probability of occurrence without any time limit and managed as FEP No. 3.2.09.01 (radionuclide transport in the gas phase). The various individual processes by which radionuclides (similar to other pollutants) can be transported in the gas phase are:

- Advection,
- Dispersion as a concomitant of the advective transport,
- Diffusion in the gas phase as a result of concentration differences,
- Convection caused by differences in density.

A detailed description of these individual processes takes place in (Wolf et al. 2012) under the corresponding FEP and is not the subject of the present study. A detailed treatment of the subject is also to be found in Rübel et al. (2004) and Rübel and Mönig (2008).

It can be assumed that transported gas comes into contact with solutions along its flow path. Mercury is thus leached out of the gas phase and its concentration decreases. Overall, the maximum amount of mercury which can be discharged via the gas phase is very limited. It depends on the volume of gas present in the affected parts of the underground storage at the time of the leakage. With a sample gas volume of 100 000m^3, a maximum of 2 kg of mercury may be in the gas phase. This is an extremely small fraction of the stored mercury. The process is thus considered negligible.

7.2.5 Propagation of dissolved mercury

The chemical behaviour of elemental mercury and mercury compounds after complete enclosure or even after a hypothetical solution inflow was previously discussed in a separate section (section 3). Basically, only reactions between mercury (and mercury compounds) with the salt rock and remaining mine air are conceivable in the planned development of underground mercury deposition. As was shown earlier, reactions with the salt rock are of no concern. Reactions with the mine air lead to the formation of mercury oxide. As long as the barriers are intact, these reactions are of no concern for long-term safety.

If solutions come into contact with mercury, a partial dissolution and mobilisation can be expected according to the reactions described in section 4. The solubility of elemental mercury (as well as mercury sulphide) is low (< 1mg/l), thus retention processes along the transport route and dilution effects should lead to a decrease in mercury concentrations in the aqueous phase to below the applicable standard values (e.g. German Drinking Water Ordinance (TrinkwV) 0.001mg/l). A detailed evaluation of these processes and of the expected concentrations along a propagation path can be conducted only in the course of a site-specific safety analysis.

7.2.6 Subsidence and ascension of elemental mercury in the salt rock

According to Buhmann et al. (2008b) the movement of waste containers due to gravity is possible as a so-called “solid-bound" pollutant transport mechanism. Solid-bound transport in this context refers to transport without the involvement of fluids. Basically, two transport mechanisms are conceivable for the host rock salt:

- Ascension of waste containers while the salt is uplifted (diapirism),
- Subsidence of waste containers because of differences in specific gravity between salt and waste containers.

The discussion regarding liquid mercury represents a special case because liquid mercury is to be understood as a “solid” in the sense of the stated definition.

The extent of the uplift of salt depends very much on the site. While salt deposits in flat stratify-cation indicate virtually show no uplift, this can be more noticeable with active salt domes. For example, an uplift of 70 m within a million years is assumed for Gorleben (Wolf et al. 2012), which is not relevant in terms of long-term safety (forecast period of 1 million years).

With regard to subsidence, the current state of knowledge was compiled by Wolf et al. (2012). For the storage of radioactive waste (corresponding with the underground storage of mercury), subsidence of waste packages due to their greater specific gravity with respect to the surrounding rock salt and its fluidity cannot be ruled out. The differences in density are as follows (rounded values):

- Salt rock: 2.2 g/cm^{3}^{3};
- Mercury: 13.6 g/cm^{3}^{3};
- Uranium dioxide (e.g. cf.): 10.96 g/cm^{3}.^{3}

Elemental mercury has a slightly higher density than the uranium dioxide contained in fuel rods. Due to the ductility of the salt rock and the fact that it has no yield point[46], it must be assumed according to Wolf et al. (2012) that the heavier tank with uranium dioxide will subside into the relatively lighter salt rock. The process is of importance insofar as the distance to the lower border of the salt barrier decreases with the subsidence of the waste packages (distance in Gorleben at the start: 2 000m). The remaining salt barrier would be insufficient in extreme cases. The speed of the subsiding waste is crucial for the safety assessment. It depends very much on the effective viscosity of the salt rocks under the location-specific pressure and temperature conditions. Other influencing factors are the shape of the tank and the humidity of the salt.

For the American WIPP site[47], Dawson and Tillerson (1978) assumed a viscosity (μμ) of $0.5\cdot10^{14}$ Pa·s, which was identified as “extremely low”. The density of the tank was assumed to be 4.1 t/m^{3}. In a test calculation, the tanks were assumed to not generate any heat. In this case, a subsidence of around 19.2 to 24 m resulted within 1000 years. In the case of heat generation,

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[46] This is the lower load limit as of which the flow velocity suddenly increases sharply.

[47] Waste Isolation Pilot Plant near Carlsbad, New Mexico, a final repository for radioactive transuranium element waste.

a counter boost of heated salt rock occurs, which large compensates for the density-driven subsidence.

A study by Chemia et al. (2009) investigated the behaviour of anhydrite clods and blocks enclosed in Gorleben salt dome. As a result of numerical modelling, it was established that a subsidence of a dense embedding in a (Newtonian, inactive)) salt dome takes place inevitably (i. e. without heat input) and even the low specific gravity difference between the studied anhydrite embeddings and the surrounding rock salt (2.8-3.0 vs. 2.2 g/cm$^{3\,3}$) is sufficient to initiate the downward movement of an anhydrite block in the salt dome. No particularly heavy waste like mercury or uranium dioxide is thus required. The subsidence velocity depends on the effective viscosity of the rock salt. At viscosities around 10^{19} to 10^{20} Pa·s, the deformations due to density-driven movements are not significant. That is consistent with the geological analysis of the Gorleben salt dome. The anhydrite clods have been in the same place for some 20 million years or the deformation was so slow that they are still at a relatively low depth (see Keller 2007). The authors concluded that viscosities of less than about 10^{18} to 10^{19} Pa·s would need to occur for the mobilisation of anhydrite block.

In a further sample calculation for the Gorleben site, Wolf et al. (2012) showed that the order of magnitude of possible subsidence velocities under the force of gravity and frictional force of viscous salt can be estimated using Stokes' law. Assuming the solid dimensions and density roughly in accordance with a Pollux container with 1.6 m or 6.5 t/m^3, the waste package would subside nearly two metres in a million years at a viscosity of salt of 10^{17} Pa·s. It was concluded that the subsidence of the waste packages in the host rock is relevant during the thermal period (during the final disposal of heat-generating waste until the heat generation abates), but is less important later.

The extent to which these findings also apply to liquid mercury could be estimated by model calculations. It should be noted that the waste containers are not likely to withstand the increasing rock pressure, and liquid mercury can leak. Between the surrounding potash or rock salt and the mercury, a density difference of 10 g/cm^3 and more occurs (mercury vs. rock salt: 13.6: 2.2 g/cm^3), which is twice as large as for radioactive waste packages. If local cracks and pores arose during the convergence, these could be filled by mercury. The average density in the deposit area would decrease as a result and thus the subsidence speed.

As a result of the studies, it can be assumed that the subsidence of waste within a period of a million years has no relevance for the long-term safety of an underground landfill, at least if the effective viscosity is consistent with the values found in Gorleben or exceeds them. It is indeed possible that elemental mercury subsides faster than the radioactive waste packages considered in the model calculations because the specific gravity difference is linear in the fall rate of the underlying Stokes' equation for the stationary fall rate. Even if the speed was ten times higher than a Pollux container, only 20 m would be achieved in a million years, thus a large distance to the lower strata limit of the salt rock would still be preserved.

Even in the highly unlikely or only in the very distant future (>> 10 million years) case of a subsidence to the lower border of the salt rock strata, this would not necessarily result in a

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48 For an "active" salt dome, the ongoing upward movement of salt can compensate for a fall of the waste tank or even exceed it.

failure of the entire system. In reality, it depends on the overall geological situation at a site whether failure of the horizontal salt barrier of an underground landfill involves safety-relevant effects on the overall system.

In fact, all German underground storage sites have additional geological strata, which also act as a geological barrier. The extent to which these would prevent the propagation of pollutants after a fall of waste has not been included in previous safety cases because the Landfill Ordinance concentrates on the barrier effect of the salt rock. It is outside the capabilities of this study to evaluate the performance of German underground storage sites in the hypothetical case of a subsidence of liquid mercury. At this point, only a few basic considerations are mentioned.

- The subsidence of wastes in the salt rock is very slow. The barrier effect of salt is thus superior to other geological formations that are in constant contact with solutions.
- The very low solubility of elemental mercury in saline solutions (<0.03 mg/l) indicates no immediate potential hazards for near-surface aquifers, even if a container subsides in the vicinity of an aquiferous underlying geological formation (e.g. sandstone). All underground storage sites have salt deposits with a significant horizontal extension. Possible pathways from the base of a salt deposit up to near-surface groundwater aquifers are so long that a significant transport duration result, and any pollutant (mercury) concentrations along this path are substantially lowered by dilution, diffusion, dispersion, and possibly sorption as well.
- If the deposited mercury contains contaminants from more soluble compounds to a limited degree, higher mercury concentrations could occur initially. Significant dilution and possibly further retention processes can be expected here also.
- The considerations apply similarly to mercury sulphide (density 8.1 g/cm^3).

In addition to the above observations, it must be noted that investigations of processes relating to the final disposal of radioactive waste are limited in many cases to a defined period of time in which the radioactivity of waste has largely ceased due to natural decay processes. The criteria for the safety case thus require the safety assessment to cover a period of a million years (BMU 2010). However, the long-term assessment for underground storages according to the Landfill Ordinance (and formerly in the Technical Instructions on Waste) is not bound to a specific forecast period, but is conducted via proof of the complete and permanent isolation of the wastes from the biosphere. The geotechnical safety case is provided if it can be shown that the waste is enclosed by the salt rock after the end of the operational phase. The Landfill Ordinance does not consider the case that the waste could leave the salt rock, even if this would be in the very distant future. The safety case would then no longer be met. It would thus be advisable to set a forecast period similar to the safety criteria for final repositories so that processes which occur later no longer have to be taken into account.

7.2.7 Conclusion

Rock salt in an undisturbed state is regarded as impermeable to liquids and gases (Popp et al., 2010). A potential hazard emanating from liquid mercury in an underground storage exists primarily in its spatial and temporal connection with mining activities. A potential pollutant propagation (both via the gas phase and the liquid phase) is thus mainly limited to the excavation damaged zone and a limited period of time after closure of the underground storage, as long as the inner structure of the salt deposit has no safety-related inhomogeneities or other disturbances and its consequences can be analysed. A gradual healing of any pathways can be expected in the post-operational phase (Pamnani et al., 2010). A safety-relevant increase of gas pressure is not to be expected in a deposit chamber for elemental mercury – in contrast to radioactive waste disposal under certain conditions. However, limited gas production could result from corrosion of the containers under certain constraints (presence of moisture). For a final, facility-related assessment, site-specific concepts and data, as well as a scenario analysis have to be used. Since outer container corrosion and a related potential hazard are not specific to mercury, this process will not be examined in more detail in the course of the present study. For more information on this subject, see Buhmann et al. (2008b) or Brasser et al. (2008).

8 Summary

A volume of approximately 11 000 tonnes of metallic, thus elemental mercury is expected in the EU over the next 40 years, which must be disposed of as waste in accordance with the regulations of the EU mercury export ban. According to the current regulatory and licensing situation disposal may take place only in underground storages in salt mines. The present study investigated the risks for operational and long-term safety of underground storages that result from the specific properties of metallic mercury. On this basis, measures were derived, which may help to reduce the risks to an acceptable level. A similar analysis was undertaken for mercury sulphide, which results from most procedures for the stabilisation of metallic mercury.

8.1.1.1 Measures to reduce risks caused by metallic mercury during the operational phase of an underground storage -

Metallic mercury is a liquid and has a partial pressure of approximately $2.5 \cdot 10^{-3}$ hPa at room temperature. This is equivalent to 20.6 mg/m^3 which exceeds the occupational exposure limit of 0.02 mg/m^3 by a factor of 100. A release of liquid or gaseous mercury is unlikely to occur during failure-free handling above ground and underground when using leak-proof containers. It is to be expected that there will be neither an endangerment of occupational safety nor of the environment (air, water, soil) during normal operation.

There is a risk that liquid or gaseous mercury will be released during unforeseeable events such as leakages or accidents with mechanical or thermal load on the waste or of a waste package. If mercury leaks, it can form very small droplets, which can penetrate into the finest cracks and form a permanent source of contamination. A leakage of metallic mercury should be avoided underground because a contamination is difficult to remove and can be the cause of a sustained exceedance of workplace concentration.

Safety measures should be aimed at minimising the risk of such events and their impact. These include

- Metallic mercury to be disposed of should comply with specific purity criteria (minimum 99.9% by weight). The testing for purity and consistency with the accompanying documents should be conducted in the course of an advanced acceptance control at the waste producer’s site in the presence of an independent expert. Hereby an opening of the containers and open handling of mercury could be avoided at the underground storage site.
- To increase safety for internal transport and loading processes, the transport and storage containers should be designed to be accident-proof (multi-barrier concept). The containers should ensure that there is no fear of a release of mercury, even in the case of underground mechanical and thermal loads which cannot technically be excluded. Such events include a load drop during loading processes, collision during a transport accident or the fire of a transport vehicle. One possible technical implementation of an accident proof container could be achieved by the combination of an inner container (e.g. 1 tonne pressure container with an outer container (e.g. steel box), which are separated from each other by a mechanically stable thermal insulation layer (e.g. concrete). An additional approach to prevent a thermal impact would be the use of self-extinguishing systems on the transport vehicles.

- Storage areas for liquid mercury should be located separately from other storage areas. They should be specially prepared, e.g. have a lower floor level than the access drift.
- The emplacement of containers in the underground storage should take place in campaigns in order to avoid the simultaneous handling of mercury containers and other types of waste. The storage sections should be backfilled and walled off immediately afterwards. As long as the storage sections are open, the concentration of mercury in the air should be regularly measured and the containers should be visually inspected.

The proposed measures are summarised in Tab. 17. They are based on a conservative, quailtative and location-independent assessment of the risk of accidents involving potential release. Quantitative statements about the propagation of mercury through the air and water path in the event of accidents were not possible in the course of this project. Extensive calculations based on site-specific data would be necessary for this purpose.

8.1.1.2 Measures to reduce risks caused by metallic mercury sulphide during the operational phase of an underground storage

Compared to metallic mercury, mercury sulphide is much easier to handle. It is solid and does not exhibit any relevant mercury vapour pressure. Although mercury sulphide can leak during accidents with mechanical load, it remains in place as a solid and can be collected easily. For the same reason, emergency retrieval of waste, as is currently being prepared in Stocamine and Asse II mine, is more feasible for solid mercury sulphide than for liquid metallic mercury. The requirements recommended for permanent storage of mercury sulphide are summarised in Tab. 17. Compared to metallic mercury, fewer additional measures are required. Even though the permanent storage of mercury sulphide is already practised, efforts should be undertaken for reasons of operational safety to prevent a release of mercury in the hypothetical event of a fire.

Mercury sulphide is thermally decomposed at fire temperatures and can be oxidised by atmospheric oxygen at approximately 250-300°C to gaseous mercury and sulphur dioxide. The potential risk due to thermal effects is thus also comparable for mercury and mercury sulphide. Measures must thus be taken to avoid a heating of mercury sulphide to over 129°C or to prevent the release of mercury even in the event of a fire. This can be done by using accident-proof containers. The use of self-extinguishing systems is an option.

Additional requirements for the mechanical strength of containers, preliminary acceptance inspection and the design of the storage areas (apart from a spatial separation from other landfill areas) are not required.

8.1.1.3 Relevance of the deposition of metallic mercury or mercury sulphide on the long-term safety of a underground storage

In the event of complete enclosure of waste, releases into the biosphere by solution or gas-bound transport are not likely because the enclosing salt rock is impermeable to liquids and gases. Although, there can be an asymmetrical force acting on the deposited waste in the course of the convergence. This does not result in its displacement, but to its deformation at most. The process of “extruding” liquid mercury, sometimes referred to in the literature, is of no concern as long as the barriers are intact as intended.

Tab. 17: Recommended additional requirements for the permanent storage of metallic mercury and mercury sulphide

Process / Event	Recommended requirement for the permanent storage of metallic mercury	Recommended requirement for the permanent storage of mercury sulphide
Certification / Labelling	Permanent labelling of inner and outer containers, certificate of producers, amount, and test results similar to Directive 2011/97EU, additional test result of the independent expert.	Permanent labelling of inner and outer containners, certificate of producers, amount, and test results similar to Directive 2011/97EU.
Acceptance control	Advanced acceptance control (purity, identity) by an independent expert and an accredited testing laboratory. No open handling of mercury in the underground storage.	-
Container corrosion	Minimum purity of mercury 99.9% by weight, absence of aqueous, oily, or solid phases. Containers should be corrosion-proof with respect to storage conditions.	-
Underground mechanical impact	Use of containers from which no mercury leaks during mechanical impacts (impact, crash) which cannot technically be excluded. For multi-walled containers: increase in geomechanical stability due to pressure-resistant elements, e.g. concrete.	For multi-walled containers: avoidance of cavities to increase geomechanical stability.
Thermal impact	Use of containers from which no mercury leaks during mechanical and subsequent thermal impacts (vehicle fire) which cannot technically be excluded. Example: multiple-walled containners with thermal insulation.	Use of containers from which no mercury leaks during mechanical and subsequent thermal impacts which cannot technically be excluded. Example: multiple-walled containers with thermal insulation.
Storage area	Facility separate from storage areas for other types of waste Storage in stages Immediate backfilling and closure Lower floor level.	Facility separate from storage areas for other types of waste Storage in stages Immediate backfilling and closure.
Occupational safety	Multiple daily concentration measurement in open storage sections in which work is being done Visual inspection of open storage sections at least once a month Providing personal protective equipment.	Providing personal protective equipment.
Fire protection	Minimising fire loads and ignition sources in the storage area. Avoiding oncoming traffic and overtaking on transport routes. Setting a maximum speed and avoiding above-ground and underground interim storage Storage area can be separated from the remaining mine operation by ventilation structures.	Minimising fire loads and ignition sources in the storage area. Avoiding oncoming traffic and overtaking on transport routes. Setting a maximum speed. Storage area can be separated from the remaining mine operation by ventilation structures.
Emergency planning	Preparation of plans and measures for the event that a release of mercury has occurred (e.g. leakage or fire).	Preparation of plans and measures for the event that a release of mercury has occurred (e.g. fire).
Emergency planning	Preparation of plans and measures for the event that a release of mercury has occurred (e.g. leakage or fire).	Preparation of plans and measures for the event that a release of mercury has occurred (e.g. fire).

The subsidence of waste in the salt rock is a process which is not exactly quantifiable. It is caused by the fact that the deposited waste has a higher density than the free-flowing salt rock. Due to new research and modelling, it is assumed that non-heat-generating waste subsides extremely slowly, only a few metres even after a million years. A leakage from the salt formation is thus not likely even in geological periods.

Metallic mercury and mercury sulphide do not react with salt rock under deposit conditions, thus an impairment of the effectiveness of the geological barrier is of no concern. Thus it must be concluded that neither elemental mercury nor mercury sulphide exhibit properties that threaten the long-term safety of an underground landfill. No mercury-specific risks are likely after closure of the underground landfill.

8.1.1.4 Long-term chemical behaviour of mercury, mercury compounds and mercury waste in the event of a hypothetical solution inflow from the overburden

If, after the operational phase and closure of the underground landfill, but prior to the completion of the convergence, a (hypothetical) failure of the technical barriers occurs, contact between solutions and waste cannot be excluded in the event of a solution inflow.

Elemental mercury and mercury sulphide are only slightly soluble in saline solutions. The experimentally observed solution concentrations are mostly under and otherwise just over 1-3 mg/l in the long term. This is in the range of solution concentrations which have also been found in experiments with mercury wastes. On the basis of the information in the literature, it is assumed that the solubility of pure metallic mercury is significantly lower. The slightly higher solution concentrations observed in the experiment of this study are caused by more easily soluble minor constituents and not fully eliminated traces of oxygen. Thus, only a minor mobilization of mercury can be expected even with a hypothetical solution inflow. If more soluble contaminants, such as mercury oxide or mercury(II) chloride, are present or can be formed by oxidation with existing oxidising agents or atmospheric oxygen, these are likely to dissolve almost completely. The aim should be to deposit mercury, either in elemental form or stabilised as mercury sulphide, in as pure a form as possible. Low levels of oxygen in the enclosed mine air cannot be prevented. If necessary, one could consider adding simple reducing agents such as pyrite or Fe(II) compounds to supply a redox buffer, which can lead to a rapid degradation of oxygen after the end of the operational phase. While oxidation reactions involving oxygen can affect both elemental mercury and mercury sulphide, corrosion of mercury by saline solutions or salt rock is of no concern.

From a geochemical perspective, both elemental mercury and mercury sulphide are suitable for deposition in salt mines. In the hypothetical event of a solution inflow, the low solubility of elemental mercury and mercury sulphide acts as an internal barrier.

8.1.1.5 Long-term behaviour of mercury sulphide and mercury compounds in an above-ground landfill

Mercury sulphide is currently not classified as hazardous waste and may be deposited in above-ground landfills in many countries. It is expected that its surface sealing will be permeable to air in the long term. Mercury sulphide can then come into contact with atmospheric oxygen and become oxidised to elemental mercury and sulphate. The formation of methylmercury may occur under suitable geochemical conditions.

Both reaction processes are slow, but a landfill with mercury sulphide would inevitably become a local source of mercury emissions. Both elemental mercury as well as methylmercury can leave the landfill via the gas circuit (landfill gas). For this reason, the deposit of mercury sulphide as well as of other strong mercury waste should be prohibited in above-ground landfills.

8.1.1.6 Conclusion

The permanent storage of metallic mercury in underground storage in salt mines is regarded as technically feasible and acceptable from a safety perspective. With regard to operational safety, specific health and operational risks must be taken into account and counteracted by organisational and technical measures due to the characteristics of metallic mercury. These consist, inter alia, of requirements for the purity of mercury, a bringing forward of the substance-based acceptance control, the use of accident-proof containers for internal transport and the establishment of separate storage areas.

Liquid mercury no longer poses a specific risk after the closure of an underground storage. The geological processes which have a long-term effect, such as hypothetical hydrogeological incidents, do not have a waste-specific effect. No special features that specifically threaten the long-term safety of the facility could be identified for mercury either. Additional requirements for the long-term safety case are not required.

An alternative concept is the prior stabilisation and solidification of metallic mercury and the subsequent permanent storage in underground landfills. It is also considered feasible and safe to perform. Stabilised mercury has the advantage over metallic mercury in that it is solid and has no significant vapour pressure. Thus fewer additional safety measures and changes to the present operating mode are required. Even if the underground disposal of mercury sulphide is already practised, additional precautionary measures are recommended in order to take into account the thermal instability of mercury sulphide in the event of a fire. Accident-proof containners are recommended for internal transport, as for metallic mercury.

9 References

Remark: all internet links were checked on 24.10.2012 if not stated otherwise.

9.1.1.1 Literature sources

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9.1.1.2 Legal sources

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Annex: Additional experimental data

Experiments with mercury oxide

Tab. 18: Experiments with HgO: initial compositions

Solution	Batch	Solution volume [ml]	Weighted mass of HgO [g]
NaCl	1	45	3,001
	2	45	3,000
	3	45	3,000
Synth. IP21	1	45	2,999
	2	45	3,001
	3	45	3,001
Synth. IP9	1	45	3,000
	2	45	3,001
	3	45	3,000
$MgCl_2$-mixing solution	1	22,5	1,50224
	2	45	3,07783
	3	45	3,02495

Tab. 19: Experiments mit HgO: final solution concentrations

Solution	Batch	Duration of experiment [months]	Density [g/l]	Hg [mg/l]	Na [mg/l]	K [mg/l]	Mg [mg/l]	Cl [mg/l]	SO$_4$ [mg/l]
NaCl	1	6,5	1,200589	1 897	117 900	<BG	<BG	178 500	26,08
	2	6,5	1,197998	1 756	117 200	<BG	<BG	180 100	20,79
	3	6,5	1,200855	1 870	117 800	<BG	<BG	181 500	4,99
Synth. IP21	1	6,5	1,338641	64 030	5 397	76 830	14 100	228 700	24 592
	2	6,5	1,33886	60 944	5 372	75 260	14 260	227 400	23 865
	3	6,5	1,339172	61 992	5 473	76 970	14 380	231 000	25 480
Synth. IP9	1	6,5	1,290883	62 298	57 000	13 500	29 890	151 700	33 650
	2	6,5	1,289731	60 794	58 580	14 440	32 120	158 800	30 260
	3	6,5	1,290843	62 576	61 410	15 020	33 320	167 700	31 430
MgCl$_2$-„Anmachlösung“	1	6,5	)[1]	62 740	< BG	97 070	200	280 000	18 030
	2	6,5	1,352205	64 000	1 168	95 260	708	284 600	17 020
	3	6,5	1,352011	63 868	1 204	96 970	717	281 300	17 440

)[1] No measurement, because sample was depleted

Experiments with mercury sulphide

Tab. 20: Experiments with HgS(black): initial composition

Solution	Batch	Solution volume [ml]	Weighted mass of HgS (black) [g]
NaCl	1	7	10,0040
	2	7	10,0069
	3	7	10,0085
Synth. IP21	1	7	10,0046
	2	7	10,0050
	3	7	10,0068
	reference experiment	17,5	10,0125
Synth. IP9	1	7	10,0082
	2	7	10,0112
	3	7	10,0115
$MgCl_2$-„Anmnachlösung“	1	5	10,00035
	2	5	10,00027
	3	4,5	10,00065
IP21 (Asse-CLV)	1	1	0,01359640
	2	1	0,01283416
	3	1	0,01469287

Tab. 21: Experiments with HgS(red): initial composition

Solution	Batch	Solution volume [ml]	Weighted mass of HgS (red) [g]
NaCl	1	7	10,0115
	2	7	10,0304
	3	7	9,9838
Synth. IP21	1	7	9,8882
	2	7	9,9544
	3	4	9,9874
Synth. IP9	1	7	10,0172
	2	7	10,008
	3	7	9,9949
$MgCl_2$-mixing solution	1	3,5	4,00026
	2	4	4,00064
	3	4	4,00072
IP21 (Asse-CLV)	1	5	2,09680