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

Summary

by

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Need for permanent safe disposal of mercury

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.

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 exceeding 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. 1.. They are based on a conservative, qualitative 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.

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. 1. 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.

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

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.

Tab. 1: 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 containers, 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 containers 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).

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.

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.

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 containers are recommended for internal transport, as for metallic mercury.