

European Commission, Brussels



Extended summary on pre-treatment technologies for metallic mercury

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1 Legal background

The legal basis for pre-treatment technologies for metallic mercury is Regulation 1102/2008. It lays down that metallic mercury resulting from specific sources (e.g. chlor-alkali-plants) has to be considered as waste from 15 March 2011. In combination with the export ban of metallic mercury from 15 March 2011 a safe storage for considerable amounts of surplus mercury has to be ensured within the Community to prevent the metallic mercury from re-entering the market.

Disposal of elemental mercury presents due to its liquid phase and high vapour pressure several emission risks. To reduce these risks, solidification of elemental mercury shall be considered as a possible alternative. Article 8 (2) of the Regulation foresees that the Commission shall keep under review ongoing research activities on safe disposal options, including solidification of metallic mercury. The Commission shall submit a report to the European Parliament and the Council by 1 January 2010. On the basis of this report, the Commission shall, if appropriate, present a proposal for a revision of this Regulation as soon as possible and not later than 15 March 2013.

In section (18) this researches to solidify metallic mercury is described to involve “techniques for stabilisation or other ways of immobilising mercury.”

Decision 2000/532/EC defines stabilisation and solidification in the following way: ‘Stabilisation processes change the dangerousness of the constituents in the waste and thus transform hazardous waste into non-hazardous waste. Solidification processes only change the physical state of the waste by using additives, (e.g. liquid into solid) without changing the chemical properties of the waste’.

Against this background all literature and practical approaches concerning stabilisation, solidification and encapsulation of elemental mercury have been investigated and conclusions as well as recommendations have been elaborated.

2 Technology overview

The identified existing technologies for the pre-treatment of metallic mercury can be differentiated in 6 major groups (Figure 2-1).

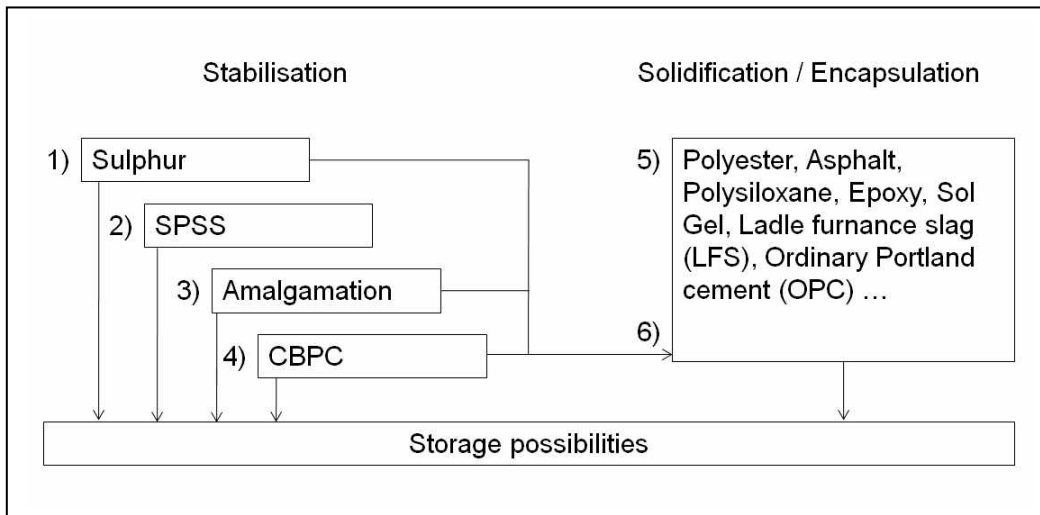


Figure 2-1: Overview on stabilization, solidification and encapsulation techniques for elemental mercury

2.1 Sulphur stabilisation

In case of sulphur stabilization elemental mercury and elemental sulphur are mixed together, to form mercury (II) sulphide.



This technique can be realized by simply mixing the compounds with a slight stoichiometric excess of sulphur, resulting in a powdery product. The weight increase of the resulting product compared to elemental mercury can be as low as 16 % and the volume increase is about 400 %.

The advantage of this technique is the simple, low energy consuming process that can be easily installed once the parameters have been adjusted. Another advantage is the high mercury concentration (86 wt %) and high stability of the resulting product. By proper application of this technology the vapour pressure of the final product is not detectable and the product shows the lowest solubility in water compared to the products of other stabilisation techniques, including elemental mercury.

To avoid the formation of unwanted by-products such as HgO the process should be performed at low pressure or in an inert atmosphere (e.g. N₂).

The resulting mercury sulphide products are stable until a pH value of about 11. This has to be considered for the final disposal according to the landfill directive 1999/31/EC and the WAC Decision 2003/33/EC.

Concerning the long term behaviour of HgS, little is known.

It shall be highlighted that in case of above ground disposal any kind of waste has to fulfil long term requirements as requested in the WAC Decision and the Landfill Directive and in case of landfilling in an underground storage site specific risk assessment have to be made to guarantee a safe long term disposal.

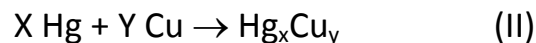
2.2 Sulphur Polymer Stabilisation/Solidification SPSS

This technique is similar to the sulphur stabilization as mentioned before, but uses some modified input materials. Instead of elemental sulphur a mixture of elemental sulphur (95 wt %) and sulphur polymer cement (SPC) (5 wt %) is used. The elemental mercury and the sulphur compounds are mixed in a two step process and heated to an elevated temperature (~ 135 °C) at which the reaction product is liquid. The liquid is cast from the vessel into a mould and the product is set to harden. The shape of the product can be chosen arbitrary, only defined by cooling behaviour limitations.

The final product has a low ratio of surface to volume, which is advantageous for the leaching behaviour and includes about 33 wt% of mercury. The behaviour of the final product from the SPSS product concerning vapour pressure and leaching is comparable with the stabilised products from the sulphur stabilisation.

2.3 Amalgamation

For this technique elemental mercury and fine powder of elemental metals are mixed together. The metals which can be used are in particular zinc, nickel, tin or copper, with copper being the most recommended metal. The ratio of mercury to metal can be as low as 1:1 but is often suggested to be 1:3 which means that the weight increase of the resulting product is about 400%.



The elemental mercury bonds to the corresponding metal forming an alloy, the so called amalgam. The amalgams have comparatively poor leaching behaviour and high vapour pressure. To achieve better leaching values and lower vapour pressures a subsequent treatment (encapsulation) has to be applied.

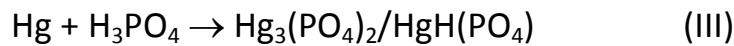
Apart from the poor performance of the amalgam concerning stabilization, the huge input of elemental metals leads to high costs of this process and the subsequent disposal.

A subgroup of the amalgamation process is the use of selenium, which is a semi-metal. The reaction with elemental mercury takes place in the vapour phase at a temperature above 580 °C (above boiling point of elemental mercury). The resulting product has good leaching behaviour but the input of the expensive selenium (~ 35.000 €/t) is five times the input of elemental mercury resulting in very high costs for this process. This technology is therefore more promising to be used for mercury contaminated wastes instead of elemental mercury.

2.4 Chemical bonded phosphate ceramic CBPC

This stabilization process consists of two reactions, including a chemical bondage of the elemental mercury as well as a microencapsulation within a matrix. Both reactions take place at the same time.

In one reaction the elemental mercury is bond to the phosphate as provided in equation (III)



In a second reaction the ceramic matrix is builds up, within which the mercury compounds are microencapsulated in.



For the use of this technique for elemental mercury it is recommended to add Na₂S or K₂S to the reaction. Therefore the process becomes comparable to a sulphurisation technique, followed by an encapsulation technique. Even so the mercury phosphate products have relatively low water solubility, the leaching values of the resulting product is quite high and therefore an uncompleted reaction and/or impurities can be expected.

The technique is well established for mercury containing waste but promising data even on a laboratory scale for treating elemental mercury are missing.

2.5 Encapsulation techniques without pre-stabilisation

Encapsulation techniques for mercury containing solid waste are already well known and realised, using asphalt, cement, ladle furnace slag, Portland cement or polyethylene as a matrix. Encapsulation of liquids such as elemental mercury is, however, a more challenging task. Even if the encapsulation of liquid mercury is successful, cracks due to aging or mechanical loads can lead to leachate of mercury which immediately results in the same environmental and human risks as elemental mercury without encapsulation. Due to this problematic no tests for the encapsulation of elemental mercury have been done so far.

2.6 Encapsulation with pre-stabilisation

Any type of stabilization can be used as a first step before encapsulation. The combination of both techniques then often leads to acceptable leaching values and low vapour pressures. The encapsulation after the stabilisation process has several benefits. One is the reduced surfaces to volume ratio compared to the pre-treated powdery product and therefore the lower leaching value. Another benefit is in general the increased physical strength and bearing capacity of the encapsulated product.

One major disadvantage of this combined process is the reduced concentration of mercury in the final product which increases the total amount of waste to be disposed. Furthermore, additional steps in the combined process have the disadvantage of increasing production costs. Therefore an encapsulation step should only be taken into account in case the first pre-treatment step did not fulfil the criteria for a safe disposal.

3 Minimum requirements for pre-treatment technologies and the resulting material

An in-depth investigation of the pre-treatment technologies has been performed in order to come to one of the following conclusions:

- i An appropriate technology for pre-treating elemental mercury is available and already realised to handle the expected quantity of elemental mercury.
- ii An appropriate technology for pre-treating elemental mercury is available but not realised in a scale to handle the expected quantity of elemental mercury. It is expected that it could be realised by March 2011.
- iii An appropriate technology for pre-treating elemental mercury is available but not realised to handle the expected quantity of elemental mercury. It is not expected that it will be realised by March 2011.
- iv An appropriate technology for pre-treating elemental mercury is not available and is not expected to be in place in a reasonable time to handle the expected quantity of elemental mercury.

For the investigation a two step methodology was developed.

- 1) Minimum requirements were developed in order to identify *appropriate* technologies. These minimum requirements are described in the following subchapters and each of them has to be fulfilled in order a technology is considered as an appropriate technology.

Table 3-1: Minimum requirements for pre-treatment technologies

Outline of the minimum requirement	
Technical minimum requirement	> 1 kg of elemental mercury can be treated in one batch
Environmental minimum requirement	Vapour pressure below "Limit Of Detection"(0.003 mg/m ³)
	Leaching limit value of the stabilized product < 2 mg/kg dry substance (L/S =10; EN 1247/1-4)
Economic minimum requirement	< 20,000 € per metric tonne of metallic mercury

- 2) Pre-treatment technologies which are fulfilling the minimum requirements are considered for the second step of investigation which concerns the present and/or future availability of the technology. Detailed and up to date data are gathered by interviews, reports, site visits and questionnaires to assess the current and/or future status of each technology. This assessment is the base for the identification of the correct statement out of the four which are described above.

3.1 Technical minimum requirements

The technical minimum requirements shall ensure that a technically feasible solution is achievable. If there are only theoretical considerations a solution cannot be considered as “appropriate” as experiences on feasibility are missing.

A technical minimum requirement requesting a full large scale application would be desirable as it would neglect any uncertainties about the usability in the future. But this requirement would have the disadvantage that technologies, which are currently not yet available in a large scale application, but could be realised within the needed time frame, would not be considered.

The question for the establishment of a technical minimum criteria was therefore, which status of process realisation is required to prove that the process is more developed than just laboratory scale but to leave enough space for promising processes that still need up-scaling. According to various experts judgements the project team decided to use the following criterion:

Available process capable of stabilizing > 1 kg of elemental mercury can be treated in one batch

With this criterion the possible upgrading potential has to be evaluated for each technology additionally.

3.2 Environmental minimum requirements

The environmental minimum requirements focus on the necessary quality of the stabilised/encapsulated product. They define limits to reduce the risk for human health and environment to a reasonable level.

The following environmental minimum requirements have been set for stabilised products:

Vapour pressure below “Limit Of Detection” LOD (0,003 mg/m³)

Leaching limit value of the stabilized product < 2 mg/kg dry substance (L/S =10; EN 1247/1-4)

Elemental mercury has a high vapour pressure with the danger of air emissions and risks for human health. A minimum requirement of the vapour pressure below LOD ensures, that in the final product elemental mercury is only present in trace amounts and that emissions from the final product to the environment can be considered as negligible.

The second requirement concerns the leaching behaviour of the stabilised product. All stabilisation techniques follow the target to obtain a mercury compound which has a very low solubility in water. In case the process is not well under control mercury compounds/impurities such as HgO or HgCl are produced which have a significant higher solubility in water and lead to unacceptable leaching values.

According to the Decision 2000/532/EC, stabilisation is defined as a process transforming hazardous

waste into non-hazardous waste. For the above ground disposal the leaching limit values of the corresponding landfill class have to be fulfilled according to the WAC Decision 2003/33/EC. By setting the minimum requirement of the leaching value $< 2 \text{ mg/kg}$, at least a disposal on a landfill for hazardous waste is possible.

With the minimum requirement of the leaching value below 2 mg/kg dry substance it can be guaranteed that the amount of easily dissolvable impurities is kept within a given range and it can be considered that, in case the stabilised product is brought in contact with water, the acute risk for the environment is low.

3.3 Economic minimum requirements

The economic minimum requirements focus on the costs for each tonne of elemental mercury which has to be treated. The purpose of this requirement is to accept a wide range of feasible pre-treatment technologies but to exclude options without any chance to be implemented in practice.

The following economic minimum requirement for the stabilised products has been set:

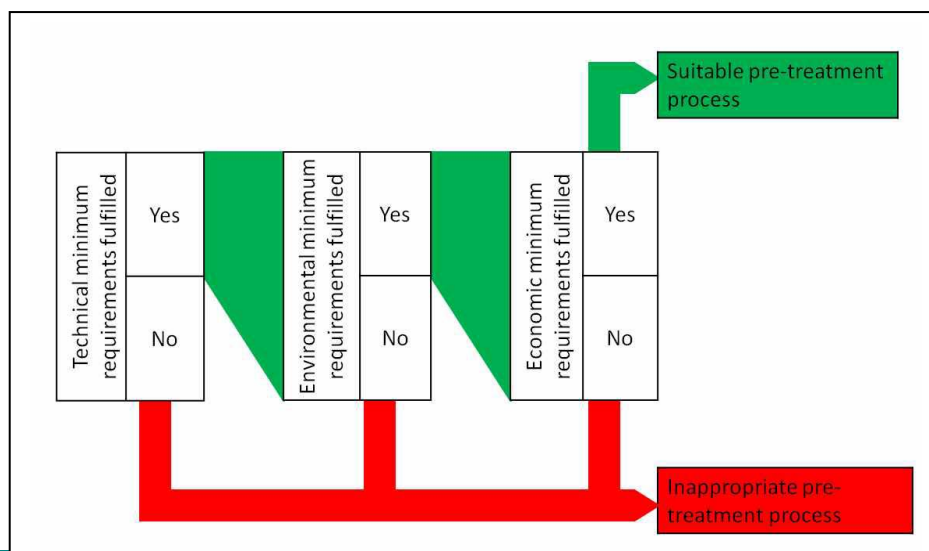
Costs of stabilisation $< 20,000 \text{ €}$ per metric tonne elemental mercury

4 Overview of technologies currently fulfilling the minimum requirements

The identified pre-treatment technologies have been evaluated against the developed minimum requirements.

Each of the different requirements is a knock-out criterion, which means that in case a technology does not fulfil a single criterion it is automatically considered as an "inappropriate pre-treatment process".

Figure 4-1: Pre-treatment evaluation against technical, environmental and economic minimum requirements



It has to be stated that the result of the evaluation can only represent the current state of development and that further technologies might arise before Regulation 1102/2008 is applicable.

The information gathered for the evaluation has been obtained directly from the industry (especially in case of technologies fulfilling the minimum requirements) or by literature. The following pre-treatment technologies have been evaluated to fulfil the minimum requirements

Table 4-1: Evaluation of pre-treatment technologies fulfilling the minimum requirements

Overview of pre-treatment technologies fulfilling all minimum requirements						
Process	Product	Minimum requirements fulfilled?			Suitable pre-treatment process	Additional comments
		Technical	Environmental	Economic		
1) Sulphur stabilisation	HgS	Yes	Yes	Yes	✓	
2) SPSS	HgS	Yes	Yes	Yes	✓	
6) Encapsulation HgS/Cement	HgS/ cement	Yes	Yes	Yes	✓	Intensive ongoing development

All these technologies include a sulphurisation step.

There are several producers worldwide which are using these technologies in batch sizes exceeding 1 kg mercury. According to the industry the repeatability and stability, concerning leaching value and vapour pressure, could be proven to be below the set minimum requirements and is much lower compared to elemental mercury.

5 Technologies not fulfilling the minimum requirements

The following Table gives an overview of those pre-treatment technologies which currently do not fulfil the set minimum requirement.

Table 5-1: Evaluation of pre-treatment technologies not fulfilling the minimum requirements

Overview of pre-treatment technologies not fulfilling all minimum requirements						
No Process	Product	Minimum requirements fulfilled?			Suitable pre-treatment process	Additional comments
		Technical	Environmental	Economic		
3) Amalgamation	HgX	No	No	No	×	Encapsulation needed
4) CBPC	Hg ₃ (PO ₄) ₂	No	No	No	×	Stabilisation

Overview of pre-treatment technologies not fulfilling all minimum requirements						
No Process	Product	Minimum requirements fulfilled?			Suitable pre-treatment process	Additional comments
		Technical	Environmental	Economic		
						needed
4) CBPC Na ₂ S/K ₂ S	HgS/Hg ₃ (PO ₄) ₂	No	Yes	No	x	High physical strength
5) Encapsulation techniques with OPC, Polyethylene, Asphalt, Polyester / Epoxy resin, Synthetic Elastomers, , Sol Gel, Dolocrete TM, Ladle furnace slag	Hg in matrix	No	No	No	x	Stabilisation needed
6) Encapsulation techniques with stabilisation and OPC, Polyethylene, Asphalt, Polyester / Epoxy resin, Synthetic Elastomers, , Sol Gel, Dolocrete TM, Ladle furnace slag	HgX / OPC	No	Yes	No	x	

3) Amalgamation

Several patents have been submitted and approved in the last decades concerning the amalgamation of elemental mercury to receive a stable product. None of these technologies have exceeded laboratory scale realisation. Due to the low quality of the final product concerning, leaching behaviour and vapour pressure the amalgamation stabilisation is not considered to be a very favourable stabilisation technology.

4) CBPC / CBPC + Na₂S/K₂S

For many waste types chemical bonded phosphate ceramics are considered to be a useful encapsulation technology to bond heavy metals. Little was done so far to transpose this technology to elemental mercury but it was discovered that addition of Na₂S or K₂S is advantageous concerning the leaching value and vapour pressure. The technique was yet not realised with a batch size of 1 kg of elemental mercury and the technology is at the present stage not developed enough to provide a satisfactory product.

5) Encapsulation without stabilisation

Broad experience is available as concerns the encapsulation of contaminated waste, but not for the encapsulation of elemental mercury. No literature is available related to direct encapsulation of elemental mercury due to the simple fact that small cracks in the matrix would immediately lead to a leachate of elemental mercury and therefore the encapsulation matrix would lose its function.

6) Encapsulation with stabilisation

The encapsulation of waste is only appropriate for solid waste, which means that elemental mercury has to be pre-treated before it can be encapsulated. Looking at the existing stabilisation techniques sulphurisation is considered to be the most promising and should be used for the pre-treatment step before encapsulation, as described in the chapter before. This combination of sulphur stabilisation followed by an encapsulation step is currently tested. Even so that an amalgamation pre-treatment step followed by an encapsulation step could also result in an advantageous end product no company is presently known to follow this combination of amalgamation and encapsulation. It is considered that this is due to the high costs for the metals used for the amalgamation.

6 Feasibility study for pre-treatment of metallic mercury

In the feasibility study it was assessed if the technologies are able to handle the expected amounts of metallic mercury. For this purpose it was considered that a facility has to be capable to stabilise about 1,000 t of metallic mercury per year. In case the technology was not capable to stabilise this amount already now it was estimated if this would be realised before 15 March 2011.

Another crucial part is that this facility has to be within the EU (Export ban for metallic mercury from March 2011). Therefore technologies only available in the USA can be considered as an example of positive realisation of such a facility, but as long it is not realised in Europe not as a practical solution.

In the following the technologies fulfilling the minimum requirements are briefly described and evaluated in the view of their feasibility.

a) A German company has realised a sulphur stabilisation process with a batch size of 5 kg elemental mercury. The process time takes about 2 hours. Therefore to stabilise ~ 1,000 tonnes/year about 50 lines with a capacity of 5 kg would have to be installed Europe wide. The operator has chosen a different approach and has installed a full scale application, which will be able to cover the whole quantity of elemental mercury to be stabilised/encapsulated from the industry (1,000 t/year). The permit as well as the proper function and the product quality of the full scale application are still missing, but it is stated by the operator that the shortcomings will be solved within the year 2010. Due to their experience in the field of treating mercury contaminated waste, handling metallic waste and the proper functioning of the pilot plant this seems reasonable.

b) A company from the US applies a sulphur stabilisation process with a batch size of 45 kg of elemental mercury. The batch size could be increased to 90 kg but for a 24 hour cycle the 45 kg option is more convenient. It is planned to install 10 to 20 of such units to one feeder which can stabilise about 500 to 1000 kg per day. Therefore to cover the expected amount of 1,000 tonnes/year of elemental mercury 3 to 6 lines would have to be installed. The technology is capable to stabilize mercury in a larger extend, but the realisation to cover the quantity need of elemental

mercury is not planned. Furthermore this technology would have to be installed in Europe due to the export ban of elemental mercury from 2011. Even if a European subsidiary would be considered a realisation before March 2011 cannot be expected.

c) Another company from the US currently runs a SPSS treatment installation with a throughput of about 250 kg /day. Therefore to cover 1,000 tonnes/year of elemental mercury 11 lines would be required. (The technology is already operating but additional lines are needed to cover the quantity need of elemental mercury which has to be stabilised.) Furthermore this technology would have to be installed in Europe due to the export ban of elemental mercury from 2011. Even if a European subsidiary would be considered a realisation before March 2011 cannot be expected.

d) A Spanish company uses a sulphur stabilisation process combined with an encapsulation step. They are currently capable to stabilise about 96 kg metallic mercury/day. To cover the expected amount of 1,000 tonnes of elemental mercury about 30 lines would have to be installed. According to their own statement they expect to install a large scale facility in the next three to five years. The following table summarizes the availability of a feasibility option by March 2011:

Table 6-1: Overview of the proposed findings on feasibility for each technology

Proposed statement of the different technologies	
Findings	Comment
Technology	
1) Sulphur stabilisation	It is expected that this technology is most probably capable to stabilise the expected amount of metallic mercury, and will be installed before 2011. The operation of a large scale application has been started but during the finalisation of the report, detailed data have not been available
2) SPSS	It is not expected that by March 2011 this technology will be available in Europe (currently only in the US) to be capable to stabilise the expected amount of metallic mercury
6) Encapsulation HgS/Cement	This technology might be available in a large scale application within the following 3 to 5 years.

Taking also the feasibility study into account the Options realised outside of Europe have to be unconsidered

7 Conclusion of the evaluation of pre-treatment technologies and recommendations

After the analyses of the different technologies, conclusion ii) is considered to be relevant:

“An appropriate technology for pre-treating elemental mercury is available but not realised to handle the quantity from the industry of elemental mercury to be stabilised/encapsulated. It is expected that it will be realised by March 2011.”

Proper stabilised elemental mercury fulfilling the set minimum requirements bears a lower risk to human health and environment compared to untreated liquid mercury. Furthermore it could be verified that currently technologies exists which can be used and it is expected that at least one company will have the capacity to cover the need before March 2011. No reason can be found to exclude a pre-treatment step from further consideration and therefore should be included in the further work of amendments and decision finding.