



**Conference of the Parties to the
Minamata Convention on Mercury
Fifth meeting**

Geneva, 30 October–3 November 2023
Item 4 (e) of the provisional agenda*

**Matters for consideration or action by the Conference
of the Parties: releases of mercury**

Best available techniques and best environmental practices to control releases from relevant sources

Note by the secretariat

1. The annex to the present note sets out a technical reference document to support the use of the draft guidance on best available techniques and best environmental practices to control releases from relevant sources,¹ to be adopted pursuant to paragraph 7 of article 9 of the Minamata Convention on Mercury.
2. The group of technical experts on mercury releases, established by the Conference of the Parties in decision MC-2/3, developed both the technical reference document and the draft guidance. The technical reference document does not form part of the guidance to be adopted by the Conference of the Parties; it is intended to provide technical information to facilitate the use of the guidance in controlling the releases of mercury and mercury compounds to land and water from relevant sources.
3. The technical guidance document is also available on the Convention web page on intersessional work² and will continue to be available on the Convention web page on guidance and forms,³ with updated technical information as appropriate.

* UNEP/MC/COP.5/1.

¹ UNEP/MC/COP.5/8, annex I.

² <https://minamataconvention.org/en/meetings/cop5#sec1563>.

³ <https://minamataconvention.org/en/about/forms-guidance>.

Annex***Guidance on best available techniques and best environmental practices to control mercury releases to land and water from relevant sources:****Technical reference document****Introduction**

1. This document is intended to provide technical information that may be helpful in using the guidance document on best available techniques and best environmental practices (BAT/BEP) to control releases of mercury to land and water from relevant sources, adopted by the Conference of the Parties to the Minamata Convention at its fifth meeting in 2023, pursuant to paragraph 7 of article 9 of the Convention.
2. This document has been developed by the group of technical experts on mercury releases, established by the Conference of the Parties in its decision MC-2/3 and mandated to develop the guidance document pursuant to decision MC-4/5. In the process of developing the guidance document, the Organization on Economic Cooperation and Development (OECD) submitted a report “Best Available Techniques to Prevent and Control Mercury Releases to Land and Water, Series on Risk Management No. 72”, which reviewed technical information on best available techniques from technical reference documents used by OECD member states as well as non-member states. The report provided a basis for developing the guidance document and may be useful for exploring further technical information on BAT/BEP.
3. Part I of this document provides an overview of existing technical information on release control techniques commonly used for different sources of releases, mentioned in chapter III of the guidance document. Part II of this document addresses techniques used for specific sources. Technical information has been extracted from technical documents used by parties, as well as information submitted during the intersessional process. At present, much of the information come from BAT reference documents under the EU Industrial Emissions Directive, US EPA Effluent Limitations Guidelines and Standards Database and other literature in developed countries, which have been developed based on the situation on those countries. Further information may be obtained from the original technical documents.
4. Parties to the Minamata Convention are encouraged to provide to the Secretariat information on the use of this technical reference document or updated technical information that may support parties in controlling the releases of mercury to land and water from relevant sources. The secretariat of the Minamata Convention will work to keep this document up to date within the available resources.

* The annex has not been formally edited.

Part I: Common techniques

5. This part provides technical information on control techniques which are commonly used to control releases of mercury to land and water from different sources, in line with Chapter III of the BAT/BEP Guidance.

I. Removal of solid contents

A. Description

6. Gravity separation (grit separation, sedimentation, clarification) means the separation of suspended particles and floating material from water by gravitational settling. The settled solids are removed as sludge from the bottom of the container, whereas floated material is skimmed as scum from the water surface. When the particles cannot be separated by simple gravitational means, *e.g.* when they are too small and their density is too close to that of water or they form colloids, special chemicals are added to cause the solids to settle, such as:

- (a) aluminium sulfate (alum);
- (b) ferric sulfate;
- (c) ferric chloride;
- (d) lime;
- (e) polyaluminium chloride;
- (f) polyaluminium sulfate;
- (g) polymers.

7. These chemicals cause the destabilisation of colloidal and small suspended particles (*e.g.* clay, silica, iron, *metals*, dyes, organic solids and oil in waste water) and emulsions entrapping solids (coagulation) and/or the agglomeration of these particles into flocs large enough to settle (flocculation).

8. The sedimentators (or settlers) commonly operated are:

- (a) sedimentation or flat tanks, either rectangular or circular, both equipped with an appropriate scraper;
- (b) hopper-bottom tanks, with vertical flow, usually not equipped with mechanical sludge removal systems; and
- (c) lamina or tube settlers, where plates are used to enlarge the sedimentation surface.

B. Cross-media effects

9. Sedimented sludge and skimmed scum, if not suitable to recycle or reuse, must be disposed of as waste. Depending on the wastewater origin, this waste might contain hazardous compounds to be treated accordingly. These compounds can be carbonates, fluorides, sulfides, or hydroxides (or oxides) of metals, oily scum, etc. and, under certain circumstances, even dioxins.

10. Sources of noise are the pumps, which can be enclosed, and the sludge/scum removal system.

11. When the wastewater contains odorous substances, it might be necessary to cover the sedimentation tank, or at least the coagulation or flocculation unit, and to duct the arising waste gas, if necessary, to a treatment system. The necessary equipment (ducts and vents) may likely requires an appropriate safety system, *e.g.*, a pressurised nitrogen gas flow system to avoid explosion risk.

C. Applicability

12. Sedimentation is a separation technique widely used for many purposes and is usually not used alone. The main examples are:

- (a) clarifying collected rainwater from solid content such as sand or dust in a sedimentation tank or pond;
- (b) clarifying process wastewater from inert contents such as sand or comparable particles;

- (c) clarifying process wastewater from reaction material such as emulsified metal compounds, polymers and their monomers, supported by the addition of appropriate chemicals;
- (d) separation of metals or other dissolved compounds after precipitation, often with chemical support, often followed by filtration processes; and
- (e) removal of activated sludge in a primary or secondary clarifier of a biological wastewater treatment process, often supported chemically.
- (f) Sedimentation upstream of other treatments.

13. Application limits and restrictions are given in Table 1.

Table 1

Application limits and restrictions associated with the sedimentation of solids

| <i>Issue</i> | <i>Limit/restrictions</i> |
|--|--|
| Particle size | Particles must be large enough to be settleable, otherwise coagulation and/or flocculation chemicals need to be applied |
| Presence of volatile substances | Volatile substances must be avoided because of the long residence time in the tank (as well as the mixing action when coagulation and/or flocculation are used) and thus the potential release of VOCs |
| Solid concentration | No limits, provided the aqueous phase is still separable |
| pH (in the case of coagulation/flocculation) | Controlled pH range is essential during operation, otherwise performance of clarification is poor |
| Emulsions | Stable emulsions cannot be separated and broken by coagulation/flocculation; preceding emulsion breaking is required |

Advantages and disadvantages

Advantages

- Simplicity of the installation
- Removal efficiency can be increased by the addition of coagulation and/or flocculation chemicals

Disadvantages

- Unsuitable for fine material and stable emulsions, even with coagulants and flocculants
- Floc can embed other contaminants that might cause problems in disposing of the sludge

Economics associated with the sedimentation of solids are given in Table 2.

Table 2

Economics associated with the sedimentation of solids

| <i>Equipment</i> | <i>Investment costs (million)</i> | <i>Operating and maintenance costs</i> |
|------------------------|-----------------------------------|--|
| Sedimentation tank | EUR 1.2 (1) | NI |
| | EUR 0.2–0.3/m ³ (2) | |
| | EUR 0.25 (3) | |
| Lamina or tube settler | EUR 0.15 (4) | Up to EUR 2.5 per m ³ (6) |
| | EUR 0.02 (5) | |

Per 1 000 m³ tank volume.

Cost per 1 000 m³ of concrete tank volume. Costs can be higher if the bottom of the sedimentation tank is slanted [63, VITO 2010].

Scraper blade of maximum 5 metre diameter [63, VITO 2010].

Capacity of 240 m³/h [63, VITO 2010].

Capacity of 20 m³/h [63, VITO 2010].

The use of a flocculation process can induce a rise in the costs as flocculating agents need to be bought. In this case the cost would vary according the matrix contents [216, Viavattene et al. 2010].

NB: NI = no information provided.

14. Investment costs are closely related to the size (surface) of the unit used to treat the wastewater volume. An economy of scale effect is evident, as large tanks cannot easily be constructed in dense urban areas and the cost of land could affect the total cost.

II. Precipitation of metals

A. Description

15. Precipitation is a process to form insoluble particulates (*i.e.* solid precipitate) that is followed by an additional process of separating the water portion (European Commission 2018). Precipitation processes are a technology used to treat mercury-contaminated groundwater and wastewater. The effectiveness of this technology is less likely to be reduced by characteristics or contaminants that may affect other technologies, such as hardness or other metals. Systems that use this technology generally require skilled operators; therefore, precipitation is more cost-effective at a large scale where labor costs can be spread over a larger amount of treated water produced. (US EPA 2007). This technique may be complemented with other treatment techniques to improve treatment efficiency. The best performances found consist of combinations of precipitation with filtration, co-precipitation, and adsorption.

16. Precipitation usually involves pH adjustment and the addition of a chemical precipitant or coagulant to transform soluble metals and inorganic contaminants into insoluble metals and inorganic salts. Mercury removal usually includes changing the pH of the water to be treated because removal is maximized at the pH where the precipitated species is least soluble. The optimal pH range for precipitation depends on the waste treated and the specific treatment process. The precipitated solid is typically removed by clarification or filtration (US EPA 2007).

17. Typical precipitation chemicals are:

- (a) lime (with lime milk, the preparation devices are part of the treatment unit) to precipitate metals;
- (b) dolomite to precipitate metals;
- (c) sodium hydroxide to precipitate metals;
- (d) sodium carbonate to precipitate metals;
- (e) calcium salts (other than lime) to precipitate sulfate or fluoride;
- (f) sodium sulfide to precipitate metals, e.g. arsenic, mercury, chromium, cadmium, nickel; and
- (g) polyorganosulphides to precipitate mercury.

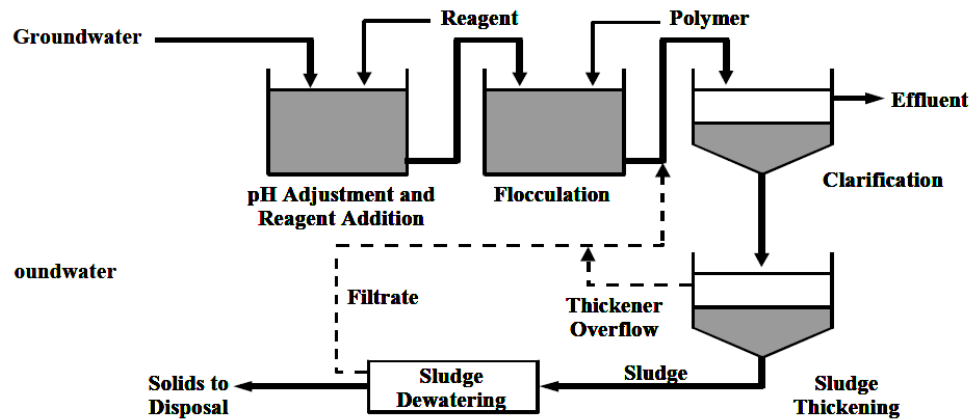
18. These are often accompanied with flocculants to assist further separation, such as:

- (a) ferrous and ferric salts;
- (b) aluminium sulfate;
- (c) polymers (cationic, anionic or non-ionic); and
- (d) polyorganosulfides.

19. Chemicals and Methods Used for Mercury Precipitation:

- (a) Ferric salts (for example, ferric chloride), ferric sulfate, or ferric hydroxide;
- (b) Alum;
- (c) pH adjustment;
- (d) Lime softening, limestone, and calcium hydroxide;
- (e) Sulfide reagents such as sodium sulfide; and polyorganosulfides
- (f) Lignin derivatives

Figure 1
Model of a Precipitation System (US EPA 2007)

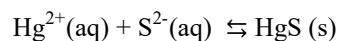


20. Precipitation usually involves pH adjustment and addition of a chemical precipitant or coagulant to transform soluble metals and inorganic contaminants into insoluble metals and inorganic salts. Mercury removal usually includes changing the pH of the water to be treated because removal is maximized at the pH where the precipitated species is least soluble. The optimal pH range for precipitation depends on the waste treated and the specific treatment process. The precipitated solid is typically removed by clarification and/or filtration.

21. For metals, precipitation is generally accomplished as close to the source as possible to avoid dilution. A precipitation facility usually consists of one or two stirred mixing tanks, where the agent causing precipitation (*i.e.* precipitation chemicals) and possibly other chemicals (*e.g.* flocculants) are added, a sedimentation tank, and storage tanks for the chemical agents. If needed, as mentioned above, further treatment equipment is added. The sedimentation tank might be replaced downstream by other sludge collecting systems. (European Commission 2016).

22. Sulfide precipitation is a common technique used to remove inorganic mercury from wastewater. Mercury ions dissolved in the wastewater can be removed by precipitation with the addition of sulfide reagents. In this process, the adjusted pH range is between 7 and 9, and a sulfide precipitant (such as sodium sulfide) is added to the wastewater stream. The sulfide precipitant converts dissolved mercury to the relatively insoluble mercury sulfide form. Typical chemicals used to precipitate mercury sulfide are sodium sulfide and polyorganosulfides (European Commission, 2016).

23. Harmful effects to occupational health may be generated during the metal sulfide precipitation (MEE, 2012[47]). The simplified chemical reaction is illustrated below:



24. European Commission (2014) indicates that removing mercury from wastewater initially starts by a settling technique to remove large mercury droplets. Afterwards, oxidising agents, such as hypochlorite, chlorine or hydrogen peroxide are used to fully convert mercury into its oxidised form (metallic cation), which is followed by sulfide precipitation of the wastewater, and then solid/liquid separation. The precipitate is then managed as solid waste and disposed of in an environmentally sound manner.

B. Achieved environmental levels

25. Precipitation is used to remove metals and other inorganics (*e.g.* phosphorus or phosphate compounds), fats, oils, greases and some other organic compounds from waste.

26. Achievable emission levels for metals vary greatly, depending on the situation. Variables may include:

- (a) the removal of a single metal species from the inorganic wastewater matrix;
- (b) the removal of a metal mix from the inorganic wastewater matrix; and
- (c) the removal of metals from the organic wastewater matrix with a tendency to form metal complexes, *e.g.* dye agents.

27. Chemical precipitation has a high yield, and the achievable final concentration is determined by the compound's solubility product. It is difficult to determine the final concentration for a combination of pollutants due to the interaction between substances.
28. According to US EPA, three plants that treated groundwater reduced the mercury concentration to less than 2 µg/L (US EPA 2007). At the Squamish Mercury Remediation Project in British Columbia, Canada, the coprecipitation and coagulation treatment reduced the mercury concentration from 15 µg/L to 1 µg/L. Precipitation, carbon adsorption, and pH adjustment were used at the Olin Corporation McIntosh Plant Site in Washington County, Alabama, to treat mercury-contaminated groundwater and reduced the average influent concentration of mercury from 44 µg/L to 0.3 µg/L.
29. Other examples of reducing mercury to achieve environmental levels are exhibited by eight projects that treated mercury -contaminated wastewater, five of which treated wastewater at chlor-alkali plants. The influent mercury concentration ranged from 362 µg/L to 0.07 µg/L, and the effluent concentration was reduced to less than 2 µg/L in all projects. However, some of the processes used multiple precipitation steps and additional treatment with other technologies such as activated carbon to reach these levels.

C. Cross-media effects

30. The precipitants usually must be disposed of as sludge. Often, this sludge is classified as chemical waste if metals are involved. This waste may contain carbonates, fluorides, hydroxides (or oxides), phosphates, sulfates, and sulfides of metals depending on the precipitating agent used.
31. However, excess use of the chemical sulfide precipitants can form soluble mercury polysulfide complexes. Mercury can resolubilize from sulfide sludges under conditions that exist in landfills, which could lead to mercury contamination of leachate and potential groundwater pollution.
32. The effluent from mercury precipitation may also require further treatment, such as pH adjustment, before discharge or reuse. Sulfide precipitation of mercury may generate residual sulfide in the effluent. Treatment to remove residual sulfide may be needed before discharge.
33. Substantial sources of noise are caused by pumps and sludge removal facilities. Appropriate measures for noise control should be taken (e.g. equipment enclosure).
34. If the release of volatile and odorous substances can be expected (e.g. when precipitating metals as sulfides, H₂S gas evolution can occur if pH is not appropriately controlled), precipitation should be operated in closed tanks or covered basins with ducts to gas abatement facilities.
35. Consumables are given in Table 3 below.

Table 3

Consumables associated with chemical precipitation

| <i>Consumable</i> | <i>Amount</i> |
|---|---|
| Precipitation agent (e.g. lime, dolomite, ferrous and ferric salts, ferrous sulfate, sodium sulfide, aluminium sulfate, polymers, polyorganosulfides) | Dependent on contaminant load Theoretical consumption of some precipitation agents in kg to precipitate one kg of metal ions is: CaO: 0.88 for Cu, 0.96 for Ni, 1.62 for Cr, 0.86 for Zn Ca(OH) ₂ : 1.16 for Cu, 1.26 for Ni, 2.13 for Cr, 1.14 for Zn NaOH: 1.26 for Cu, 1.36 for Ni, 2.31 for Cr, 1.22 for Zn |

Source: European Commission 2016.

D. Applicability

36. Precipitation can be applied at different stages of the wastewater stream, for example:
- directly at the source to remove metals to avoid dilution by unloaded streams;
 - as the central treatment technique for the removal of phosphates, sulfate and fluoride, provided inadequate dilution is not expected; and
 - to remove phosphates after the biological stage in a central wastewater treatment process, where the sludge is collected in the final clarifier;
 - precipitation upstream of other treatments.

37. The performance of further liquid/solid separation normally depends on factors such as pH, mixing quality, temperature, or residence time at the precipitation step. The optimum conditions are usually determined on a case-by-case basis.

38. Application limits and restrictions are given in Table 4.

Table 4

Application limits and restrictions associated with chemical precipitation

| <i>Issue</i> | <i>Limits/restrictions</i> |
|----------------------------|---|
| pH adjustment | Optimum pH range for metals, phosphate, fluoride (generally pH 9–12) with lime. A broader pH range is available with sodium sulfide. When sulfides are used, hydrogen sulfide is generated under excess sulfide and acidic conditions |
| Complex-forming substances | Can prevent precipitation of metals, such as copper, nickel |

Source: European Commission 2016

E. Factors Affecting Precipitation/Coprecipitation Performance and Cost (US EPA 2007)

(a) **pH:** In general, mercury removal will be maximized at the pH where the precipitated species is least soluble. The optimal pH range for precipitation/coprecipitation depends on the waste treated and the specific treatment process. The most effective precipitation of mercury for the sulfide precipitation process occurs within a pH range of 7 to 9. The most effective precipitation of mercury for the hydroxide precipitation process occurs within a pH range of 7 to 11.

(b) **Presence of other compounds:** The presence of other metals or contaminants may affect the effectiveness of precipitation/coprecipitation.

(c) **Chemical dosage:** The cost generally increases with increased chemical addition. Larger amounts of chemicals added usually results in a larger amount of sludge, which requires additional treatment or disposal. Excess use of sulfide precipitant can form soluble mercury polysulfide complexes.

(d) **Treatment goal:** For some applications, a single precipitation step or using precipitation alone may not achieve the treatment goals. Multiple precipitation steps or the use of additional technologies may be needed to meet stringent cleanup goals, effluent guidelines, or disposal standards.

(e) **Sludge disposal:** Sludge produced from the precipitation/coprecipitation process could be considered a hazardous waste and require additional treatment before disposal as a solid waste or disposal as hazardous waste.

Advantages and disadvantages

General advantages

- Chemical precipitation is a well-established technique with ready availability of equipment and many chemicals
- Some treatment chemicals, especially lime, are inexpensive
- Completely enclosed systems are often conveniently self-operating and low maintenance, requiring only replenishment of the chemicals used

General disadvantages

- Competing reactions, varying levels of alkalinity and other factors typically make calculation of proper chemical dosages challenging. Therefore, frequent jar tests are necessary for confirmation of optimal treatment conditions. Overdosing can diminish the effectiveness of the treatment
- Chemical precipitation may require working with corrosive chemicals, increasing operator safety concerns
- The addition of treatment chemicals, especially lime, may increase the volume of waste sludge by up to 50 %
- Large amounts of chemicals may need to be transported to the treatment location
- Polymers can be expensive

Advantages with lime as an agent

- Prevention of increased salt content in the wastewater
- Increase of the buffering capacity of the central biological wastewater treatment process
- Improvement in sludge sedimentation
- Sludge thickening
- Improvement of mechanical dewaterability of sludge
- Reduction of dewatering cycle time
- Low cost

Disadvantages with lime as an agent

- Operating problems associated with the handling, storage, and feeding of lime
- Increase of sludge amount due to an excess of calcium hydroxide
- Maintenance problems more likely

Advantages for sodium sulfide

- Precipitation occurs over a broad pH range
- Decrease in amount of sludge (about 30 % in volume, compared to lime treatment)
- Decrease in amount of chemicals used (about 40 %, compared to lime treatment)
- Produces lower metal levels in treated effluent
- No pretreatment or post-treatment needed
- Highly efficient at removing suspended and dissolved metals from a wastewater stream

Disadvantages of using sodium sulfide

- Generation of hydrogen sulfide gas under excess sulfide conditions if the batch becomes acidic by pH control failure
- Odour problems

F. Economics

39. The costs for precipitation are expected to be similar to those presented for the sedimentation process associated with flocculation. The operating and maintenance costs will depend on the agents used in the precipitation process and on the required quantity regarding the matrix composition and can be estimated at EUR < 0.03 per m³ (European Commission 2016).

IV. Ion-exchange**A. Description**

40. Ion exchange is the removal of undesired or hazardous ionic constituents of wastewater and their replacement by more acceptable ions from an ion exchange resin, where they are temporarily retained and afterwards released into a regeneration or backwashing liquid. The undesirable ions are temporarily retained by the resin and then released into a regeneration or backwashing liquid (European Commission 2016, European Commission 2019). For removal by ion exchange, mercury must first be oxidised to the mercuric cation (Hg²⁺) with oxidising agents such as hypochlorite, chlorine, or hydrogen peroxide (European Commission 2014).

41. The equipment of an ion exchanger usually consists of:

- (a) a vertical cylindrical pressure vessel with a corrosion-resistant lining that contains the resin, usually as a packed column with several possible configurations;
- (b) control valves and piping system, directing the flow of wastewater and regeneration solution to the proper locations; and

- (c) a system to regenerate the resin, consisting of salt-dissolving and dilution control equipment.
42. An affixed inlet distribution system provides even distribution of the influent wastewater to prevent the hollowing out of flow channels in the resin bed. It also acts as a collector for backwash water.
43. Though not all are used for mercury removal, ion exchangers commonly in use are macroporous granule resins with cationic or anionic functional groups, such as:
- (a) strong acid cation exchangers, neutralising strong bases and converting neutral salts into their corresponding acids;
- (b) weak acid cation exchangers, able to neutralise strong bases and used for dealkalisation;
- (c) strong base anion exchangers, neutralising strong acids and converting neutral salts into their corresponding bases; and
- (d) weak base anion exchangers, neutralising strong acids and used for partial demineralisation.
44. The ion exchange operation cycle is comprised of:
- (a) the actual ion exchange operation;
- (b) the backwash stage, including removal of accumulated particles and reclassification of the ion exchange resin bed;
- (c) the regeneration stage, using a low volume/high concentration solution, reloading the ion exchange resin with the respective ion, and releasing the unwanted ion species to the regeneration solution;
- (d) the displacement, or rinse with a slow water flow, of the regeneration solution through the bed; and
- (e) the fast rinse, removing the remaining traces of the regeneration solution, including any residual hardness, from the resin bed.
45. Storage facilities for the regeneration chemicals are necessary.
46. Ion exchange implies the consumption of ion exchange resins, regeneration liquids, water for backwashing and rinsing, and energy for the pumps. The addition of other chemicals, *e.g.* to suppress microbiological fouling, may be necessary.

B. Achieved environmental levels

47. Typical effluent ion concentrations that can be achieved are in the range of 0.1–10 mg/l with influent concentrations of 10–1 000 mg/l (European Commission 2016).
48. Achieved environmental benefits associated with ion exchange are given in Table 5 below.

Table 5. **Abatement efficiencies and emission levels associated with ion exchange**

| <i>Parameter</i> | <i>Emission level (mg/l)</i> | <i>Abatement efficiency (%)</i> | <i>Comments</i> |
|------------------|----------------------------------|-------------------------------------|--|
| Effluent ion | 0.1–10 | 80–99 (1) | Influent concentrations of 10–1 000 mg/l |

Source: European Commission 2016

C. Cross-media effects

49. The regeneration of ion exchange resins results in a small volume of concentrated acid or salt solution, which contains the removed ions originating from the resin. This enriched liquid has to be treated separately to remove these ions, *e.g.* metals by precipitation.
50. The rinsing water from regeneration contains the same ions as the brine, but in relatively low concentrations. Whether this part can be discharged directly or must undergo treatment depends on the concentrations. In some instances, this rinsing water can be reused. At a plant in Germany, the rinsing water from regeneration is reused in waste gas scrubbers.

51. Ion exchange implies the consumption of ion exchange resins, regeneration liquids, water for backwashing and rinsing, and energy for the pumps. The addition of other chemicals, *e.g.* to suppress microbiological fouling, may be necessary.

52. To reduce noise, pumps can be enclosed.

D. Applicability

53. Ion exchange is applied to remove unwanted ionic and ionisable species from wastewater, such as:

(a) metal ions, cationic or anionic, *e.g.* Cr^{3+} or cadmium and its compounds, with low feed concentrations, CrO_4^{2-} also with high feed concentrations;

(b) ionisable inorganic compounds, such as H_3BO_3 ;

(c) soluble, ionic or ionisable organic compounds, *e.g.* carboxylic acids, sulfonic acids, some phenols, amines as acid salt, quaternary amines, alkyl sulfates.

54. Ion exchange is not commonly used for mercury treatment, as it is more likely to be affected by characteristics of the media and contaminants other than mercury, than affected by co-precipitation and sulfide precipitation (US EPA 2007). As such, adsorption and ion exchange are more appropriate for: applications where mercury is the only contaminant to be treated, for smaller capacity systems, and for polishing of pre-treated effluent.

55. Ion exchange is feasible as an end-of-pipe treatment, but its greatest value lies in its recovery potential. Ion exchange is commonly used as an integrated operation in wastewater treatment, *e.g.* to recover rinse water and process chemicals. Suspended particles in the feed should be less than 50 mg/l to prevent plugging. Thus, solid/liquid separation is an appropriate pretreatment. Application limits and restrictions are given in Table 6 below.

Table 6

Application limits and restrictions associated with ion exchange

| <i>Issue</i> | <i>Limits/restrictions</i> |
|-----------------------|---|
| Ion concentration | High ionic strength can cause swelling of resin particles |
| Temperature | Thermal limits of anion resins are generally in the vicinity of 60 °C |
| Corrosive agents | Nitric acid, chromic acid, hydrogen peroxide, iron, manganese, and copper can damage the resins |
| Interfering compounds | Inorganic compounds such as iron precipitates or organic compounds such as aromatics can cause irreversible adsorption to the resin |

Advantages and disadvantages

Advantages

- In principle all ions and ionisable species can be removed from aqueous liquids; it operates on demand, and is relatively insensitive to flow variations
- High efficiency possible
- Recovery of valuable species possible
- Water recovery possible
- A variety of specific resins are available

Disadvantages

- Prefiltration is required
- Bacteria growth on the resin surface and fouling caused by precipitation or adsorption
- Interference of competing ions in the wastewater
- Attrition of resin particles due to regeneration or mechanical impacts; the brine and sludge resulting from regeneration has to be treated or disposed of

E. Economics

56. Investment and operating costs depend on the nature of the feed stream. Economics associated with ion exchange are given in Table 7 below.

Table 7

Economics associated with ion exchange

| <i>Type of costs</i> | <i>Costs</i> | <i>Comments</i> |
|----------------------|--|--|
| Investment costs | GBP 60 000 (EUR 73 000) ⁽¹⁾ + GBP 20 000 (EUR 24 000) ⁽¹⁾ | Packed height of 1 m and diameter of 1 m; vessel, valves, and resin included for additional 0.5 m of diameter |

Source: European Commission 2016

V. Adsorption on activated carbon

A. Description

57. Adsorption has been used to remove inorganic mercury from groundwater and wastewater. This technology can reduce concentrations of inorganic mercury to less than 2 µg/L. Its effectiveness is sensitive to a variety of contaminants and characteristics of the untreated water. It can be a primary treatment method but is often used as a water treatment processes (US EPA, 2007).

58. Adsorption is the transfer of soluble substances (solutes) from the wastewater phase to the surface of solid, highly porous particles (the adsorbent). The adsorbent has a finite capacity for each compound to be removed. When this capacity is exhausted, the adsorbent is 'spent' and must be replaced by fresh material. The spent adsorbent is either regenerated or incinerated.

59. One of the most important characteristics of an adsorbent is the quantity of adsorbate it can accumulate. Important characteristics that affect adsorbate capacity are surface area, pore size distribution, and surface chemistry. Water is passed through a bed or adsorbent in adsorption treatment for mercury. Mercury or mercury compounds are adsorbed as the contaminated water passes through the adsorbent, removing them from the water.

60. Activated carbon, a highly porous carbonaceous substance, is usually used to remove organic materials from wastewater. It also has applications in the removal of mercury and precious metals (European Commission 2017b).

61. The effectiveness of adsorption is sensitive to a variety of water characteristics. Pretreatment is used in many adsorption systems to alter the characteristics of the untreated water and ensure effective adsorption. For example, adsorption may be preceded by filtration to remove solids that may plug the adsorption bed. Ultraviolet (UV) light treatment may be used to control bacterial growth, which can also plug the adsorption bed and reduce its adsorption capacity. Equalization tanks are often used to ensure a constant flow rate through the bed. This constant flow helps ensure that the residence time is sufficient to remove the contaminants. Additionally, high flow rates can cause channelization and erosion of the adsorption bed, which can reduce effectiveness.

62. Adjustment of pH to the range where adsorption is most effective is also a common pretreatment step. After adsorption treatment, the pH may require further adjustment to acceptable criteria of the receiving waters. Once the adsorbent bed is saturated, the bed may be regenerated or disposed of (US EPA, 2007).

63. As a pretreatment, reducing agents such as hydroxylamine can be used to fully convert ionic mercury into its elemental form, with subsequent removal by coalescence and recovery of metallic mercury, followed by adsorption on activated carbon (European Commission 2014).

64. Granular activated carbon (GAC) has a wide efficiency range and is not restricted to polar or non-polar compounds. GAC can be impregnated, e.g. with oxidants such as potassium permanganate or with sulfur compounds, improving the retention of heavy metals. GAC adsorption is applied to remove organic contaminants, mainly those with refractory, toxic, coloured and/or odorous characteristics, and residual amounts of inorganic contaminants, including nitrogen compounds, sulfides, and heavy metals. Granular medium filters, e.g. sand filters, are commonly used upstream of the GAC adsorber to remove the suspended solids present.

65. According to the European Commission (2016), potential adsorbents for adsorptive wastewater purification are given in Table 8 below.

Table 8
Commonly used adsorbents for Hg and their properties

| Adsorbent | Form | Specific surface area (m ² /g) | Pore volume (cm ³ /g) | Bulk density (g/l) |
|------------------|----------|--|----------------------------------|-----------------------|
| Activated carbon | Granular | 500–1 000 | 0.3–0.8 | 300–550 |
| | Powder | 600–1 500 | 0.3–1.0 | |
| Adsorber resins | Granules | 400–1 500 | Porosity 35–65 vol-% | 650–700 |

66. Adsorption processes are divided into:

- (a) mixing, usually used for batch-wise treatment;
- (b) percolation, applicable to continuous treatment, normally with a fixed-bed adsorber packed in two columns that are alternately on duty and undergoing backwashing; and
- (c) pulse-bed or moving-bed process, as continuous percolation with wastewater and adsorbent led countercurrent through the column.

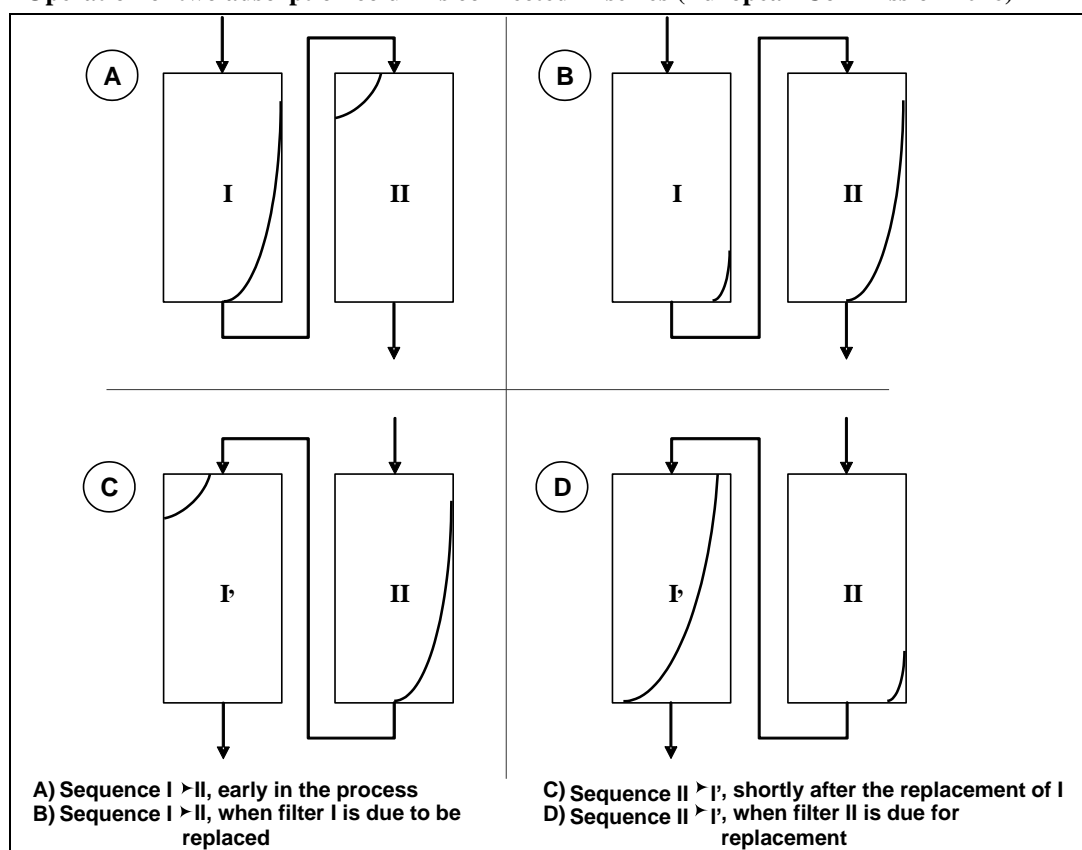
67. Since the adsorbent-active surface is often subjected to clogging and blockage, the wastewater needs to be as free of solid content as possible, which often makes an upstream filtration step necessary.

68. An example of the operating stages of a two-column fixed-bed adsorber connected in series is illustrated in Figure 2 below.

69. Adsorber vessels are usually built of corrosion-resistant material, e.g. lined carbon steel, stainless steel or fibreglass-reinforced plastic (FRP). Storage facilities for the adsorbent are necessary.

Figure 2

Operation of two adsorption columns connected in series (European Commission 2016)



B. Achieved environmental levels

70. The efficiency of adsorption processes varies widely with wastewater composition and feed concentration, which should be borne in mind when references to achievable emissions or removal efficiencies are cited. Data collected during the development of the United States Effluent Limit Guidelines (US EPA ELG) show that carbon can be extremely effective when used on individual

wastewater streams. However, the data showed the breakthrough of certain pollutants even with careful monitoring. In particular, in all cases, the concentrations of many metals increased across the carbon units.

71. Abatement efficiencies for Hg associated with adsorption are given in Table below.

Table 9

Abatement efficiencies associated with adsorption

| Parameter | Abatement efficiency (%) | | Comments |
|--------------|--------------------------|--------|--------------|
| | Granular | Powder | |
| Inorganic Hg | 80 (1, 2) | NI | Feed 29 µg/l |
| Organic Hg | 80 (1) | NI | Low feed |

Source: European Commission 2016

72. Powdered activated carbon (PAC) treatment systems are reported to treat wastewater with a COD higher than 60 000 mg/l, including toxic volatile organic compounds higher than 1,000 mg/l with a reduction of specific toxic organic chemicals to below the limit of detection, i.e. about 100% reduction.

73. According to the US EPA, the effectiveness of adsorption treatment can be evaluated by comparing influent and effluent contaminant concentrations. Performance data were available for three of the four full-scale processes. Influent concentrations ranged from 3.3 to 60 µg/L in these treatments. The effluent mercury concentration was below 2 µg/L for all three of these projects. Of the two pilot-scale applications, one (Project 5) reported a mercury influent concentration of 2,500 µg/L and a removal rate of 98 %. Data on the effluent concentrations were not available for this project. Project 6 reported a mercury influent concentration of 60 µg/L and an effluent concentration below the detection limit. The detection limit was not provided, however.

74. A testing laboratory in Massachusetts generates wastewater containing thimerosal concentrations averaging 60 µg/L before treatment. In 1992, the laboratory conducted pilot testing of carbon adsorption and constructed a full-scale system. The full-scale system includes a 15-micron bag filter, UV light, an equalization tank with pH adjustment to the 4 to 5 range, granular activated carbon filters, a mixing tank with pH adjustment to 5.5 to 9.5, and a neutralization tank. The micron bag filter was necessary to remove solids that tended to plug the filters. UV light was introduced to control bacterial growth in the carbon adsorption system. Flow equalization was provided to establish constant detention time and avoid channelization of the beds caused by increasing flows experienced when equalization was not included. The pH was adjusted to the range where the adsorptive capacity of the carbon filter is greatest (4 to 5). After the carbon filter, the pH is readjusted to the 5.5 to 10.5 range before the wastewater flows into the neutralization tank. Treated water is finally neutralized to the range accepted by the receiving water body. This acceptable range was not reported, however. *This system reduced the concentration of thimerosal in the wastewater from 60 µg/L to below the goal of 1 µg/L.* (US EPA 2007)

C. Cross-media effects

75. When the adsorptive capacity of the adsorbent has been exhausted, it will be replaced and subsequently regenerated (with the exception of PAC which is disposed of together with other wastewater sludge). As mentioned above, the adsorbents have their own distinct regeneration methods. Common to these methods is, however, that they need energy and/or chemicals for their operation.

76. Granular activated carbon (GAC) is thermally regenerated at temperatures up to 750–1,000 °C. Resins, zeolites, and activated aluminium oxide carrying inorganic loads are eluted with chemicals, either organic solvents or inorganic solutions.

77. For example, the regeneration process of GAC releases off-gases that contain the thermal and chemical decomposition products of the adsorbed compounds. With each regeneration, a proportion of about 10 % will be lost and must be replaced by fresh GAC. This continuous renewal should be adequate to maintain the overall quality of the GAC in the bed. The regeneration of GAC would normally be carried out by specialist companies, which operate regeneration furnaces. These companies will transport GAC from the consuming treatment plant to the regeneration furnaces and vice versa. As regeneration is relatively expensive, plants are usually designed to have a period of at least six months between regeneration cycles.

78. The generation of off-gases with regeneration requires subsequent waste gas treatment, either at the chemical site itself or at the site of the regenerating company.

79. If the GAC cannot be regenerated, it must be disposed of as chemical waste and incinerated. This might be the case if the GAC is contaminated with PCBs, PCDDs/PCDFs, metals or dichlorobromopropane.

80. Consumables are given in Table 10 below.

Table 10

Consumables associated with adsorption

| <i>Consumable</i> | <i>Granular</i> | <i>Powder</i> |
|-------------------|----------------------------------|---|
| Adsorbent | About 10 % loss per regeneration | 0.1–1 g PAC/l of effluent or 10 g PAC/kg of suspended solids |

Source: European Commission 2016

81. Further impacts of adsorption on the environment are:

- (a) the transport of spent GAC to and from regeneration;
- (b) the regeneration operation itself at the site of a specialist company;
- (c) the energy consumption for the regeneration process;
- (d) the release of contaminants to water and/or air during this regeneration process; and
- (e) sources of noise, e.g. the pumps, which can be mitigated through enclosures.

D. Applicability

82. The effectiveness of adsorption is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organic compounds, and biological growth can cause fouling and plugging. Pretreatment with flocculation, settling, filtration, or oil-water separation may be used to reduce suspended solids and organic compounds. UV light treatment has been used to reduce biological growth before the process is used to adsorb mercury. Spent adsorption media must be regenerated or disposed. Competition for adsorption sites could reduce the effectiveness of adsorption because other constituents may be preferentially adsorbed, resulting in a need for more frequent bed regeneration or replacement.

83. The adsorbent most used in the chemical sector is activated carbon. It is used as granulate (GAC) in columns or as powder (PAC) dosed to a treatment tank or basin. Other commonly used adsorbents are lignite coke, activated aluminium oxide, adsorber resins, and zeolites.

84. **GAC adsorption** is applied to remove organic contaminants, mainly those with refractory, toxic, coloured and/or odorous characteristics, and residual amounts of inorganic contaminants, such as nitrogen compounds, sulfides and *metals*. Granular medium filters, e.g. sand filters, are commonly used upstream of the GAC adsorber to remove the suspended solids present.

85. Representative applications of GAC adsorption are:

- (a) textiles and dyestuffs: removal of TOC, colour, dyes;
- (b) petrochemical industry: removal of COD, BOD;
- (c) detergents, resins, chemicals: removal of TOC, COD, xylene, alcohols, phenols, resin intermediates, resorcinol, nitrated aromatics, polyols;
- (d) herbicides, insecticides: removal of chlorophenols, cresol;
- (e) pharmaceuticals: removal of phenol; and
- (f) explosives: removal of nitrated phenols.

86. GAC is normally regenerated by thermal reactivation at temperatures of about 900–1,000 °C. Regeneration of granular activated carbon usually involves heating to desorb contaminants, which could release volatile mercury compounds. Use of air pollution control equipment may therefore be necessary to remove mercury from the off-gas produced. Further treatment may be necessary before spent adsorption media from mercury treatment systems can be disposed.

87. PAC is dosed to the wastewater to be treated as a slurry and subsequently removed by separation processes such as sedimentation and filtration. PAC can also be added to the wastewater stream at the same point as the inorganic coagulants and removed by existing sedimentation and filtration devices. It is usually preferred where the requirement for adsorptive removal of pollutants is intermittent or variable. It can be dosed individually as needed. Another application is its use in

emergency cases to remove refractory, hazardous or toxic substances that have escaped into a sedimentation tank, activated sludge tank or other vessel. PAC can also be added to the aeration basin of an activated sludge system where the microbiological processes are enhanced by the adsorption process. PAC adsorbents are typically used with a mixer-settler or slurry adsorber arrangement in combination with coagulation/flocculation agents, with the PAC being added in the flocculation, sedimentation, or filtration step.

88. Normally PAC is not regenerated but becomes part of the sludge to be disposed of.

89. Application limits and restrictions are given in Table 11 below.

Table 11

Application limits and restrictions associated with adsorption

| <i>Issue</i> | <i>Limits/restrictions</i> |
|------------------------------|---|
| TSS (Total Suspended Solids) | < 20 mg/l with fixed-bed adsorbers ⁽¹⁾ < 10 mg/l with moving-bed adsorbers ⁽²⁾ |
| Pollutant concentration | < 100 g/l (without adsorbent recovery) ⁽²⁾ < 500 g/l (with adsorbent recovery) ⁽²⁾ |
| Molecular mass | Decreased efficiency with low molecular mass |
| Length of carbon chain | Increased efficiency with increasing carbon chain (free oil does not adsorb) |
| Branching of carbon chain | Decreased efficiency with increasing branching |
| Polarity | Decreased efficiency with high polarity |
| Solubility in water | Increased efficiency with high solubility (free oil does not adsorb) |
| Degree of dissociation | Decreased efficiency with increasing dissociation |
| Macromolecules | Decreased efficiency with macromolecular structure |

Source: European Commission 2016

Advantages and disadvantages

Advantages

- High removal efficiency (not lignite coke) enables the removal of refractory and/or toxic organic compounds (GAC, PAC, lignite coke, resins)
- Usually low extra space requirements
- Systems automated
- Recovery of compounds possible (preferably with zeolites)

Disadvantages

- Mixtures of organic compounds may cause a significantly reduced adsorption capacity
- High content of macromolecular compounds decreases efficiency and may cause irreversible blockage of active sites
- Scouring effect in the activated sludge unit may cause a major erosion problem (PAC)
- Spent adsorbent must be regenerated (high energy consumption) or disposed of (potentially causing waste to be incinerated)

E. Factors Affecting Adsorption Performance and Cost

(a) Contaminant concentration: Competition for adsorption sites can reduce the effectiveness of adsorption if competing contaminants are adsorbed instead of, or in addition to, mercury resulting in a need for more frequent bed regeneration or replacement. In addition, the capacity of the adsorption media decreases with increasing contaminant concentration. High contaminant concentrations can exhaust the adsorption media quickly, requiring frequent regeneration or replacement.

(b) Fouling: The presence of suspended solids, organic compounds, and solids may cause fouling of adsorption media.

(c) Flow Rate: Increasing the flow rate through the adsorption media can decrease adsorption of contaminants and erode the adsorbent bed.

(d) Wastewater pH: The optimal pH to maximize adsorption of mercury by granular activated carbon is acidic (pH 4-5). Therefore, pH adjustment may be needed both before and after adsorption treatment.

(e) Spent Media – Spent media that can no longer be regenerated would require treatment or disposal.

F. Economics

90. Economics associated with adsorption are given in Table 12 below.

Table 12
Economics associated with adsorption

| | <i>Investment costs</i> | <i>Operating and maintenance costs</i> |
|-------------|---|--|
| GAC | EUR 50 000–1 000 000 ⁽¹⁾ EUR 0.3–0.5 per m ³ (for up to 1 000 m ³ /d) ⁽¹⁾ | EUR < 0.5 (for > 1 000 m ³ /d and without considering the regeneration of adsorbent) ⁽¹⁾ |
| Active coal | EUR 1.28–2.06/kg ⁽²⁾ | EUR 0.1/kg (removal cost for landfilling) ⁽²⁾ EUR 0.5/kg (removal cost as chemical waste) ⁽²⁾ |
| PAC | EUR 150 000 ⁽³⁾ | NI |

Source: European Commission 2016

91. Investment costs are relatively high for small units treating less than 100 m³ per day. However, economy of scale is possible for larger units. Economy of scale is also observed for the operating and maintenance costs. Operating and maintenance costs are related to the replacement of the adsorbent bed. The regeneration or the destruction of the adsorbent are more expensive than the treatment itself. As regeneration is relatively expensive, the technique is generally unattractive for highly contaminated streams that consume large amounts of carbon.

VI. Adsorption on chelating media

92. Chelating resins are resins with functional groups that form chelates (complexes) with metal ions, and they capture metal ions by forming chelates with specific metals. They are used to remove toxic metals such as mercury, copper, zinc, and cadmium, as well as to recover precious and valuable metals such as gold, platinum, and palladium.

93. Selective adsorption and removal of mercury is generally performed by resins with sulfur-containing chelate-forming groups such as thiol group (-SH), thiourea group (-NH · CS · NH₂), thiocarbamic acid group, and dithizone group. After filtering and separating suspended matter and insoluble mercury compound particles in wastewater, a small amount (about 5 mg/l) of chlorine is added under acidic conditions (pH 2~6) to completely ionize mercury and make the liquid pass through a reaction tower filled with chelating resin to adsorb and remove mercury. Since the sulfur functional group of the mercury chelating resin is sensitive to chlorine, the amount of chlorine added should be limited to 5 mg/l.

94. Chelating resins treat mercury in wastewater to less than 0.0005 mg/L and may last longer but are difficult and expensive to regenerate. Therefore, it is desirable to remove most of the mercury by the sulfide method in advance when the mercury concentration is high.

Table 13
Chelating resins

| Exchange group | Adsorbed ion | Feature |
|-----------------|--|---|
| Thiol system | Hg ²⁺ | <ul style="list-style-type: none"> ▪ Mercury can be selectively removed. ▪ Sensitive to oxidants since the chelate-forming group contains sulfur. |
| Thiourea system | Hg ²⁺ , Cd ²⁺ , Pb ²⁺ , Zn ²⁺ , Cu ²⁺ | |

95. Precious metals (gold, platinum, and palladium) can be adsorbed in addition to mercury.

96. The chelating resin adsorbs only mercury ions dissolved in water. Therefore, those that are not in the ionic form, e.g., metallic mercury form, need to be ionized by adding an oxidizing agent and dissolved in water to adsorb by chelating resins.

97. Factors affecting adsorption performance:

(a) The chelating resins cannot be used for oxidizing solutions since oxidizing substances will disintegrate the resin itself.

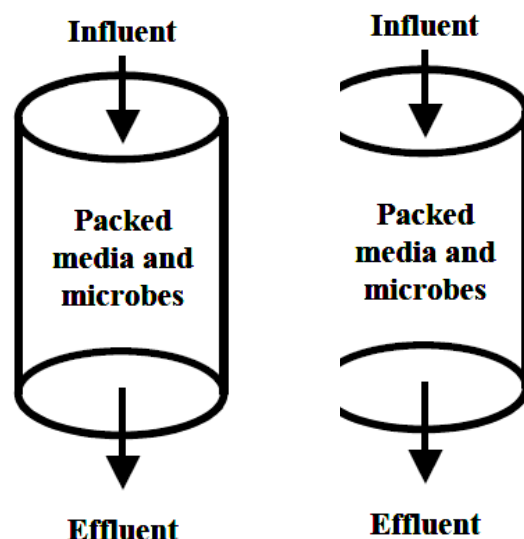
(b) Generally, chelating adsorption towers are installed in the last step of the process, as other potentially competing constituents in the waste water will then have been removed by previous steps.

VII. Biological treatment

98. Biological reduction of organic pollutants utilizes the metabolism of microorganisms to perform redox reactions rather than using chemical treatments. Biological treatment involves the use of microorganisms that act directly on contaminants or alter the surrounding conditions which lead to contaminant leaching from the soil or precipitating from water (US EPA, 2007). While mercury is an inorganic contaminant, biological treatment can be used to reduce hazardous soluble mercury compounds to less soluble forms in the wastewater, which can then be removed by additional techniques such as adsorption or precipitation (US EPA, 2007); (European Commission 2017a). This technique is based on reducing oxidised species of mercury to elemental mercury using microbial metabolism in anoxic or anaerobic conditions.

Figure 3

Model of a Biological Treatment System



99. Biological treatment is typically carried out in fixed-film bioreactors using activated carbon as a carrier for wastewater generated from the use of wet abatement systems in large combustion plants. The anoxic/anaerobic biological treatment for the removal of mercury is applied in combination with other techniques, such as adsorption on activated carbon (European Commission 2017a). Some coal-fired power plants use anoxic/anaerobic biological systems to reduce certain pollutants including ionic mercury and reported it to be more effective than sedimentation, chemical precipitation, or aerobic biological treatment processes (European Commission 2017a). On the contrary, biological treatment of mercury in the wastewater from chlor-alkali plants showed higher residual mercury concentrations than those of the other common abatement techniques (European Commission 2014).

100. Activated sludge systems combined with sludge incineration or waste gas treatment is another technique reported in the European Commission to reduce the mercury emissions to wastewater (European Commission 2016). Mercury can easily adsorb onto the sludge, which needs to be controlled if sludge is to be incinerated. However, there is no further information about the technique provided in the European Commission (2016).

A. Aerobic Biotreatment Process for Mercury

101. One process that has been applied at a pilot-scale project uses aerobic biological treatment to convert soluble ionic mercury (Hg^{2+}) into elemental or metallic mercury (Hg^0). This reaction is catalyzed by enzymes such as mercuric reductase, which is generated naturally in the cytoplasm of certain bacterial species. For example, certain strains of *Pseudomonas* are capable of reducing

mercuric ion to elemental mercury. The less soluble elemental mercury collects in the microbial mass as small droplets, which must be subsequently extracted using another technology.

102. Biological treatment technologies typically require amendments to create optimal growth conditions and provide nutrients to the microbial population. In the pilot-scale process, the treatment system includes pretreatment to adjust the pH to the optimal range of 6.5 to 7.5 using sodium hydroxide and phosphoric acid. An adequate amount of nutrient is required to support microbial growth. Nutrient additives used in this process include sucrose, sodium chloride (NaCl), and yeast extract.

103. The contaminated water is passed through a packed bed bioreactor. The reactor bed is usually made of materials suitable for microbial growth, such as silica (SiO₂) and alumina (Al₂O₃). Before treatment begins, the microbial inoculum is distributed throughout the bioreactor bed through a series of steps that involves pumping combinations of nutrients, microbes, and wastewater through the bed. After biological treatment, the bioreactor effluent is usually treated by activated carbon to remove residual mercury. The biological treatment process results in solid residuals consisting of dead bacteria and elemental mercury. (US EPA, 2007).

B. Aqueous Biocyanide Process

104. Another process that has been applied at a pilot-scale uses a series of aerobic and anaerobic biological treatment steps to remove mercury from wastewater. This process is designed primarily to treat cyanide in mining wastewaters, but also removes metals, including mercury. This process uses a fixed-bed reactor with a combination of microbes, including proprietary microbial cultures and microorganisms isolated from the contaminated wastewater. The equipment used in this process includes an aerobic unit and an anaerobic unit, each consisting of a microbial culture tank and a bioreactor vessel. The treatment process involves alternating cycles of treatment and inoculation with periodic flushing between the two cycles. Contaminated wastewater is passed through the aerobic fixed-bed reactor system made of porous ceramic medium. The effluent from the aerobic reactor is then passed through the anaerobic reactor. This biological process converts soluble forms of mercury into less soluble forms, such as sulfides and other mineral phases. However, the references used for this report did not contain more specific information about the mechanism of mercury removal in this process. (US EPA, 2007).

105. **Technology Description:** Biological treatment of mercury-contaminated wastes is catalyzed by microbial enzymes. In one process, the soluble, ionic form of mercury is aerobically converted to insoluble elemental mercury by an enzyme called mercury reductase. The less soluble elemental mercury must be extracted using another technology. In another process, a combination of aerobic and anaerobic treatment methods is used to convert soluble forms of mercury into insoluble mineral phases, such as sulfides. The effluent from the biological treatment system is normally subjected to further treatment by an activated carbon bed or precipitation before disposal.

- (a) Microbes Used:
 - i. Mercury-tolerant strains of *Pseudomonas* spp.
 - ii. Proprietary microbial cultures
- (b) Technology Types Used:
 - i. Fixed-bed aerobic bioreactor
 - ii. Fixed-bed bioreactors, with series of aerobic and anaerobic treatment steps
- (c) Media for Bed Packing:
 - i. Al₂O₃ and SiO₂
 - ii. Porous ceramic medium

C. Applicability, Advantages, and Limitations

106. Biological treatment of mercury involves conversion of soluble mercury into a less soluble elemental form or into insoluble mercuric sulfide. High concentrations of contaminants such as mercury or chlorine can inhibit microbial activity. Nutrients, pH, and temperature must be maintained at levels that optimize biological activity and growth. Pretreatment with pH amendment agents such as NaOH or H₃PO₄ is essential to maintain an optimal pH range. Nutrient additives such as sucrose, yeast, and NaCl may be required to support the growth of microbes. The bioreactor effluent typically

requires further treatment by methods such as activated carbon adsorption or precipitation to ensure residual mercury is removed before disposal.

107. Factors Affecting Biological Treatment Performance and Cost

- (a) **pH:** Neutral pH of 6.5 to 7.5 is optimal for aerobic biotreatment processes.
- (b) **Contaminant concentration:** High concentrations of mercury may be toxic to microorganisms used in biological treatment.
- (c) **Available nutrients:** The presence of sufficient amount of nutrients, such as sucrose and yeast extract, is crucial to the performance of a biological system because nutrients are essential for the growth of microorganisms.
- (d) **Temperature:** Lower temperatures (0 to 10 °C) decrease biological reaction rates. Heating may be required to maintain biological activity. Temperatures higher than 30 °C may be harmful to the microorganisms.
- (e) **Chloride concentration:** The presence of chloride at concentrations greater than 0.5 mg/L may inhibit microbial growth.

D. Achieved environmental levels

108. Performance information is available for one pilot-scale application for electrolysis wastewater from a chlor-alkali manufacturing plant and one pilot-scale application for metal mining wastewater. For the first one, the initial concentration of mercury ranged from 2,000 to 5,000 µg/L. The concentration of mercury in the effluent ranged from 30.7 to 40.7 µg/L. For the second, initial concentration of mercury ranged from 151 to 164 µg/L. The concentration of mercury in the treated effluent ranged from 3 to 11 µg/L. Although significant mercury reductions were achieved, this technology did not reduce the concentration to less than 2 µg/L in either of these applications. However, information on the treatment goals for these applications was not available, and these applications may not have been designed to treat mercury to less than 2 µg/L.

109. An innovative bioremediation process was tested at pilot scale to treat mercury in wastewater from the Echo Bay/McCoy Cove Mine (US EPA 2007). This project was evaluated by the U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program. The treatment method used is a proprietary process known as the Aqueous Biocyanide Process. This process consists of aerobic and anaerobic fixed-bed bioreactor units. This application of the Aqueous Biocyanide Process used microorganisms isolated from the mine stream in combination with proprietary microbial cultures. A biofilm of the microbial mass was formed on the reactor bed, which was made of a porous ceramic medium. This biofilm converted the soluble ionic form of mercury (Hg²⁺) into more stable mineral phases, primarily mercuric sulfide (HgS). The treatment process in this pilot test included aerobic and anaerobic pathways with the following three steps: (1) inoculation of the culture tanks with microbial cultures; (2) treatment of contaminated media fed into the inoculated tanks; and (3) flushing to remove process wastes from the culture tanks. Influent concentrations of mercury ranged from 151 to 177 µg/L. Final concentrations of mercury ranged from 3 to 11 µg/L. The information sources used for this report did not provide data about the total amount of waste treated during this project. The sources also did not provide information about the treatment goals for this project and the disposal methods for the flush water and treated effluent.

E. Membrane filtration

110. Membrane filtration can remove a wide range of contaminants from water. This technology has been used in a limited number of full-scale applications to treat wastewater contaminated with mercury. Before membrane filtration, a pretreatment step may be used to cause mercury to form precipitates or coprecipitates that can be more effectively removed by this technology. Membrane filtration can reduce concentrations of mercury to less than 2 µg/L (US EPA 2007).

F. Technology Description and Principles

111. Membrane filtration passes water through a semi-permeable, microporous membrane to concentrate contaminants into a smaller volume of water. This technology separates the influent into two effluent streams:

112. The permeate, or effluent stream, is the fluid that passes through the membrane. It usually contains reduced levels of contaminants. This stream may or may not contain contaminants at concentrations below the desired levels. If a reduction in concentration is still required, this stream

may be sent to additional treatment units. In the case study described later, the permeate is neutralized and sent to an equalization and disposal unit.

113. The concentrate, or reject stream, contains water and contaminants that have not passed through the membrane. The reject may be recycled back through the membrane filtration system to further concentrate the contaminant and reduce the volume of reject. If the concentrate is not recycled, further treatment may include processing in a filter press, as in the case study described later, or dewatering in solar evaporation ponds.

114. **Technology Description:** Membrane filtration separates contaminants from water by passing it through a semi-permeable barrier or membrane. The membrane allows some of the constituents to pass through while blocking others.

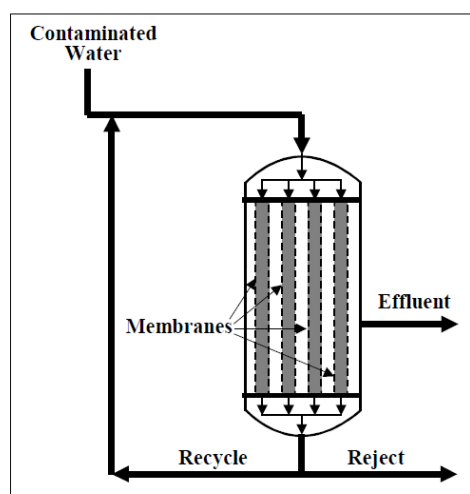
(a) **Media Treated:**

- i. Drinking water
- ii. Groundwater
- iii. Surface water
- iv. Industrial wastewater

(b) **Types of Membrane Filtration Processes:**

- i. Microfiltration
- ii. Ultrafiltration
- iii. Nanofiltration
- iv. Reverse osmosis

Figure 4
Model of a Membrane Filtration System



115. Membrane filtration processes vary based on the pore size of the membrane. The pore size is selected based on the molecular weight or size of the target contaminant and the pressure required to move wastewater through the filter. The four types of membrane filtration processes, from largest to smallest filter pore size, are:

- (a) Microfiltration
- (b) Ultrafiltration (UF)
- (c) Nanofiltration
- (d) Reverse osmosis

116. UF has been used in a treatment train with precipitation/coprecipitation to treat wastewater that contains mercury. There is no information on the use of microfiltration, nanofiltration, or reverse osmosis to remove mercury. Therefore, these technologies are not discussed in this technology summary.

117. UF units are used to remove oils, suspended particles, and biological solids. UF requires a pressure of 5 to 100 pounds per square inch (psi) to move the fluid through an ultrafiltration filter. UF filters can filter out contaminants with a molecular weight greater than 1000 g/mole.

H. Applicability, Advantages and Limitations

118. UF is primarily used to remove high-molecular weight contaminants and solids. This technology is usually preceded by precipitation/coprecipitation to cause the mercury species to form or adsorb onto a suspended solid because dissolved mercury species are typically too small to be effectively removed by UF. The energy required to operate membrane filtration units is related to the pressure requirements. This type of treatment may be run in either batch or continuous mode. This technology's effectiveness is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organic compounds, colloids, and other contaminants can cause membrane fouling.

Q. Achieved efficiencies

119. At a Hazardous Waste Combustor, ultrafiltration was included as part of a treatment train used to treat a variety of contaminants in wastewater generated by the APC equipment of a hazardous waste combustor. The wastewater treatment system included a primary and secondary treatment loop. The secondary treatment loop contained a stage for precipitation with sodium hydroxide followed by sedimentation and ultrafiltration. Analysis of samples collected at the influent and effluent of this treatment loop showed that the mercury concentration was reduced from 0.4 µg/L to below the detection limit of 0.2 µg/L.

120. Membrane filtration is effective for the treatment of mercury but is used less frequently because its costs tend to be higher, and it produces a larger volume of residuals than other mercury treatment technologies. In addition, it is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organic compounds, colloids, and other contaminants can cause membrane fouling.

Part II: Techniques for specific sources of releases

121. This part provides technical information on control techniques used to control releases of mercury to land and water from specific release sources, in line with Chapter IV of the BAT/BEP Guidance.

I. Releases from air-pollution-control systems

122. The following table, taken from European Commission (2017a), summarizes techniques for controlling water pollution from plants operating flue-gas treatment.

Table 14

Techniques for the prevention and control of water pollution from plants operating flue-gas treatment with emissions to water

| <i>Technique</i> | <i>Technical description</i> | <i>Achieved environmental benefits</i> | <i>Environmental performance and operational data</i> | <i>Crossmedia effects</i> | <i>Technical considerations relevant to applicability</i> | <i>Economics</i> |
|--------------------------------|--|---|---|---------------------------|---|------------------|
| 1. Mechanical treatment | | | | | | |
| Filtration | Separation of solids from wastewater effluents passing through a porous medium | Reduction of oil and solids in the wastewater discharge | NA | Sludge production | Generally applicable | Plant specific |
| Oil separation | Separation of oil and water by gravity | Reduction of oil in the wastewater discharge | | Sludge production | Generally applicable | Plant specific |

| <i>Technique</i> | <i>Technical description</i> | <i>Achieved environmental benefits</i> | <i>Environmental performance and operational data</i> | <i>Crossmedia effects</i> | <i>Technical considerations relevant to applicability</i> | <i>Economics</i> |
|--|---|---|---|---|--|------------------|
| 2. Physico-chemical treatment | | | | | | |
| Flocculation, sedimentation, precipitation, neutralisation | Addition of special chemicals to cause solids that cannot be separated by simple gravitational techniques to settle | Removal of fluoride, metals, TOC, suspended solids | NA | Sludge production | Generally applicable | Plant specific |
| Softening, crystallisation, evaporation | Crystallisation is closely related to precipitation. In contrast to it, the precipitate is produced on seed material such as sand or minerals | Reduction of the pollutants in the wastewater discharge. Avoidance of water discharge | | Concentrated wastewater or sludge production Energy consumption. | Applicable to ZLD (zero liquid discharge) system | Plant specific |
| Stripping | Wastewater is brought into contact with a high flow of a gas current in order to transfer volatile pollutants from the water phase to the gas phase | Reduction of ammonia content in wastewater | | Transfer of ammonia to air by stripping | Applicable if high ammonia content in wastewater because of SCR/SNCR | Plant specific |
| Ion exchange | Removal of undesired or hazardous ionic constituents of wastewater and their replacement by more acceptable ions from an ion exchange resin | Removal of ions and ionisable species from wastewater | | Sludge and brine production | Generally applicable | Plant specific |
| Reuse of water | Mixing the wastewater from wet flue-gas desulfurization for ash transport, by-products, etc. | Avoidance of water discharge | NA | Stabilised material can be used as filling material in opencast mines | Applicable to plants close to opencast mines | Plant specific |
| Water recycling | Return of wastewater to the production process | Reduction of water discharge | | High salt content in water discharged | Generally applicable. Compulsory for soft water used as make-up water for wet flue-gas desulfurization | Plant specific |
| Biological treatment | Degradation of dissolved organic substances with microorganisms | Reduction of organic content, nitrogen and | EPA-821-R13-002 | It may contribute to the release of odours and | Nitrification may not be applicable in the case of high chloride | Plant specific |

| <i>Technique</i> | <i>Technical description</i> | <i>Achieved environmental benefits</i> | <i>Environmental performance and operational data</i> | <i>Crossmedia effects</i> | <i>Technical considerations relevant to applicability</i> | <i>Economics</i> |
|------------------|-------------------------------------|--|---|---------------------------|---|------------------|
| | (i.e. bacteria) as oxidising agents | metals in wastewater | | volatile substances | concentrations (i.e. around 10 g/l) | |

123. Under the EU Industrial Emissions Directive, the Applicable Emission levels associated with the best available techniques (BAT-AELs) for direct discharges to a receiving water body from flue-gas treatment: 0.2–3 µg/l

(a) Concentrations, expressed as mass of emitted substance per volume of water.

(b) BAT-AELs refer to daily averages, i.e. 24-hour flow-proportional composite samples. Time-proportional composite samples can be used if sufficient flow stability can be demonstrated.

124. As indicated in the US EPA Effluent Limitations Guidelines and Standards Database (US EPA ELG) for Steam Electric Power Generating, the BAT limits for FDG wastewater are ranging between 0.034-0.356 µg/l (monthly average) and 0.103-0.788 µg/l (daily maximum) expressed in concentration.

II. Oil and Gas

125. European Commission (2015) provides information on techniques used in wastewater treatment plants for cooling water, process water, sanitary sewerage water, storm water, etc., at oil and gas refineries. It includes information on techniques used to treat wastewater and average range of the water effluents from European refineries, mostly gathered in 2008 – 2010.

126. The report concludes that the BAT to reduce the load of pollutants in the wastewater discharge to remove insoluble and soluble polluting substances by using all the techniques given below:

(a) Removal of insoluble substances by recovering oil

(b) Removal of insoluble substances by recovering suspended solids and dispersed oil

(c) Removal of soluble substances including biological treatment and clarification

127. The report concludes that the Applicable Emission levels associated with the best available techniques (BAT-AELs) for mercury in direct waste water discharges are 0.0001 - 0.001 mg/l

128. As indicated in US EPA Effluent Limitations Guidelines and Standards Database (US EPA ELG) for Oil and Gas Extraction, BAT mercury limitation is 1 mg/kg dry weight (instantaneous maximum) for offshore drilling fluids and drill cuttings and coastal drilling fluids, drill cuttings, and dewatering effluent (expressed in quantity).

III. Primary mercury metal production

129. Mercury mines pose an environmental concern because of the presence of mine tailings, commonly termed calcines, and waste rock that contribute mercury-enriched sediment to watersheds. At some mines, mine drainage that is often acidic and that contains elevated levels of mercury and other metals also impacts water quality and biota. Mercury ores consisting primarily of cinnabar are processed in rotary furnaces and retorts and elemental mercury is recovered from condensing systems. During the roasting process mercury phases more soluble than cinnabar are formed and concentrated in the mine tailings. Differences in mineralogy and trace metal geochemistry are reflected in mine drainage composition. Mercury and methylmercury concentrations in mine drainage are relatively low at the point of discharge from mine workings. The concentration of both mercury species increases significantly in mine drainage that flows through and reacts with calcines.

130. Besides this, during the process of mercury purification wastewater and sludge are generated and discharged into primary treatment (sedimentation). Overflow is further discharged into an evaporation pond. After liquid components are removed, mercury rich solids are returned from both the sedimentation and the evaporation pond to the rotary kiln for mercury extraction. Wastewater and sludge from metallurgical production are separated from other industrial effluents of the plant. For instance, the concentration of Hg in wastewater released from the metallurgical plant from Khaidarkan Mercury Mine is 0.020 µg Hg/l.

131. As indicated in the US EPA Effluent Limitations Guidelines and Standards Database (US EPA ELG) for Ore Mining and Dressing, the BAT limits of Hg concentration in mercury ore production are:

- (a) for mine drainage - 0.001 mg/L (monthly average) and 0.002 mg/L (daily maximum)
- (b) for mill discharge where annual precipitation exceeds evaporation - 0.001 mg/L (monthly average) and 0.002 mg/L (daily maximum)

IV. Non-ferrous metals industry

132. European Commission (2017b) notes that the most appropriate treatment technique or combination of different treatment methods can only be chosen on a site-by-site basis by considering the site-specific factors, including:

- (a) the process that generates the waste water;
- (b) the amount of water;
- (c) the pollutants and their concentrations;
- (d) the possibilities for internal reuse; and
- (e) the availability of water resources

133. The document summarizes techniques for wastewater treatment as follows:

Table 15
Summary of advantages and disadvantages of common wastewater treatment techniques

| <i>Treatment technique</i> | <i>Advantages</i> | <i>Disadvantages</i> |
|----------------------------|--|--|
| Precipitation | Cheap and simple technique Long history of successful use Does not require large expenditure in a new plant Capable of treating a wide range of metal contaminants particularly if two-stage precipitation with hydroxide and then sulfide reagents is used Under the correct conditions, can give excellent removal of metals Specified precipitants are commercially available Allows absorptive precipitation Precipitates can often be returned to the feed | Acid effluents can be difficult to treat Non-selective: gives a high water content sludge that contains a cocktail of toxic and non-toxic metals The sludge may have to be disposed of, sometimes at great cost The presence of other salts, organic complexing agents and solvents can severely compromise the precipitation efficiency Cannot always be used to treat low concentrations of metals Some hydroxides inefficiently precipitated |
| Sedimentation | Cheap and simple technique; Long history of successful use | Can only remove solid particles For particles with a small density difference to water, sedimentation takes a long time and large basins are required |
| Filtration | Cheap and simple technique Long history of successful use Filtration (e.g. sand filter) is best used for a known solid matter | Can only remove solid particles The filtration efficiency decreases if the particles are very small Filtration efficiency decreases with increased velocity |
| Flotation | Cheap and simple technique; Long history of successful use | Can only remove solid particle complexes that are floatable Air needs first to be dissolved in pressurised water to be dispersed |
| Ultrafiltration | Simple technique Very fine particles, even molecules, can be removed from the wastewater Very fine membranes will also filter solutes as small as metals Virtually zero solids emissions | Limited flow rate and filtration velocity Membranes can quickly decompose in corrosive effluents No separation of metals Old membranes can leak Membranes can be easily fouled |
| Electrolysis | Can be used to recover and recycle metals Can be used to treat concentrated metal effluents (about 2 g/l) in a single step | Better than ppm level of clean-up is difficult Ineffective cells are expensive to maintain and operate Electrolysis not selective |

| | | |
|-------------------------|---|--|
| | Technology mostly available Tried and tested with good track record in electroplating industries Can be used to clean up organic contaminants simultaneously Can be used in batch or continuous flow modes | Needs constant monitoring Poor at treating variable content, high-volume effluents |
| Electrodialysis | Can be used to recover and recycle metals Can be selective Already used in desalination and electroplating industries Capable of sub-ppm level of clean-up | Suffers from the same disadvantages as ion exchange methods (e.g. membrane fouling) Needs constant monitoring Poor at treating variable content, high-volume effluents |
| Reverse osmosis | Virtually zero emissions Technology exists and equipment is commercially available Can be used for recycling metals Can be operated in continuous flow or batch mode Can deal with a large range of metal concentrations Can be used to remove organics in effluent Efficacy is not strongly dependent on the concentration of non-corrosive contaminants in effluent | Limited flow rate and filtration velocity Membranes can quickly decompose in corrosive effluents No separation of metals Old membranes can leak Membranes can be easily fouled Membranes need frequent monitoring and replacement Equipment is specialised and expensive Uses high pressure Restriction of a minimum flow rate of approximately 200 l/min Concentrated bleed is produced that needs further treatment |
| Ion exchange | Relatively inexpensive Commercial products available Tried and tested in industrial applications (e.g. rhenium and selenium removal and recovery) Capable of clean-up to ppb level (selective ion exchange capable of ppt level) Can be easily used in conjunction with other techniques (e.g. precipitation) as part of an integrated waste water treatment Can be selective for metals Can be applied to many flow types: intermittent, continuous, relatively large volume Selective ion exchange has been used in isolated cases, such as the treatment of nuclear industry effluents | Cannot handle large concentrations of metal Matrix easily fouled by solids and some organics Traditional ion exchange is not selective Exhausted exchanger must usually be disposed of as toxic waste Matrices can decompose over time Performance is sensitive to effluent pH Large-volume effluents require very large ion exchange columns Selective ion exchange has not been extensively used on an industrial scale to date Regeneration of selective ion exchange columns is time-consuming Long contact times with effluent may be needed |
| Activated carbon | Can be used for a wide range of applications (e.g. the removal of mercury or PCDD/F from effluent) Can be added after coagulation and sedimentation as a layer in sand filters Technology exists and equipment is commercially available | Activated carbon is expensive Activated carbon can become a breeding ground for microorganisms High emissions of SO ₂ generated from the heating process in manufacturing carbon from coal |

134. European Commission (2017b) concludes that that the Applicable Emission levels for mercury associated with the BAT as a daily average for direct emissions to a receiving water body from the production of copper, lead, tin, zinc (including the wastewater from the washing stage in the Waelz kiln process), cadmium, precious metals, nickel, cobalt, and ferro-alloys:

- (a) Copper production: 0.005–0.02 mg/l
- (b) lead, tin, zinc, cadmium, precious metals, nickel, cobalt, and ferro-alloys: ≤ 0.05 mg/l

135. As indicated in the US EPA Effluent Limitations Guidelines and Standards Database (US EPA ELG) for Ore Mining and Dressing⁴, the BAT limits of Hg concentration for copper, lead, zinc, gold, silver, platinum, and molybdenum ores production are 0.001 mg/L (monthly average) and 0.002 mg/L (daily maximum) for the following processes:

⁴ Title 40 Code of Federal Regulations Subchapter N Part 440 ("40 CFR Part 440), US Environmental Protection Agency, 1988

- (a) mill discharge from froth-flotation process alone, or in conjunction with other processes;
- (b) mine drainage or mill discharge from dump, heap, in-situ leach or vat leach processes to extract copper from ores or ore waste materials where annual precipitation exceeds evaporation;
- (c) mill discharge from cyanidation process to extract gold or silver where annual precipitation exceeds evaporation;
- (d) mine drainage and open pit or underground operations and except placer deposits.

V. Management of Waste from Extractive Industries

136. European Commission (2018) covers wastes resulting from the prospecting, extraction, treatment, and storage of mineral resources and the working of quarries. It only covers:

- (a) extractive waste from onshore oil and gas extraction, including drilling muds, flow back water and well completion fluids;
- (b) extractive waste from quarrying;
- (c) extractive waste from peat extraction;
- (d) extractive waste besides extractive waste from mineral processing and extractive waste from excavation, such as sludge from decantation processes applied in the management of extractive waste.

137. The document includes information on wastewater management techniques being used, levels of mercury in such wastewater, and BAT conclusions on the management of extractive waste influenced water.

VI. Chlor-alkali Production

138. European Commission (2014) contains information on wastewater management techniques used in chlor alkali plants, levels of mercury in wastewater, and BAT conclusions.

139. Mercury-contaminated wastewater includes:

- (a) the process wastewater: brine purge, (back)washing water from brine purification, condensate and wash liquor from the treatment of chlorine and hydrogen, condensate from caustic concentration units, brine leakage, ion-exchange eluate from process-water treatment;
- (b) the wash water from the cell cleaning operations: inlet and outlet boxes;
- (c) the rinsing water from the cell room: cleaning of the floors, tanks, pipes and dismantled apparatuses;
- (d) the rinsing water from maintenance areas outside the cell room if they are cleaned with water.

140. Techniques to reduce mercury emissions and releases include:

- (a) Management system, including:
 - (i) detailed service routines;
 - (ii) training and motivation of personnel;
 - (iii) mercury balance to better understand mercury consumption and emission levels, including:
 - a. use of a recognised standard methodology;
 - b. purging of all equipment where mercury may accumulate before making the balance, if possible;
 - c. accurate inventory of mercury in cells and in store;
 - d. use of high-performance monitoring systems.
- (b) Suitable cell room that is:
 - (i) equipped with a smooth, crack-free, light-coloured, and impervious floor that is sloped towards open floor gutters;

- (ii) well-lit to enable easy identification and clean-up of spills;
 - (iii) free of obstructions and debris that may absorb mercury and/or hinder the clean-up of spills;
 - (iv) avoiding equipment where mercury may accumulate (e.g. hang cable trays vertically);
 - (v) connected to a wastewater treatment system.
- (c) Monitoring and leak detection/repair, including:
- (i) continuous mercury monitoring in the cell room;
 - (ii) leak detection using equipment sensitive to hydrogen;
 - (iii) scheduled programme of preventative maintenance for seals and valves;
 - (iv) immediate repair of identified leaks, if possible.
- (d) Cleaning and recovery of mercury, including:
- (i) immediate isolation of recovered mercury in closed vessels;
 - (ii) immediate removal of mercury spillages by using vacuum cleaners equipped with activated carbon filters;
 - (iii) daily cleaning of the floor by gentle flushing with water; avoidance of high-pressure washing due to the potential formation of micro droplets of mercury.
- (e) Storage of mercury and of waste contaminated with mercury in suitable areas (see description of cell room above);
- (f) Process-integrated techniques during normal operation to stabilise operating conditions and to reduce the frequency of cell opening, including:
- (i) use of high-purity salt;
 - (ii) verification and cleaning of inter-cell buses for good current distribution;
 - (iii) monitoring of mercury pressure and flow;
 - (iv) optimisation of mercury quantity in cells;
 - (v) adjustment of anodes over different cell segments;
 - (vi) computerised control of electrode gap, current and voltage;
 - (vii) computerised system for tracking the life of cell components;
 - (viii) graphite reactivation without opening the decomposer, if possible, for example by treatment with sodium molybdate, ferric sulfate or cobalt.
- (g) Process-integrated techniques during maintenance and repair operations to reduce mercury evaporation, including:
- (i) scheduled programme of preventative maintenance;
 - (ii) detailed service routines for cell dismantling;
 - (iii) reduction of duration of cell opening by ensuring the availability of personnel and spare parts, including a spare decomposer completely assembled with carbon, if possible;
 - (iv) suitable working areas (see description of cell room above);
 - (v) cell cooling during maintenance;
 - (vi) avoidance of use of rubber hoses for mercury transfer, as they are difficult to decontaminate;
 - (vii) removal of all residual visible mercury by using vacuum cleaners equipped with activated carbon filters;
 - (viii) cleaning of the cell bottom with an alkaline sodium peroxide solution and water; check cleaning operation with portable mercury analysers;

- (ix) avoidance of stepping into the cell bottom, as shoes are difficult to decontaminate;
 - (x) covering of all equipment from which mercury may evaporate, in case of interruption of operation.
- (h) End-of-pipe techniques, including:
- (i) mercury removal from process exhaust originating from:
 - a. closed end-boxes and separate end-box ventilation;
 - b. vacuum cleaners;
 - c. mercury pump seals;
 - d. brine circuit and salt dissolver;
 - e. mercury distillation/retorting;
 - (ii) mercury removal from hydrogen;
 - (iii) mercury removal from waste water;
 - (iv) mercury removal from caustic soda.

141. An overview of techniques applied by two plants that achieved low mercury emission levels from 2005 to 2011 is given in Table 16 below. These two plants were put into operation around 1970. Since beginning operation, the operators took the abatement of mercury emissions into consideration. The low emission levels were achieved by implementing a variety of techniques and continuous improvements.

Table 16
Overview of applied techniques and mercury emission levels at the two plants from 2005 to 2011

| <i>Mercury source</i> | <i>Applied techniques</i> | <i>Residual mercury concentration (annual average)</i> | <i>Flow</i> | <i>Hg emission/loss in g/t annual chlorine capacity (annual average)</i> | <i>Recipient medium</i> |
|--|--|--|--------------------------------|--|-------------------------|
| INEOS ChlorVinyls plant in Stenungsund (Sweden) | | | | | |
| All sources | Detailed service routines Training and motivation of personnel Continuous mercury monitoring Computerised control of current and voltage Vacuum salt | NA | NA | NA | All |
| Waste water | <u>Treatment with hydrazine, followed by sedimentation, sand filtration and activated carbon filtration</u> | < 20 µg/l (in waste water) | <37 000 m ³ /yr | 0.00–0.01 | Water |
| | Total | | | 0.13–0.18 | Air, products and water |
| Solvina plant in Antwerp-Lillo (Belgium) | | | | | |
| All sources | Detailed service routines Training and motivation of personnel Continuous mercury monitoring Computerised control of current and voltage Adjustment of anodes over different cell segments Monitoring of mercury flow | NA | NA | NA | All |
| Waste water | <u>Treatment with sulfide, followed by sedimentation and sand filtration</u> | < 20 µg/l (in waste water) | < 1 000 000 m ³ /yr | 0.01–0.04 | Water |
| | Total | | | 0.26–0.45 | Air, products and water |

NB: NA = not applicable; NI = no information provided.

Source: [55, Euro Chlor 2014], [116, Euro Chlor 2013]

142. The document concludes that BAT-AELs for mercury emissions to water, expressed as Hg, at the outlet of the mercury treatment unit during decommissioning or conversion, are 3 – 15 µg/l in 24-hour flow-proportional composite samples taken daily.

143. In the US EPA Effluent Limitations Guidelines and Standards Database (US EPA ELG) the BAT Mercury Limitations for Chlor-alkali production (Mercury Cell Process) are 0.1 g/t of product (monthly average) and 0.23 g/t of product (daily maximum), expressed in quantity.

VII. Waste Incineration

144. European Commission (2019) contains information on wastewater management techniques used in waste incineration plants, levels of mercury in wastewater, and BAT conclusions.

145. The document covers wastewater from the flue-gas cleaning, as well as other wastewater including the following:

A. Bottom ash collection, treatment, and storage

146. Wastewater from ash handling activities can normally be reused as the water supply for a wet bottom ash discharger, so it will not need to be discharged. It is, however, important to have sufficient storage (and treatment) capacity to cope with fluctuations in storage levels caused by rainfall. Generally, the treatment options for excess water are: discharge to an available process waste water treatment system; discharge to the local sewerage system; and/or special disposal. This type of waste water can be reused in the FGC system if the quality is suitable, generally after treatment by sedimentation, filtration, etc.

B. Boiler operations

147. Wastewater from the boilers (resulting from the preparation of boiler feed water and boiler drainage) can normally be reused in the incineration and FGC system so it will not need to be discharged. However, the recycling of wastewater to the FGC system is only possible in the case of semi-wet or wet systems if the quality is suitable; otherwise, the waste water is discharged (mainly due to the high salt content).

C. Sanitary wastewater

148. This originates from toilets, kitchens, and cleaning. It is normally discharged to the sewerage system, for treatment in a municipal wastewater treatment plant. A septic tank may be used if connection to the local sewage system is not possible. As this category of wastewater is not specific to waste incineration, it is not discussed further in this document.

D. Clean rainwater

149. This arises from rain falling on unpolluted surfaces, such as roofs, service roads, and parking places. Normally this 'clean' water is collected separately from process water and discharged directly to the local surface water or via soakaways. Pre-treatment may be required for rainwater from roads or parking areas.

E. Polluted rainwater

150. This arises from rain falling on polluted surfaces, such as unloading areas. It is usually segregated from clean rainwater and may be treated before use or discharge.

F. Cooling water

151. By far the largest cooling capacity is required where water condenser cooling is used, *i.e.* for electricity production with a steam turbine. Depending on the design of the plant, various cooling water streams will need to be disposed of, including:

- (a) water from convection cooling of the condenser, which is connected to the steam turbine;
- (b) water drained off from an evaporation cooling water system;

(c) water from various other pieces of equipment which require cooling; waste chute, hydraulic systems, strippers, etc.

152. These cooling water streams are not specific to waste incineration; they are described in the Reference document on the application of Best Available Techniques to Industrial Cooling Systems, published in December 2001

G. Condensed wastewater from the partial pre-drying of sewage sludge

153. This type of wastewater is specific to sewage sludge incineration, although it does not arise in all cases, as the steam generated during drying is sometimes evaporated with the incinerator flue-gas instead of being condensed. It generally has a high chemical oxygen demand (COD) and contains substantial concentrations of nitrogen (mainly NH₃), as well as other pollutants that were originally present in the treated sludge. The high nitrogen content can form a bottleneck for treatment; in this case stripping of nitrogen may be used, although there may be a risk of fouling and additional energy requirements for its operation. A solution in this case may be recycling into the furnace when the recovered ammonia solution (concentration approximately 10 %) can be used for SNCR (selective non-catalytic reduction) de-NO_x feed. At the NL05 sewage sludge incineration plant, high amounts of volatile fatty acids (VFA) were found in the condensed wastewater from the pre-drying of sewage sludge. Since VFA can interfere with the stripping of nitrogen, the condensate is treated in the on-site wastewater treatment plant.

154. Mercury in the effluent originates from mercury contained in the waste. It is common practice that incinerators apply an input limit for the content of mercury in the waste incinerated.

155. For one plant incinerating hazardous waste and equipped with wet gas scrubbing, it is calculated that the total mercury input via the waste amounts to 2,000 kg/yr for an incineration capacity of 100 000 t/yr. Taking into account a maximum yearly emitted mercury flow via the waste water of less than 4 kg/yr, a removal efficiency higher than 99.8% can be reached based on M-trimercaptotriazine precipitation and subsequent efficient removal of the precipitate.

156. The emission levels generally range between close to the limit of quantification and 0.006 mg/l as an average and 0.027 mg/l as a maximum. Higher emissions have been reported by 10 plants, possibly associated with other than-normal operating conditions of the wastewater treatment plant and, in some cases, with inconsistent use of the units when reporting the data to express the concentration of this pollutant.

157. The document concludes that applicable BAT-AELs for emissions to water: 0.001–0.01 mg/l expressed mass of emitted substances per volume of wastewater. In cases where an operator demonstrates that the achievement of these BAT-AELs would lead to disproportionately higher costs compared to the environmental benefits, *e.g.* to the technical characteristics of the installation concerned, the applicable emission limit value for discharges of waste water from the cleaning of natural gas is 0.03 mg/l for mercury

158. As indicated in the US EPA Effluent Limitations Guidelines and Standards Database (US EPA ELG), the BAT Mercury Limitations for Commercial Hazardous Waste Combustor (wastewater) are 1.3 µg/l (maximum monthly average) and 2.3 µg/l (daily maximum), expressed in concentration.

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⁵ In this document, the BAT Reference Documents are referred to as European Commission, without the name of the individual authors.