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Guidelines on Best Environmental Practices for the environmental sound management of mercury contaminated sites

Centro Tecnológico Nacional
de Descontaminación
del Mercurio

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Foreword

These Guidelines have been commissioned by MED POL and the Regional Activity Center for Sustainable Consumption and Production (SCP/RAC) of the Mediterranean Action Plan (MAP/UNEP) to the Spanish National Technological Center for Mercury Decontamination (CTNDM), which counts with a vast technological experience in mercury management and offers scientific and technological support to eliminate the hazards related to the presence of mercury in products, emissions and wastes.

The Guidelines have been prepared by Manuel Ramos, Javier Carrasco, Ana Conde and Engracia Delacasa, from the CTNDM and from Minas de Almadén (MAYASA), with collaborations of Marc Pujols and Gracia Ballesteros from ACUAMED; Antoni Malet and Antonio Caprino from SOLVAY IBÉRICA, and Josep Maria Chimenos from the University of Barcelona.

The Directorate General for Risk Prevention (Service of Technological Risk, Management of Contaminated Sites) of the French Ministry of Ecology, Sustainable Development and Housing, and the Waste Agency of Catalonia have contributed with comments and suggestions.

The coordination and technical supervision was ensured by SCP/RAC.

1. Introduction

In general, a *contaminated site* is a place where there is an accumulation of toxic substances or residues which may affect the soil, groundwater, sediments and even air in the case of mercury to levels that pose a risk to the environment or human health or be above the safe limits recommended for a specific use.

Metallic mercury is a liquid at room temperature, the only metal with this property and also evaporates at room temperature. Mercury is one of the most problematic toxic substances that may be found at contaminated sites: the special physical and chemical characteristics of mercury make a challenge the management of mercury contaminated sites, especially when it comes to remediate large industrial sites and mercury mining sites. Due to its properties, once mercury has entered the environment, it remains there adopting different physical and chemical forms reaching all of the environmental compartments to a greater or lesser extent: air, soil, water, sediments and even the buildings used for the activity.

Inorganic mercury can be transformed by bacteria into methylmercury in sediments and soils, at a rate depending of the physic-chemical characteristics of the soil. Methylmercury (CH_3Hg+) is a highly toxic bioavailable form of organic mercury and cumulative throughout the food chain. Consumption of fish and shellfish poisoned by direct dumping of methylmercury in the wastewater from a chemical factory in the Minamata bay (Japan) during decades was the cause of one of the worst episodes of chemical pollution recorded in the past century.

The three major forms (speciation) that can be found in the environment are:

- Metallic mercury (Hg°), in liquid and gas equilibrium depending of the temperature.
- Inorganic mercury (Hg^{2+}, HgO, $HgCl_2$, HgCl…) [1]
- Organic mercury (CH_{3}-Hg-CH_3, CH_{3}-Hg-NH_2, CH_{3}-Hg-SH…)

Various activities have led historically to mercury-contaminated sites, generally as a result of lack of environmental regulations, use of pollutant technologies and poorly waste management practices. These activities mainly include: mercury mining and quarrying[2]; the chlor-alkali industry; coal-fired power-plants; cement industry; production of pig iron, steel and non-ferrous metals; the waste sector; the production of chemical substances, chemical fertilizers, pharmaceutical products and catalysers; batteries and fluorescent lights.

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[1] Mercury can easily change its chemical state in the environment because of the low Hg2+/Hg° standard potential, thus causing drastic changes in its mobility and toxicity.

[2] The most common ore form of Hg is cinnabar (HgS). It has been exploited in the Mediterranean region mainly in Spain and also in Algeria, Slovenia, Turkey and Italy.

Currently the most important source of emission of mercury in the Mediterranean region are the coal-fired power plants[3].

Remediation of a contaminated site is a corrective measure to mitigate or eliminate the pollution. The first step towards achieving this is to thoroughly examine the origin, extent, type and amount of existing contamination. Once these parameters have been defined, the next step is to determine how and to what extent the environment and human health is or may be affected. Finally, and only after having investigated the aforementioned aspects, corrective measures should be proposed and adopted to remediate safely the environmental damage and limit or eliminate the risk of the contamination to any environmental vector and to the human health.

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[3] “Diagnosis of Mercury in the Mediterranean Countries”. CP/RAC, 2010.

2. International Legislation

2.1 Minamata Convention on Mercury [4]

The Minamata Convention on Mercury provides for control and reductions across a range of products, processes and industries where mercury is used, released or emitted.

With regard to contaminated sites, the global Convention on mercury shall adopt guidance on managing contaminated sites, but does not pose an obligation on remediation of contaminated sites.

The parties are encouraged to cooperate in the formulation of strategies and the execution of activities to identify measure, classify depending on priorities, manage and, as appropriate, remediate contaminated sites.

2.2. Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean (Barcelona Convention)

2.2.1 **Common Measures**, adopted in the 5th Conference of the Parties (1987) of the Barcelona Convention.

- The maximum concentration of mercury in effluent before dilution in the Mediterranean Sea is 50 µg/l.
- New outlets for mercury-containing effluents in the Mediterranean Sea should be designed and constructed to prevent an increase of mercury concentration in the biota and sediments to above 50% of the background level in a 5 km radius from the discharge point.

2.2.2 Regional Plan on the reduction of inputs of Mercury (2012).

In the framework of the implementation of article 15 of the Protocol of Land Based Sources of pollution, the Mediterranean Action Plan (MAP) of the Barcelona Convention adopted in 2012 a legally binding text in order to reduce Mercury pollution, by which the Parties should establish limits of emission (ELVs) to different industrial sectors, among other measures.

An inventory of contaminated sites - including mercury mines and chloralkali facilities which use or have used in the past mercury cells-, has to be forwarded to the Secretariat of the Barcelona Convention. The countries have also to **identify and envisage appropriate measures for these sites.**

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[4] Open for signature in 2013 and enter into force in 2018

2.3. European Union Legislation

2.3.1 Surface water and Groundwater

2.3.1.1 **Council Directive 98/83/CE** of 3 November 1998, on the quality of water intended for human consumption. Sets a limit for Mercury of 1 microgram per litre.

2.3.1.2 **Directive 2006/118/EC** of 12 December 2006, on the protection of groundwater against pollution and deterioration.

- Indicates criteria for assessing good chemical status of groundwater.
- Set the threshold values of the analytical parameters.
- Mercury is included in the minimum list of pollutants or groups of pollutants and indicators of pollution that member states should establish.

2.3.2 Soils

2.3.2.1 **Council Directive 86/278/EEC** of 12 June 1986 on the protection of the environment, and in particular of the soil when sewage sludge is used in agriculture.

2.3.2.2 **Council Directive 91/156/EEC** of 18 March 1991 establishes the obligation to draw up inventories of contaminated sites.

2.3.2.3 The thematic strategy for soil protection, ***Communication COM[2006]231-final***, includes concepts like:

- the establishment of a legal framework to protect and use the soil sustainably;
- the integration of protection policies;
- the identification of risk areas
- the inventory of contaminated land and facilities
- the restoration of degraded soils.

2.3.2.4 The implementation of the Strategy and ongoing activities since 2006 were presented in document **COM (2012) 46 final**.

2.3.2.5 **Directive 2010/75/EU** on Industrial Emissions (IPPC). The industrial activities dealing with hazardous substances will have to establish through a baseline report the state of soil and groundwater before the start of activities and after the cessation of the activities.

2.3.2.6 **Directive 99/31** on landfill of waste. The operator shall be responsible for the maintenance, monitoring and control in the after-care phase for as long as may be required by the competent authority, taking into account the time during which the landfill could present hazards. In some countries this period is not inferior to 30 years.

2.3.3 All media

Regulation EC no.166/2006, concerning the establishment of an European pollutant release and transfer Register (E-PRTR), setting as compulsory to inform on emissions to air, water and soil above given limits.

2.3.4 Health and safety at work

Commission Directive 2009/161/EU establishing a list of indicative occupational exposure limit values.

2.3.5 Transport of hazardous waste

2.3.5.1 **Basel Convention. Draft updated technical guidelines for the environmentally sound management of wastes consisting of, containing, or contaminated with mercury or mercury compounds** (Draft of 20 November 2014 - Rev.35)

Mercury wastes should be transported in an environmentally sound manner in order to avoid accidental spills and to track their transportation and ultimate destination appropriately. Prior to transportation, contingency plans should be prepared in order to minimize environmental impacts associated with spills, fires and other emergencies that might occur. During transportation, such wastes should be identified, packaged and transported in accordance with the “United Nations Recommendations on the Transport of Dangerous Goods: Model Regulations (Orange Book)”. Companies transporting wastes within their own countries should be certified as carriers of hazardous materials and wastes, and their personnel should be qualified and certified as handling of hazardous materials and wastes as required by national or local legislation. Transporters should manage mercury wastes in a way that prevents breakage, release of their components into the environment and exposure to moisture.

2.3.5.2 European Agreement concerning the **international carriage of dangerous goods by road (ADR)**

2.3.5.3 **Regulation EC 1013/2006** on shipments of waste specifies the procedures for controlling waste shipments to improve environmental protection.

2.3.5.4 **Directive 2008/98** on waste (Framework Directive), includes the conditions for transportation of waste, including minimum standards of transporters.

3. Identification of mercury-contaminated sites

The first step is to produce a census of current and former industrial sites that hosted industrial activities likely to have used - intentionally or unintentionally - mercury in the process or be emitted or dumped into the environment (see list of activities in the introduction). To this list, sites can be added for which analyses and diagnoses revealed the presence of significant mercury anomalies in the soil, air, water, sediments. To detect these anomalies, it is necessary to compare the results found on the site with those of natural or anthropogenic geological background.

The realization of studies on the site to characterize the pollution in its breadth and scope is a critical phase to define the actions to undertake cleanup activities later.

To characterize the pollution it should be established:

- What are the forms of mercury present (metallic mercury, methyl mercury …);
- The amount of mercury;
- What are the environmental compartments impacted;
- What is the extent of the contaminated area;
- The behavior of mercury in environmental compartments;
- What are the consequences of the pollution, both in and out of the site.

Several tools can be implemented on the site:

- Historical studies, literature and recollection of memories from workers may reconstitute industrial and environmental practices in the site to target potentially polluted areas and type of pollutants potentially present.
- The hydro-geological studies will show the soil characteristics (granulometry, composition of soil and rock, fragmentation areas..) and underground hydrological networks (flow direction of the water, connection between groundwater tables, depth, variation in levels of the groundwater table..). This helps to identify potential transfer and the possible pollution extent.

Information gathering will also seek to identify issues to protect in the site and if the pollution exits the site: local population, uses of the environment (orchards, fishing, water consumption, swimming areas, walking areas ...), media exposure, and the protection of natural resources.

The program of investigations conducted on the site defines environmental compartments and study samples to be taken in order to ultimately develop the conceptual site layout. The latter can map the relationships between the sources of pollution, the various transfer media and issues to protect.

The environmental compartments to be studied are water (surface, groundwater); biota (fish, plants,..); soil, soil gas and sediments and air.

The sampling and analyzes have to be performed according to the protocols and standards. In the case of mercury pollution, it is convenient to associate each sampling with a collection of field observations and measurements of parameters to be able to assign bias indices to the results. These observations or parameters taken into consideration may be:

- In the air: temperature and internal pressure, temperature and pressure of the outside air.
- In the soil: environment in the area of sampling (sub-slab, bare soil, grassy floor, soil with nearby trees...), soil type (natural, backfills, lithology, homogeneity/ heterogeneity, granulometry, moisture, etc.) soil temperature, ambient air temperature, pH, Eh, dissolved oxygen, organic content (TOC), iron, sulfates, major element and/or traces characterizing the geochemical background, chlorinated solvents (HVOC, chlorinated monocyclic aromatic compounds, total hydrocarbons, etc.), types of bacteria present in the soil (anaerobic, aerobic ...)
- In the soil gas: temperature and pressure of the soil, temperature and air pressure outside.
- In the water: pH, Eh, dissolved oxygen, electron acceptors (nitrates, nitrites sulfates, iron and manganese), content of chlorides, COD.
- In sediments: pH, Eh, sulfides / sulfates, Total Organic Carbon (TOC), granulometry.

If there are droplets of mercury in soil or sediments, the results may be biased depending if the droplet is taken or not in the sample, especially if the weight of the sample is very small. Sampling sizes should be carefully considered in this case to minimize this risk. A good safety measure to validate the results is to include also sampling and measurements of soil gas.

During analysis of mercury in the sample, it is necessary to perform mercury speciation, which will let to have a precise evaluation of the toxicity, lability and the associated risks. The speciation will distinguish the different forms of mercury present: total mercury, dissolved elemental mercury, dissolved reactive mercury, gaseous mercury Hg °, particulate and colloidal mercury.

Taking into account that metallic mercury is the most present form (99%) in the air and soil gas, the speciation in the samples should preferably be carried out in water - groundwater and surface water -, soil and sediments.

Sampling is described in more detail in chapter 5.

3.1 Stage I: Preliminary report on the situation

The preliminary report should contain a theoretical model of the mercury-contaminated site that draws on all of the previously known information. Data on the following aspects will be gathered during this stage:

- ✓ The location, surface area, and details of the physiographic region of the site.
- ✓ Historical records of the site and the surrounding area (climatology, etc.).
- ✓ Past, current and future uses of the place.
- ✓ Analytical data from previous studies.
- ✓ A survey of the site and the nearby area.

One important tool that helps to identify, quantify and characterize the contamination is a list of the activities and processes that have taken place on the site associated with mercury use and the estimated amount of mercury-containing wastes.

Once these factors have been identified, stage II should be carried out. This stage involves the drafting of a more detailed additional report to assess the degree of mercury contamination.

3.2 Stage II: Additional report

This report will contain the information required to draw conclusions and determine **whether or not** a more in-depth analysis is needed.

It is advisable to carry out a preliminary site inspection to meet three specific objectives: **a) describe the site**, **b) examine the type of contamination produced** by the mercury and **c) define the mechanisms of mercury mobility and the points of exposure**.

If detailed studies of the site are required, the environmental characterization stage will be carried out (Chapter 5).

The three specific objectives are discussed in more detail below.

3.2.1 Description of the site

This should include generalities on the location of the site, climatology, hydrology, hydrogeology, the demography of the area (size and distance from the nearest population), and potential environmental affection.

The report should include at least the following data:

- **Location**. A complete description of the location of the site and access to it. Geographic information on the site. Potential movement of the material deposited there, the production processes carried out, the source of mercury waste, amounts of waste, etc.

- **Form and structure of any facilities**. Geometric characteristics, the building system and sequence, an estimation of the volume of material, the boundaries of the site and the uses of the immediately adjacent area.

- **Climatology**. A complete description of the climate using all available data, the average seasonal temperature, the annual rainfall and its distribution, the maximum precipitation, the predominant wind direction and seasonal wind patterns.

- **Geology of the area**, to discover the geological formations and the rocks found at the site, along with their characteristics.

- **Edaphology and land uses**. A complete description of the kinds of soil at the site, along with the soil characteristics and the land uses: industrial, agricultural, livestock farming, forestry, crop types, etc.

- **Surface drainage network**. A description of the fluvial flow throughout the year, permanent or seasonal rivers.

- **Socioeconomic aspects**. The demography and economy of the area.

3.2.2 Type of contamination

Unless chemical analyses have been carried out, it is difficult to accurately determine which contaminants are present at a site. However, during a site visit, it is possible to define with sufficient clarity the type of mercury contamination that has taken place. To achieve this, it is essential to find out about the activities and processes carried out in the area of interest, through interviews with the local authorities and with the population of the surrounding area. Information that is gathered in this way must always be summarized and filtered, particularly if the polluting activity was halted a long time ago.

The site should be defined in as much detail as possible in relation to the geometric and physical characteristic of the structure or structures that could potentially produce the contamination.

3.2.3 Identify the mechanisms of mercury mobility and points of exposure

A description of the site and of the type of contamination will enable us to predict the mechanisms of mercury mobility and the environmental compartments that are affected, where applicable. A good selection of points of exposure is extremely important, as environmental sampling should be comprehensive.

During the first site visit, the specialist in charge of the study should also define the areas in which there is no evidence of contamination. These areas will be used to take reference samples, which will serve to ***establish the natural or background level of mercury in the study area.***

A preliminary precautionary decision can be made to limit access and uses of the potentially contaminated area if knowledge of points of exposure gained in this first visit leads to the conclusion that there may be an exposure risk for people or animals. **The relevant local authority must be informed of this decision.**

The advisability of the measure can be reviewed later when the results of the analyses are available.

4 Identification of environmental impacts

National environmental safety and protection criteria should be used as a reference to identify environmental impacts at the contaminated site.

If no specific regulations exist, the principle of prudence should be considered in the study of the mercury-contaminated site. In this case, applicable published data, recommendations and international guidelines should be used as a reference. The conclusions obtained in this way and the decision of the relevant authority/ies will enable future actions to be evaluated.

As mercury is mobile, environmental impacts should be assessed in the various environmental compartments to determine the following risks.

Hydrological risk:

- Alterations in natural surface drainage and contamination of river beds due to runoff and leachate from the contaminated site.
- Changes in the courses of streams adjacent to the site due to the accumulation or piling up of material in the beds, which may cut off the natural flow or be washed away in a flood and pollute the downstream.

Atmospheric risks:

- Resuspension or reemission of particles of dust from the mercury-contaminated site that are carried by the winds.
- Regasification and release of mercury present in piled up or contaminated materials, due to seasonal changes in temperature.

Changes in soils:

- Occupancy by accumulation of materials.
- Nearby soil affection by dispersion of materials from the contaminated site, the deposition of dust or the runoff of rainwater.

Impact on vegetation and wildlife:

- Affection of plant species from the area and movement of wildlife to adjacent habitats.

Morphology and landscape:

- Visual impact on the main basins in the natural landscape due to the effect of piling up of material, lack of vegetation or colour changes.

5 Environmental characterization of mercury-contaminated sites

The selection of the environmental compartments that should be sampled will depend on the characteristics of the contaminated site or location: each site is different, so criteria that apply to one might not be applicable to another. In some places, surface water and sediment should be sampled; in others soil sampling may be sufficient; and in yet others emissions should be measured and soil, surface water and groundwater should be sampled.

When mercury contamination is detected at a site, it should also be sought in the surrounding area. Sampling should be carried out both ‘inside’ and ‘outside’ the site, to assess the possibility that the contamination affects adjacent surroundings.

However, in all cases, it is essential to obtain a reference sample to determine the background levels of mercury. If the site is in a mining area, a great deal of caution must be taken in defining the **reference level**. The mineral deposits could extend beyond the limits of the mine, due to the continuation of the geological formation that contains the deposit. Thus, high metal content results could be obtained that are not strictly due to the mining activity. In these cases, special attention should be paid to soils and aquifers.

Sampling

Sampling and analyses are essential elements in the assessment of mercury-contaminated sites.

The tasks of sampling, analysis and monitoring should be carried out by qualified professionals, in accordance with a well-thought-out plan, using widely accepted methods. The same methods should be used throughout the programme.

In addition, rigorous quality assurance and control measures should be applied. Sampling and analysis errors or deviation from the standard operating procedures could produce data of no value or even data that are detrimental to the programme.

The methods available for sampling, analysis and monitoring vary widely, depending of the different physical and chemical forms of mercury that can be present in a contaminated site. The OECD series (http://www.oecd.org/chemicalsafety/testing/) contains information on good laboratory practice that should be used. In addition, the WHO and UNEP document *Guidance for Identifying Populations at Risk from Mercury Exposure* contains useful information to follow on general methodological aspects.

The media to be sampled to assess mercury contaminated can be liquids, solids and gases:

a) Liquids:

- Leachates from landfills and deposits.
- Liquid collected from spills.
- Water (surface water, groundwater from wells and springs, drinking water and industrial effluents).
- Biological material (blood, urine, hair; particularly when the health of employees is being monitored).

b) Solids:

- Products and compounds that consist of mercury, that contain mercury or are contaminated with it.
- Solids from industrial treatment or elimination processes or sources (airborne ash, deposited ash, sediments, other waste, etc.).
- Containers, equipment or other materials: pipes, vessels, contaminated fabric and clothes, contaminated material used in packaging and wrapping, etc
- Soil, sediments and organic matter.
- Rubble, walls, floors, etc. from industrial facilities.

c) Gases:
- Air.

Analyses

In order to obtain significant, acceptable results, the analytical laboratory should have the required infrastructure and proven experience with the matrix and type of mercury to be analyzed. One excellent way to verify the validity of results is the participation in an inter-laboratory comparison programme.

Methods to analyse the various matrices of mercury may assess the total mercury content or the speciation of mercury. Some have been defined by the International Organization for Standardization (ISO) and the European Committee for Standardization (CEN). Other national methods have been drawn up, such as those of the United States (EPA) or Japan.

The following criteria must be met to obtain high quality results:

a) Specification of the analytical technique.
b) Maintenance of the analytical equipment.
c) Validation of all of the methods used (including the laboratory’s own methods).
d) Training of laboratory staff.

The various steps in analytical determinations are as follows:

a) Extraction
b) Purification
c) Identification with suitable detectors, such as inductively coupled plasma, atomic absorption spectroscopy, compact instruments, etc.
d) Quantification and notification of data, as appropriate
e) Presentation of reports, according to the established quality procedure

In addition, procedures such as homogenization and acceptance criteria for handling and preparing samples in the laboratory should be established.

5.1 Characterization of surface water and groundwater

Analysis of water samples is usually carried out in the lab rather than in the field. However some field testing is possible. Use of Teflon bottles washed with HCl acid is recommended as a good means of preventing cross contamination. Ensure the acid used is mercury-free, as acids can serve as a source of various contaminants, including Hg.

Speciation in water is an important topic for the understanding of mercury behavior in the environment and for the treatability of water contaminated with mercury. Various forms of Hg arising from various means of treatment of the water sample have to be distinguished (e.g. filtration of sample and treatment with BrCl yields information on $Hg_D = Hg°+ Hg_R + Hg_C$; however acid digestion followed by analysis yields information on $Hg_T = Hg_P+Hg_D$):

- Hg_T = total
- Hg_P = particulate
- Hg_D = dissolved Hg
- Hg_R= reactive
- Hg^o = gaseous
- Hg_C = colloidal / residual

Analysis of water samples for methyl-Hg may be accomplished with the use of isotopic tracers and GC-ICP-MS analysis.

5.1.1 Surface water

The mercury content of surface water at the contaminated site and in the surrounding area should be studied, as water may act as a pathway for the dispersal of contamination by leaching from the site.

To determine the impact of the contaminated site on surface water, an analysis will be carried out upstream of the supposed mercury point source and downstream of all the possible points of exposure. This analysis should focus on points at which the water is used for human consumption, recreation, cleaning clothes, etc.

Unfiltered samples are generally used to analyse surface water. In addition, mercury sampling must be carried out in ***all of the seasons***, that is, in periods of rain and drought, heat and cold.

Whenever a body of surface water is analysed, information should be gathered on the **sediments**. For this purpose, simple and surface samples (0-5 cm) should be taken at places upstream and downstream of the pollution point source.

In areas where contamination is found in water, it is important to know if the aquatic fauna is fished for food, in order to assess the possibility of fishing restrictions.

Once the drainage network has been defined in the additional report, a sampling campaign should be designed for liquids and solids (sediments). The aim is to assess:

1- the water quality in the area surrounding the site;
2- the sediment quality in stream beds in the area;
3- whether sediments are affected by contaminated material or by the contaminant itself carried by the water.

The following tasks should be carried out to design the sampling campaign:

- Inventory of surface water points.
- Field survey of all the types of water points.
- Selection of sampling points and the period (or periods) most suitable for carrying out the sampling, depending on the climate.
- Establishment of background mercury levels in the area. Sampling points should be selected upstream of the study area, to assess the levels of mercury present before the water reaches the polluted area.

Mercury levels in surface water that are above the limits established for water for human consumption (1 µg/l) should generally be sufficient to merit an in-depth analysis of the source. Such levels could be proof of contamination or due to natural enrichment.

5.1.2 Groundwater

Aquifers are one of the media that are most vulnerable to contamination in hazardous sites. Therefore, they should be monitored not only by means of man-made wells, but also through samples collected from springs and other natural underground water sources.

Hydrogeological studies should be carried out in the study area, and should include some of the following activities:

a) The design of a preliminary scheme for hydrogeological conditions in the area, including the creation of an inventory of water points (water catchment points and springs in the area).
b) Field survey of all the water points. The following data should be gathered: construction characteristics, extraction capacity, piezometric level and physicochemical characteristics of the water.
c) Selection of sampling points and the period or periods that are most suitable for carrying out the sampling, depending on the climate.

When required by the size and complexity of the situation, additional information may need to be gathered through the following activities:

d) Test drilling around the site through structures and formations of hydrogeological or hydrochemical interest. This will reveal changes in the piezometric level and enable the detection of vertical gradients.
e) Hydraulic characterization tests in areas not investigated by the test drilling, to determine the permeability of the main structures in the area through the different rocks.
f) Hydrochemical sampling along the test drill holes by clogging stretches to reveal the chemical characteristics of the underground flow at different depths of water upstream and downstream of the pollution point source.

Due to the natural variability in aquifers, they ***should be analysed at least three times a year*****,** depending on the local climate.

The following parameters should be measured in the water:

- Parameters measured in situ:

  - Temperature
  - Conductivity (salinity)
  - pH (acidity)
  - Dissolved oxygen
  - Eh (redox potential)

- Concentrations of metals:
  - Mercury
  - Arsenic
  - Barium
  - Chromium
  - Iron
  - Nickel

In addition to these analytical determinations, other tests can be carried out according to the type of production process that generated the mercury deposit, and the expected composition of the pollution point source.

Likewise, other measures can be implemented to determine the presence of anions such as sulphates, nitrates, nitrites, carbonates and ammonium.

Mercury levels in aquifers can only be compared with reference values (for example, those of the US-EPA) when the ***analysed samples have not been filtered***. The analysis should also include samples from domestic taps, as the concentration of contaminant in taps could be different from the values found in a well or spring.

In all cases, mercury levels above the reference levels for human consumption (1 μg/l) should be analysed to determine their source.

Sediment samples will be treated as follows:

  - Dried at room temperature.
  - Sieved at 200 mesh size, ASTM (75 µm).
  - Analysed to determine the presence of metals, such as mercury, chromium, iron, nickel, lead, zinc, etc.

It is difficult to define the acceptable concentration limit for mercury in sediments. Samples need to be taken at points in the environment at which it can be guaranteed that there is no contamination. However, these sampling points must have geological substrates with similar characteristics to those in the contaminated site. Under these conditions, the average concentration values at the reference points plus twice the standard deviation (given a log normal statistical distribution) can be taken as a reference level or background.

5.2 Soils

Soils in the area surrounding the site should be characterized on the basis of the data collected in the additional report on:

- Road infrastructure (entrances, paths, roads in general).
- Land uses (agriculture and livestock, residential, etc.).

Before the soil sampling campaign is designed, a site survey should be carried out to take into account various factors, including:

- Geomorphology of the site.
- Topographical and geological characteristics, land uses, identification of escarpments, slopes, steeply sloping hillsides, instability, etc.
- Accessibility of the site and sampling areas.
- Identification of areas of natural ground and areas formed by backfill due to the movement of deposited materials. This point is of particular interest in the sampling of urban areas, where it is important to determine whether soil has been removed or mixed up by urban development works.
- Historical site uses (industrial process, tanks, pipelines, waste storage, landfill areas…)

On the basis of this information and data from the additional report, guidelines will be established for the sampling campaign. Contamination is mainly dispersed by wind, through resuspension and sedimentation of fine materials (generally the distribution is marked by the directions of the main winds in the area), and by surface water.

Taking into account the distribution of the winds and the surface water that runs through the site, a rhombus-shaped sampling grid should be established with sides measuring 50 by 50 metres. The grid should be symmetrical about the direction of the prevailing winds direction, as it is considered a priori that these winds will have the maximum concentration of suspended particles in the gradient of contamination. In addition to the aforementioned grid, a series of regularly spaced points should be sampled in a concentric pattern around the boundary of the contaminated site (at around 150 m from the source), to compare and assess the impact of non-prevailing winds on the movement of solid particles.

The soil samples should be taken at three levels: simple surface (0-5 cm), at a depth of 0.5 m, and from rock samples obtained in test drill holes, if applicable. The aim of sampling at the first two levels is to discover potential variance between surface and deep soils due to mercury enrichment caused by migration from soil and concentration in the contact surface with the bedrock. The in-depth network sampling can be done at half of the points and alternating them. The hydrogeological test drill holes can be used for sampling, which should be preferably of continuous recovery of core.

Sampling should be carried out during the cold period at sites that are frequently affected by snow, and during the rainy period at sites with high rainfall that are affected by floods or surface flows of water.

Surface soil sampling will be carried out by removing a thin layer of earth and then taking the sample with a clean spatula. The deep soil sample will be taken at the same point as the surface sample using appropriate sampling equipment (auger). Samples from mechanical boreholes can be taken from the core.

Each sample could weigh approximately one kilogram, of which a portion of around 100 ml will be taken for analysis. The rest of the sample will be kept referenced and storaged for further tests, if necessary.

The solid samples will be treated as follows:

- Dried at room temperature.
- Sieved at 200 mesh size, ASTM (75 µm).
- Analysed to determine the presence of metals, such as mercury, chromium, iron, nickel, lead and zinc.

As with the sediments, it is difficult to define the acceptable concentration limit for mercury in soil. Samples need to be taken at points in the environment at which it can be guaranteed that there is no contamination. However, these sampling points must have geological substrates with similar characteristics to those in the contaminated site. Under these conditions, the average concentration values at the reference points plus twice the standard deviation (given a log normal statistical distribution) can be taken as a reference level.

5.3 Characterization of air and food

5.3.1 Air

Mercury levels in ambient air should be considered because of the high dispersion and ease of evaporation of this metal. As mentioned above, sampling points should take into account industrial activities within and outside the site, as well as meteorological conditions.

There may be many sources of mercury in ambient air. However, high levels naturally indicate that there is mercury in the area. The measurement of mercury concentration in air is a rapid way to confirm the presence of the metal. This is because contaminants are commonly dispersed in air, but do not remain in it. As a result, levels drop once the source of contamination has been removed or reduced.

In its *Air Quality Guidelines for Europe*, the World Health Organization (WHO) established a guideline value of 1000 nanograms/m^3 (1 microgram/m^3) as an annual average for mercury in ambient air.

The United States Environmental Protection Agency (EPA) selected a reference concentration of mercury of 300 ng/m^3 for exposure in residential areas.

European Directive 2009/161/EU establishes maximum occupational exposure (8 hours per day) at 20,000 ng/m^3.

Modelling can be carried out to identify the most likely pollution point sources (samples of ambient air should always be taken). Air samples can be collected in 24-hour periods according to a schedule that takes into account the meteorological conditions throughout the year.

A detailed record should be kept of the meteorological conditions and all the activities that were being carried out in the area at the time of each sampling.

5.3.2 Food

The mercury content should be determined in plant and animal samples of the food produced in the area and other food that is frequently consumed by the population. Food generated by fishing and hunting should be included, as well as those from agricultural sources.

When sediments are contaminated, sampling should include species that are bottom feeders in rivers, streams and lakes. It is not as important to include fish that feeds in the water column.

According to the principle of precaution, the intake levels described in World Health Organization (WHO) recommendations should not be surpassed. In 2008, WHO published a guidance document http://www.who.int/foodsafety/publications/chem/mercury/en. to provide information on the potential impact of mercury exposure and to help, as much as possible, to identify at-risk populations.

In the guidance document, WHO indicates that two groups are particularly vulnerable to the effects of mercury. Foetuses are particularly sensitive to the effects of mercury. Intrauterine exposure to methyl mercury due to maternal consumption of fish (especially Tuna, Swordfish, Shark..) or seafood may damage a baby’s brain and nervous system. The main consequence of methyl mercury is potential disorders of neurological development. As a result, exposure to this substance during the foetal stage may affect a child’s cognitive ability, memory, concentration ability, language, fine motor skills and spatial and visual skills. Therefore, particular attention should be paid to pregnant women, breastfeeding women and women of childbearing age.

The second group is that of people who are systematically exposed (chronic exposure) to high levels of mercury. This group includes people with fish as staple food (subsistence fishing) or those individuals occupationally exposed.

As the population’s eating habits could mean that their mercury intake approaches the limits, it is advisable to restrict access to affected foods and even to regulate the use of the land and/or the types of crops that can be grown in the affected area, to ensure that the health of the surrounding population is protected.

6. Sample preparation and analytical procedures

A well-contrasted methodology is described in the following section, taking into account that other different techniques may be used depending on each specific case, the expertise of its analysts and the technical means available.

A. SAMPLE PREPARATION

a) Soils saturated with water and Sediments

Two alternative procedures are described, the drying of the sample at room temperature and the lyophilization.

a.1 Drying at controlled room temperature (max. 20-22 ° C)

1- If the sample is saturated with water, it should be filtered to separate the liquid phase. If the original sample is dry enough, then proceed directly with the homogenization phase (point 3). In any case, the humidity content of a sub-sample shall be determined in parallel in a kiln or in a thermobalance (see footnote 6).

2- The solid part is put over absorbent paper at controlled room temperature (not above 20-22 ° C), and it is weighed periodically until the weight becomes constant.

3- Homogenize the sample.

4- If no prior information about the approximate concentration of mercury is available, an option could be to run an ESCHKA5 analysis for guidance on the most suitable technique to determine the Hg content of the sample.

5- Perform the analysis depending on the expected concentration, with the guidance given later on in point B. For this, except when using the technique of pyrolysis, it will be necessary a prior dissolution of the sample. The most common procedure is the aqua regia attack, but there are other alternative methods depending on the characteristics of the sample.

- ISO 11466.3 (aqua regia)
- EPA 3050B (HNO3-H2O2-HCl).
- MICROWAVE ASSISTED ACID DIGESTION EPA 3015, 3051, SW 846

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[5] The method ESCHKA is based on the mercury amalgamation process on a gold plate. The soil sample is introduced in a porcelain crucible and covered first with a layer of iron powder and later with a layer of zinc oxide. Then, the porcelain crucible is covered with a gold plate. After that, the crucible is subjected to a calcination process and it leads to the formation of gaseous mercury which is fixed to the gold plate. The difference on the weight of the gold plate let us to determine the mercury contained in the soil sample. The measured range of mercury can be from around 0.2% to more than 30%.

6- Give the result referring to dry matter, with the moisture correction formula (see footnote 6)

a.2 Lyophilization

Lyophilization (freeze drying) is a method that minimizes the loss of volatile components, such as mercury, in the drying process of samples with humidity, being also very convenient for organic tissues (fish, shellfish, algae, etc). The result is a sample with a very low moisture content that can be directly analyzed. Lyophilization is especially suitable for small amounts of sample.

Laboratory device for lyophilization

b) Dry soil sample

1 - Dissolution of the sample, usually in aqua regia, except when using a pyrolisis technique.
2 - Make the corresponding analyses.
3 - Reference the results on a subsample dried at 105 ° C, as described above.

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[6] Moisture correction : The resulting concentration of mercury in the original sample, expressed on dry sample will be:

$$R = \frac{L}{1000} . \frac{b.F}{M} . \frac{100}{100 - H}$$

R: concentration of mercury on dry solid sample mg/kg (ppm)
L: mercury concentration in the solution analyzed (micrograms/liter)
b: final digestion volume in mililiters.
F: dilution factor of the digestion, if any
M: weight of original solid sample digested, in grams.
H: value of loss at 105 ºC, in % of original sample.

c) Determination of Hg in liquid samples

For the analysis of mercury in liquid samples, the measurement is made directly (prior to vacuum filtering with filter size of 0.20 microns) depending on the expected range of mercury (see point B).

B. MOST COMMON ANALYTICAL PROCEDURES

1. For solid samples with mercury concentrations above 300 ppm, the exact concentration of mercury can be determined directly following the ESCHKA method (see footnote5)

2. For solid samples with a mercury concentration between 20 and 300 ppm, the exact concentration of mercury can be directly determined by pyrolysis of the sample (ie the RP-91C attachment from LUMEX company is intended for decomposition of a sample and the reducing of mercury from the bound state into an atomic state using the pyrolysis technique) and subsequent analysis by atomic absorption spectrophotometer.

3. For samples with a mercury concentration between 0.05 to 20 ppm, the exact concentration can be determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry), also referred to as Inductively Coupled Plasma Optical Emission Spectrometry (ICP -OES), performing a pre-digestion of the sample in an acid mixture.

4. Alternatively, for more than 1 ppm of Hg, the technique of cold vapor system (CVAAS) with subsequent measurement by atomic absorption spectrophotometry (based on ISO 12846:2012), which is the most extended in the Laboratories, or its equivalents FIAS and FIMS can be used. Problems that may arise are that organo-mercury compounds will not respond to the cold vapor atomic absorption technique and possible interferences may appear with chlorides, iodides, sulfides, copper and VOCs. It is recommended first to eliminate organic bonds with aqua regia in solid samples and with digestion with nitric acid in liquid samples followed by an oxidization of all mercury to its bivalent state with permanganate or dichromate, and finally reduce as usual with borohydride or stannous chloride. A safe option would be the use of the method of standard additions to confirm the results, or to change the technique if the problems persist.

5. Solid samples with a concentration of less than 0.05 ppm mercury - although it can also be used for higher concentrations- can be analyzed directly without dissolution from the original solid sample by thermal decomposition (i.e. the RP-91C attachment from LUMEX company is intended for decomposition of a sample and reducing the mercury from bound state into an atomic state using the pyrolysis technique), then amalgamation with atomic absorption spectroscopy (ie the equipment AMA-254). The method is based on norm EPA 7473 SW 846.

   In any case, when the pyrolitic process is used and mercury is suspected to be bound in silicates or other matrices that may not thermally decompose, validation of direct analysis of the solid should be confirmed with total acid digestion with an appropriate method (such as method EPA 3052), followed by analysis with AMA-254 or other equivalent mercury analytical techniques.

7. Risk assessment

The Environmental Risk assesment (ERA) will help to answer the following questions:

- Does the site represent a real or potential risk to the human population and/or to the biota?
- What is the magnitude of the risk?
- Should the site be restored to reduce the risk?
- If the site is not restored, could the risk increase and/or spread?

ERA is a process that assigns magnitudes and probabilities to the adverse effects of contamination. Consequently, it is an instrument that can help to define whether or not environmental measures should be implemented at a contaminated site. Risk assessment can establish the urgency to act: the greater the risk of the contamination affecting living beings, the greater is the need to implement restoration programmes.

Risk assessment can be used to define remediation objectives for a site, which may be to reach (a) the maximum acceptable limits established by current legislation or relevant authorities or (b) specific limits set for the site on the basis of the assessment.

ERA constitutes a tool for deciding whether to carry out corrective actions at the contaminated site and for setting the final remediation objective, thus selecting the best clean-up strategies. The ideal objective is to restore the site and its uses with concentrations to the levels found in the environment prior to contamination through techniques described in point 7.1. However, this may be economically unfeasible and other options should be considered, as it is mentioned in that point.

The establishment of a **target clean-up level on the basis of a risk assessment** means that the contamination will be reduced to its maximum accepted level, which may be not necessarily zero (speciation, lability and biodisponibility of mercury are parameters that can be taken into account). Thus, at the end point, the residual concentration of the contaminant will not constitute a risk to the human population and biota.

Risk assessment can be carried out in four clearly defined stages with specific objectives:

1. Identification and characterization of what is at risk. All analyses of these characteristics should help to assess the risk to human health and to ecosystems.

2. Analysis of the hazard level and toxicity. The aim of this stage is to identify elements or compounds that may be critical; to characterize the kind of effects they may have; and to evaluate dose-effect relationships, in order to predict the response to the

contaminant for a wide range of doses. This analysis is based on contaminant data and characteristics, referring to its environmental and toxicological behaviour.

3. Analysis of exposure. The aim is to estimate the rate of contact with the identified contaminants. The analysis is based on a description of exposure scenarios, as well as characterization of the nature and extent of the contamination.

4. Analysis of risks. The results of the previous stages are combined to objectively estimate the likelihood of adverse effects on the protected elements under the specific conditions of the site.

Other contaminants besides mercury may have an impact. Therefore, if there is evidence that other contaminants are present at the site, the responsible of the process must take the decision to include them in the study and assessment.

7.1 Characterization of toxicological effects

This section of the risk assessment evaluates and describes the effects of the significant contaminant (mercury) on the receptors identified through the different exposure routes.

Contamination receptors that are frequently at risk in mercury-contaminated sites are:

7.1.1 Humans

In humans and some animals, the potential effects and symptoms of mercury intoxication vary according to the chemical form of mercury, the exposure route (inhalation or ingestion) and the exposure dose, including the exposure time and the concentration of the mercury.

For all the inhabitants of an area where a mercury-contaminated site is located, the main potential exposure routes are as follows:

- Breathing (absorption by inhalation) of mercury and/or dust.
- Eating (absorption by ingestion). It is considered that mercury ingested in food is mainly in the form of methylmercury (an organic compound of mercury).
- Dermal contact.

7.1.2 Terrestrial animals

In general, the symptoms of intoxication reported in animals for cases of mercury poisoning are not specific and depend on the exposure route, as in humans.

7.1.3 Aquatic biota

Many factors influence the potential toxicity of mercury in aquatic biota. These include the form of mercury, the developmental stage of affected organisms, and the chemistry of the water.

Changes in temperature, salinity and the hardness of the water also alter the toxicity of mercury to the biota.

It is widely accepted that the most toxic form of mercury is **methylmercury**. Reducing conditions (i.e. low-oxygen concentration) are needed for methylation to occur. It is well known that bacterial action promotes methylation, which is the main process responsible for the transformation of inorganic mercury to an organic formulation able to enter throughout the food chain.

In aquatic systems, fish are the main receptors of mercury through ingestion, as they are exposed to mercury both in water and through the ingestion of plants and macroinvertebrates.

Fish and macroinvertebrates like shellfish can also absorb mercury through the gills.

Macroinvertebrates may also be exposed to mercury in sediments, as are species of fish that feed on material deposited on top of the sediments. Due to their position at the top of the food chain in aquatic systems, it is assumed that fish have the highest concentration of mercury of all kinds of aquatic biota.

7.1.4 Plants

Plants are generally not sensitive to inorganic forms of mercury (i.e. elemental mercury and ionic mercury), probably due to the high level of absorption of the metal by soil particles. This largely prevents the absorption of mercury and toxicity in plants, which normally do not concentrate heavy metals[7], but show greater access to organic forms of mercury, such as methylmercury, than to inorganic forms.

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[7] Preventive Measures against Environmental Mercury Pollution and its Health Effects. Japan Public Health Association, 2002.

7.2 Evaluation of exposure

By this stage, we know the exposure routes, the receptors, the concentrations and the toxicity.

The evaluation of exposure consists in combining the results of the risk assessments for humans and ecosystems with dispersion studies to assess the degree of mobility of contaminants and to analyse concentrations in the different media that are affected.

The exposure sources that should be considered at a mercury-contaminated site are the media analysed in the environmental characterization, i.e: particles in suspension (PS), gas emissions, surface water, groundwater, soil and sediments.

7.3 Risk characterization

Risk characterization is the final stage in the risk assessment. During this stage, the probability of the occurrence of adverse effects due to mercury exposure is evaluated, and the bases are established for future actions.

In addition, data and conclusions from the stages in which the toxicological characteristics and the effects of the significant contaminant were reviewed are analysed together, along with the evaluation of exposure. All of these data are combined with the reasoning behind the proposed conceptual model.

For human health, the contaminant dose received by an individual (calculated on the basis of the characterization of the exposure scenario) is compared with the toxicological reference values set for this substance and population strata.

The following results should be obtained:

a. Conclusions on the actual risk of contamination at the site for human and ecosystem receptors, as well as the risk of dispersion (future risk).

b. Estimation of the level of uncertainty in the risk analysis, in order to accurately evaluate the conclusions of the characterization.

This stage can be carried out with the help of validated software to simplify the calculations, taking into account that its suitability should be justified for the specific characteristics and conditions of the site. Otherwise another method of calculation should be used. If software is used, screenshots of the process should be provided to confirm the values that were entered and the conclusions obtained.

Different approaches have been developed for the risk characterization stage, each one with its dedicated commercial software available, like:

-Risk-based corrective action (RBCA)
-Probabilistic risk assessment (PRA)
-Biotechnology-based direct toxicity assessment

8. Remediation of mercury-contaminated sites

Remediation measures for mercury-contaminated sites depend on various factors associated mainly with the location itself and with the potential impact on the environment and human health.

One or more remediation technologies can be considered, taking into account the results of the site study, the target clean-up levels, the capacity of the available remediation technologies, and the intended future use of the site.

The main factors that influence the selection of an initial set of treatment technologies are:

a) Receptors (surface water and / or groundwater, soil, air, biota, human..).
b) The (potential) mobility of mercury in the hydrological system.
c) The possibility of leaching of mercury from soil or sediments.
d) The pollution point source.
e) Mercury concentrations in human, animal and plant receptors, which indicate exposure levels.
f) The chemical states of mercury at the contaminated site.
g) Bioavailability to the aquatic biota, invertebrates and edible plants.
h) The amount of mercury released during the operations.
i) The possibility of mercury methylation.
j) Background mercury contamination, regional atmospheric deposition of mercury that is not associated with local sources.
k) The local/national clean-up regulations for water, soils/sediments and air.
l) In the case of mining operations, it is important to know precisely the geological formations that led to mercury extraction in order to not to include them as polluted soil due to the mining activities.

Once these factors have been evaluated, a more comprehensive analysis of the appropriate remediation techniques can begin.

Depending on the gravity, magnitude, degree and type of contamination by mercury and other pollutants and on the receptors, the recovery plan is likely to involve various remediation techniques or measures to reduce or contain the amount or toxicity of the contamination as effectively and efficiently as possible.

Below, some of the treatment options for mercury-contaminated media are described. These techniques can be used – alone or in combination - in the remediation of a contaminated site. In general, the aim of the techniques listed below is to recover the area by removing the mercury.

As mention in point 3.2.3, there is the possibility to restrict use of the contaminated area and limit access to it, at least until work can be started on recovery of the site.

Alternatively, a site can be contained by making it impermeable using natural materials such as clays or geosynthetic materials such as high density polythene sheets to prevent the evaporation and leaching of mercury.

In addition, waste can be transported for safe storage in landfills enginereed for this purpose.

Another option is to propose different treatments for each area or product in a mercury-contaminated area.

8.1 Treatment of mercury-contaminated effluents and soils[8]

Numerous techniques can be used to treat mercury-contaminated effluents. Some processes are merely physical (sedimentation), others are physicochemical (coagulation-flocculation, adsorption, etc.), yet others are chemical (oxidation-reduction, precipitation, etc.). The appropriate choice depends on various factors, mainly the speciation of the element and the presence of other agents.

Point 7.1.1 treats specifically groundwater and surface water remediation

a) Precipitation

Precipitation of mercury in the form of insoluble salts is one of the most common practices in effluent treatment.

The main precipitant is sulphide. Mercury sulphide is one of the most insoluble salts and is the form in which most of the mercury on the earth’s crust is found (cinnabar).

The optimum pH for the reaction is 7. The precipitate that is formed is then subjected to a sedimentation process, which can be assisted by the addition of flocculants. Mercury concentration values after sulphide precipitation are between 10 and 100 µg/litre.

This process has some disadvantages, such as the formation of high volumes of sludge that require subsequent treatment, and the formation of soluble species due to an excess of sulphide. Therefore, it is not the most suitable treatment for mercury-contaminated effluents.

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[8] (Source EPA 1997)

b) Adsorption

Treatments involving adsorption produce lower mercury concentration levels than those obtained by precipitation. As the concentration of the adsorbent increases, the levels of remaining mercury decrease. Other factors that affect this process are pH and mercury speciation.

The most commonly used adsorbent is activated carbon. This is generally in the form of granular activated carbon, in which the carbon has a relatively large particle size and can be used to fill columns.

c) Ion exchange

This is one of the main treatments for mercury-containing effluents. A wide range of resins can capture the different species of mercury. The technology is primarily designed to bind ionic mercury. It is not highly effective for organomercury compounds or elemental mercury.

The process is carried out in columns or tanks filled with the corresponding resin and equipped with systems for intake and outlet of the effluent, as well as clean water for rinsing, and regenerating solution.

Ion exchange systems have several advantages: they operate as needed, they are relatively insensitive to variability in effluent, they can produce zero concentration values, and a wide range of resins is available. The disadvantages include sudden exhaustion of the capacity, which means that the process must be monitored continuously, generation of a saline water effluent containing mercury, which must be treated, and potential problems when the process is used with water that contains a high level of total dissolved solids.

d) Oxidation – reduction

In some cases, oxidation and reduction processes are used to change the oxidation state of the mercury and thus promote its dissolution or decantation.

Oxidation is used in effluents that contain metallic mercury or organometallic compounds to transform them into the ionic form or to dissolve them as mercury halide. The process can take place in batch or plug flow reactors. Mercury salts separate from the matrix of waste materials and are then sent for further treatment, for example acid extraction or precipitation.

The most common oxidants are: sodium hypochlorite, ozone, hydrogen peroxide, chlorine dioxide and chlorine gas.
Reduction is used as a method for removing mercury in solution in the form of metallic mercury and then to sediment, filter or centrifuge it, for example. The most common

reducing agents are: aluminium, iron, zinc, hydrazine, stannous chloride and sodium borohydride.

The decontamination rate is high in reduction processes when the mercury concentration is relatively high (up to 2 g/l). However, the efficacy of the process drops when the levels of mercury are low. In this case, further treatment is required.

e) Others

Other methods for treating mercury-contaminated effluents have given good results like membrane separation processes (such as ultrafiltration and reverse osmosis).

Others, some in the experimental stage, are biological treatments (microorganisms that can absorb mercury or reduce it), liquid emulsion membrane extraction and solar photocatalysis with titanium dioxide.

8.1.1 Technology for groundwater and surface water remediation *(Biester, 2013)*

In many cases, contaminant removal may not be possible and hydraulic containment may be necessary to protect the surrounding environment. In these cases, the most currently applied technology for groundwater and surface water remediation is Pump & Treat (P&T). Basically, P&T systems involve the installation of extraction wells below the water table within or slightly down-gradient from the zone of contamination. As the mass of contamination remains in the subsurface, P&T systems must operate in perpetuity to prevent off-site migration. As extracted water must be treated at the surface, well placement and pumping rate should be chosen to ensure capture of contaminated groundwater and limit recovery of clean water. Monitoring wells have to be installed around the contaminant plume to assess containment and evaluate hydrogeochemical conditions.

For high concentrations of mercury**,** the treatment technologies are similar to mercury recovery processes of industrial liquid effluents as described before (mercuric brine of chlor-alkali waste water, etc,.). The treatment from bulk contaminated water enabling to reach concentrations below the remediation goals encompasses several treatment steps which may include for example: sulphuration, chemical reduction (hydrazine), co-precipitation and adsorption, ion exchange. These technologies are efficient for high concentrations (over 1 mg/L) and low flow rate (less than 10 m^3/hour). It is often applied in batch processor. It has to be considered that this low flow rate treatment may reduce the ability of the pumping to capture the contamination plume.

For low concentrations (< 10 µg Hg/l), the most advisable treatment technique is groundwater filtration with sulphur-activated granular carbon (see table below).

Most frequently applied filtration technologies to remove mercury from water (HPC AG Freiburg, 2011):

	Modified activated granular carbon	**Sulphur impregnated granular activated carbon**	**Ion exchange resins (e.g. Ambolite)**
Source of information	Supplier	Supplier	Supplier
Principle	Sorption	Ion exchange and sulphuric sorption	Ion exchange on thiol group (-SH)
Efficiency (µg Hg/l)	<1	<1	<1
Adsorption capacity (g Hg/Kg filtration media)	4 (3-5)	8 (5-10)	50
Costs (€ / Kg filtration media)	3,6	4,5	40
Specific cost (€ / g Hg)	0,9 (0,7-1,2)	0,56 (0,45-0,9)	0,8

The table above shows the low filtration capacity and adsorption capacity of GAC (Granular Activated Carbon). Furthermore, the sorption kinetic on GAC is low, thus reducing the flow rate for an efficient filtration and Hg removal from water. It has also to be considered that mercury is often associated with other organic and/or inorganic compounds in complex water matrix (high or low pH, high salinity) causing competitive sorption and drastic reduction of the efficiency of traditional GAC filtration.

Low kinetic and adsorption capacity associated with high specific cost cause high capital and O&M (Operation & Maintenance) costs for traditional remedy using ion exchange technologies and GAC.

In any case, mercuric wastes such as mud, filters, saturated granular carbon are produced which have to be managed like a mercury waste.

8.2 Treatment of mercury-contaminated solid waste [9]

Mercury-contaminated solid waste treatments have been classified into four categories:

a) Thermal treatments (retorting or roasting, among others)

b) Solidification/Stabilization (including amalgamation)

c) Washing/Acid extraction

d) Vitrification

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[9] Source: *Treatment technologies for Mercury in Soil, Waste and Water, EPA 2007*

a. **Thermal treatments** Thermal desorption and retorting are two common methods for full-scale thermal treatment of mercury-contaminated waste and for the treatment of soils and sediments.

   These treatments volatilize the mercury by low-pressure heat transfer, followed by condensation on a cold surface.

   Elemental mercury that is collected in this way can be reused in processes or stored. Off-gases should be treated to avoid emissions of mercury or other components.

   a.1 Retorting/roasting (Source: ITRC 1998)

   Pre-treated waste is sent to a desorber or retort where it is heated at low pressure to volatilize the mercury. Heating may be direct through contact with combustion gases or indirect through a metal wall (e.g. electrical heating).

   When desorbers are in operation, the waste inside them is agitated continuously. The movement increases heat and mass transfer, leading to higher evaporation rates. In contrast, waste in retort and roasting equipment is static.

   The most common desorbers are directly heated rotary kilns and indirectly heated screw systems.

   Direct heating systems require high volumes of combustion gases when a large volume of waste is treated. Consequently, complex control systems are required, and gas emissions must be treated. In these cases, the investment and operating costs could be much higher than in an indirectly heated system, in which combustion gas is not mixed with the hazardous waste.

   a.2 Gas treatment

   Gases from the retort system are filtered through fabric filters to remove particulate matter. Subsequently, the gas is cooled in a condenser to transform gaseous mercury into a liquid. The gas is then treated in control systems comprised of activated carbon filters and catalytic oxidants to capture any leakage of mercury vapour and organic volatile matter.

b. Solidification/Stabilization

Solidification and stabilization are physicochemical processes that tend to reduce the mobility of mercury to a certain extent by physically enclosing it (solidification) or forming chemical bonds with it (stabilization). Amalgamation, that is, the formation of a solid or semi-solid alloy of mercury with other metals, is a form of solidification.

There are two main solidification processes:

- Macroencapsulation: the encasing material is poured over and around the waste mass.
- Microencapsulation: the waste is mixed with the encasing material before solidification occurs.

b.1 Stabilization by Sulphur

This process consists of converting liquid mercury into mercury sulphide (HgS); a form that is the most insoluble and common in nature.

There are two crystalline forms of mercury sulphide: alpha HgS and beta HgS, both of which are practically insoluble and have a very similar solubility in water.

If waste contains elemental mercury, Hg is mixed with S at room temperature and agitated rapidly. The energy produced by mixing is sufficient to cause the activation. Alternatively, a reaction can be carried out between Hg vapour and S inside a mixer with an inert atmosphere, to prevent the formation of HgO.

Oxidation of mercury to HgO should be avoided, as this species is more soluble than the sulphur. Therefore, it is advisable to work in an inert atmosphere and to add antioxidants (Na_2S).

b.2 Sulphur–polymer stabilization

This is a modification of the sulphur process. It consists in stabilizing the mercury through a reaction with sulphur, followed by solidification/microencapsulation in a polymer matrix.
It is carried out in two steps:

1. Stabilization: Reaction between elemental mercury and sulphur polymer cement (SPC, a mix of 95% sulphur and 5% polycyclopentadiene).

2. Solidification (and microencapsulation): Heating to 135°C.

There are several advantages to this process: the product that is obtained is monolithic and has a low specific surface area. Hence it is less volatile and leaching is less likely.

b.3 Amalgamation

This process consists in the formation of a mercury alloy with other metals (amalgam). As the concentration of metal increases, the amalgam becomes more solid. The metals that are most frequently used are: copper, selenium, nickel, zinc and tin.

To accelerate the process, finely divided metals are added to the mercury.

b.4 Other stabilizing agents – solidifying agents

Other substances that are used as a medium in these processes are: cement, calcium polysulfide, chemically bonded ceramic phosphate, phosphates, platinum and polyester resins, among others.

Of the various matrices used in solidification processes, we can distinguish between those that require previous stabilization and those that do not. The distinction is based on the strength of the material, to ensure that mercury is not released.

c. Washing /Extraction

Soil washing and acid extraction are used for ex situ treatment of mercury-contaminated soil and sediments.

Soil washing is a water-based process that uses a combination of physical particle size separation and aqueous-based chemical separation to reduce contaminant concentrations in soil. This process is based on the concept that most contaminants tend to bind to the finer soil particles (clay and silt) rather than the larger particles (sand and gravel). Physical methods can be used to separate the relatively clean larger particles from the finer particles because the finer particles are attached to larger particles through physical processes (compaction and adhesion). This process thus concentrates the contamination bound to the finer particles for further treatment.

Commonly used methods for treating the wastewater include ion exchange and solvent extraction.

Acid extraction uses an extracting chemical such as hydrochloric acid or sulfuric acid to extract contaminants from a solid matrix by dissolving them in the acid. The solid and liquid phases are then separated using hydroclones, and the solids are transferred to a rinse system, where they are rinsed with water to remove entrained acid and contaminants.

The precipitated solids may require additional treatment or may be disposed in a landfill, and the acid extraction fluid and rinse waters are then treated to remove the heavy metals.

The principal advantage of soil whasing /acid extraction is that hazardous contaminants are separated from soils and sediments, thereby reducing the volume of hazardous waste to be treated / disposed.

The performance and viability of soil washing depends on factors like soil type, composition, particle size distribution, homogeneity and Total Organic Carbon present. Also, complex, heterogeneous contaminant compositions can make it difficult to formulate a simple washing solution, requiring use of multiple, sequential washing processes to remove contaminants

d. Vitrification

Vitrification uses electrical current to heat, melt and vitrify the treatment material in place, thus incorporating them into the vitrified end product, which is chemically durable and leach resistant. Electric current is passed through soil by an array of electrodes inserted vertically into the surface of the contaminated zone.

The temperature of the contaminated soil can reach between 1,600 and 2,000 ^{o}C. A single melt can treat a region up to 1,000 tons.

Vitrification is used to treat wastes up to a depth of 6 meters. Large contaminated areas are treated in multiple blocks that fuse together to form one large treated zone.

The gases produced must be collected and sent to a treatment unit. Dioxins and furans may also form when excess chlorides are present and enter the off-gas treatment system.

Mercury may be difficult to treat because of its high volatility and low solubility in glass (less than 0.1 percent), but may be effectively treated at low concentrations.

Chlorides in excess of 0.5 weight percent will typically fume off and enter the off-gas. If chlorides are excessively concentrated, salts of alkali, alkaline earth, and heavy metals may accumulate in the solid residues collected by off-gas treatment. Separation of the chloride salts from the residue may be necessary, therefore, if the residue is returned to the process for treatment.

The following table presents a summary of the pros and cons of the most usual strategies and treatments:

Technology	Principle	Key advantages	Key disadvantages	Targeted mercury	Status
Source removal with excavation	Excavation of the polluted materials on the whole contaminated area or specifically on the hot spots where the mercury masses are concentrated	Provide total remedy, radical with no residual concentrations to manage if the whole area is excavated	Could be expensive due to health and safety constraints for workers and surrounding. Risk of remobilization of labile elemental mercury. Geotechnical limitation due to groundwater level and/or existing infra-structures Transport of the polluted soil to the landfill Necessity of an enginereed landfill suitable for Hg wastes If only hot spots are removed, management with other technologies of residual non excavated soils.	Total labile mercury	Reliable technology but with difficulties inherent to the occurrence of mercury
In situ containment with vertical barriers and capping	Isolation of existing contaminated areas in the subsurface from the surrounding uncontaminated environment	-Relatively simple and rapid to implement -Uses standard construction equipment -Can be more economical than excavation and removal of waste, and thermal treatment -Can be applied to large areas or volume of waste -Avoids use of monocell space and risks associated with removal and transport -Provides a total remedy that addresses all mercury present in the targeted area -Provides a relatively passive system that doesn't rely an	Mercury remains on site and there is no reduction of toxicity and masses; this represents a potential risk should containment fail / degrades Geotechnical limitations due to existing infra-structures Vertical barrier limited to depth less than 20 m due to increasing capital costs. Vapour treatment by gas-drainage-capping	Total labile mercury	A variety of barrier materials are easily available

Technology	Principle	Key advantages	Key disadvantages	Targeted mercury	Status
		active management			
Soil-washing with pre processing (mechanical separation)	Ex situ technique where soils and polluted materials are washed, generally with water and/or oxidative acid solutions. Wash water and wash solutions can be treated and recycled	Possible reuse of treated material on site for filling. Reduction of waste to be treated /landfilled	-Source removal required -Pre-processing with physical separation, sorting, grinding of the material may be required -Technical difficulty increases depending of the type of soils and contaminats -Technology only viable for important volumes to treat due to costs.	Hg° and inorganic mercury	Soil washing units have efficiently treated soils and mercury wastes in different countries.
On-site immobilisation: stabilisation & solidification, amalgamation with on-site or off-site disposal	Chemical reaction (stabilization) and physically encapsulation (solidification) to reduce the hazard potential of a contaminated material by converting the contaminant into less soluble, less volatile, less mobile, and/or less toxic forms . On-site or off-site disposal in special engineered landfill licensed to receive mercury wastes.	-Lower waste classification by reaching the acceptance criteria for leaching; -Reducing the risk during transportation -Enable containment in special engineered landfill (monocell).	-Required excavation -Required site-specific testing at laboratory and pilot scale prior to full-scale application -possible passivation of elemental mercury during mixing and inefficiency of the treatment when Hg° droplets occurs (high elemental mercury content) -Increase of the bulk waste volume -the long term stability of stabilized media is uncertain or has not been assessed with some reagents --Carbon fingerprint when transportation of the waste off site -Elevated cost for large volume of waste (800 to 1000 € per tonne) -Long term monitoring required	Total labile mercury, especially Hg°	

Technology	Principle	Key advantages	Key disadvantages	Targeted mercury	Status
In situ thermal desorption (ISTD)	In situ heating of contaminated soils causing direct volatilisation – removal of volatilized products through soil vapour extraction.	-No excavation required -Selective extraction of labile mercury (which is the environmental issue) -Short duration of operation	- Could be expensive and technically difficult to conduct -Requires dense combined borehole networks for both soil vapour extraction + heating -mercury captured in the vapour treatment system must be managed, -Fugitive emissions of mercury vapour must be controlled, -Secondary treatment of wastewater streams from condensed water would be complex -Large energy consumption	Hg° and inorganic mercury	ISTD has been demonstrated commercially at full scale for high boiling point organic compounds remediation.

Technology	Principle	Key advantages	Key disadvantages	Targeted mercury	Status
Ex situ Thermal Desorption (ESTD)	Ex situ thermal desorption is a continuous process normally conducted in rotary kilns (or equivalent)	-Recovery of mercury and separation from material that could be reused for filling on site -High abatement efficiency	-excavation and temporary storage required -re-treatment would be required -Large energy consumption -Fugitive emissions of mercury vapour must be controlled -mercury captured in the vapour treatment system must be managed -Secondary treatment of wastewater streams from condensed water would be complex	Hg° and inorganic mercury	ESTD has been demonstrated commercially at full scale for mercury remediation only for low concentration (< 10 mg Hg/kg).
Batch retorting	Ex situ process where contaminated soils are heated in a controlled manner – volatizing contaminants (e.g. mercury) which is then recovered from off-gases.	-Thermal desorption under controlled conditions -Recovery of mercury and separation from material that could be reused for filling on site -High abatement efficiency	-excavation and temporary storage required -limited to treatment capacities of the order of one to five tons per day -expensive, high energy requirements, require vapour treatment, and significant handling effort and long treatment times (1 to ten years based on the capacity of 5 tons per day)	Hg° and inorganic mercury	It has been demonstrated commercially at full scale for small volume of highly polluted materials

Technology	Principle	Key advantages	Key disadvantages	Targeted mercury	Status
In situ Vitrification (ISV)	High temperature process that immobilizes contaminants by incorporating them into a vitrified matrix which is durable and leach resistant	-High abatement efficiency, -No excavation required	-Operation and maintenance would likely be technically difficult and expensive -Required site-specific testing at pilot scale prior to full-scale application -Required dense combined borehole networks for both soil vapour extraction + heating - Mercury captured in the vapour treatment system must be managed Fugitive emissions of mercury vapour must be controlled -Secondary treatment of wastewater streams from condensed water would be complex -Large energy consumption -the long term stability of in situ immobilized media is uncertain or has not been assessed (metastability of glassy material)	All forms and combination of mercury	One application reported at full scale with ex-site treatment in the USA for mercury wastes.

8.3 Safety measures. Prevention of occupational risks during clean-up work

Remediation tasks may lead to mercury exposure and all the risks that this entails, in addition to all the usual risks associated with the activity itself. To avoid risks, it is essential to know the mercury levels that workers are exposed to.

Environmental monitoring of the concentration of a toxin in air is the main instrument in the prevention of health-related occupational risks in general, and in relation to mercury in particular. There are two forms of environmental monitoring. **The first** involves sampling the air in a work area. **The second** focuses on staff and involves sampling the level of exposure of workers during their working day, as staff normally moves from one place to another during the day.

Another control for each exposed worker individually is the biological monitoring. This occupational health procedure measures a potential toxin, in this case mercury, its metabolites or an unwanted chemical effect in a biological sample, in order to assess individual exposure.

These measurements are known as biological exposure indicators or biomarkers. Biological monitoring measures the amount of the agent that has been absorbed, regardless of the pathway. It takes into account the elimination pathways, the toxicokinetics and the toxicodynamics of the corresponding substance. As a preventative measure, biological monitoring should be carried out regularly and repeatedly, but should not be confused with procedures for diagnosing occupational illness.

The daily environmental exposure limit values for mercury and for divalent inorganic compounds of mercury, including mercury oxide and mercury chloride (measured in mercury), is 0.02 mg/m^3, measured or calculated for a reference period of 8 h. These values are in accordance with Commission Directive 2009/161/EU establishing a third list of indicative occupational exposure limit values.

There are several procedures for the environmental determination of mercury. Both active and passive systems can be used. The choice of system will depend on the type of evaluation that is required, the instrumental conditions and the available techniques, as well as on the form of the contaminant. Devices for taking direct readings can be used to measure a specific concentration.

The most common method involves trapping mercury as a vapour. This is usually achieved through the use of adsorbent tubes (hopcalite, manganese bioxide and activated carbon, among others) or passive monitors (for example, gold and silver plates) that amalgamate the mercury. When mercury is trapped in adsorbent tubes, the amount is usually determined using atomic absorption spectrophotometry. If passive monitors have been used, variations in electrical conductivity are generally measured. If the mercury is in the form of particulate

matter (powder), it is trapped in filters and analysed by Atomic Absorption spectrophotometry. Electrochemical techniques, such as polarography and stripping potentiometry, can also be used for the analytical determination.
Biological indicators can be established for elemental mercury and inorganic compounds. These are appropriate parameters in biological media from a worker (urine and blood), and can be measured at a specific time.

The biological limit value for total inorganic mercury in urine can be set at 35 µg/g of creatine before the working day, i.e. after 16 hours without exposure. The limit value for total inorganic mercury in blood can be set at 15 µg/l at the end of the working week, that is, after 4 or 5 consecutive days of exposure at work. These values correspond with the Occupational Exposure Limits for Chemical Agents in Spain (National Institute of Safety and Hygiene at Work, 2012).

Preventative measures can reduce workers' levels of exposure. These include ventilation systems that increase air renewal in working spaces. Clean air is brought into the work area and contaminated air is extracted to treat it in activated carbon filters. In addition, protective clothing can be worn, such as mouth and nose masks with Hg P3 filters, in accordance with European Respiratory Protection Standards (EN 141: 2000).

8.4 Environmental monitoring required during remediation work

Environmental remediation projects for mercury-contaminated sites should include an Environmental Monitoring Plan (EMP) in addition to the remediation activities themselves.

The aim of the EMP is to determine and assess the environmental impact or damage to the area around the contaminated site to be remediated, in all stages of the remediation work. Thus, the EMP will describe appropriate measures for mitigating or avoiding negative environmental effects of the remediation activity. Measures will apply to the design and location of the remediation activity, the remediation procedures, purification, and general mechanisms for protecting the environment.

The EMP for remediation activities at a mercury-contaminated site will define monitoring and measurement activities. Measurements will be divided into two groups:

1. Those made during implementation of the remediation work.
2. Those made after the remediation work or monitoring activities.

In these two groups, there will be a particular focus on:

- Surface water and groundwater quality.
- Particle and gas emissions that affect the quality of life of inhabitants of the area.

In addition, remediation activities will be monitored by means of topographic control and a photographic record. Meteorological data will also be gathered.

The EMP will establish the method for monitoring remediation actions: the kind of reports that are required, the content of the reports, their frequency, and when they will be issued in the framework of the remediation project.

Quality control of the remediation work and of the significant environmental aspects that were identified for the project (in the design, implementation and maintenance stages) will be carried out according to the guidelines established in the Environmental Monitoring Plan.

An exemple of the main aspects to include in an EMP for a remediation project at a mercury-contaminated site is showed at the end of the chapter.

8.5 Monitoring and control of the expected results and of implemented activities

Once the option of remediation has been selected, a monitoring plan should be designed, implemented and run. This plan will determine the times and places at which monitoring will be carried out to assess the progress of the remediation actions and confirm that the targets have been met and that the site is not a risk to human health or the environment.

The design and implementation of a monitoring plan (MP) is highly specific to the type of remediation carried out and the contaminated site. Monitoring should be accompanied by assessment of the indicators, to verify whether or not progress has been made in the various activities that form part of the system or project under evaluation.

The aim of the basic control and monitoring indicators should be to verify that:

- Processes within the contaminated site that has been remediated are carried out according to plan.
- The environmental protection systems work exactly as proposed in the remediation project.
- There is compliance with the conditions of authorized use of the contaminated site.

At least the following indicators should be evaluated during the period established by the relevant authority:

1. Meteorological data. It is essential to establish the meteorological data that will be collected from the site:

- Volume of precipitation (daily and monthly values)
- Minimum and maximum temperature (monthly average)
- Direction and strength of the prevailing wind
- Evaporation (daily and monthly values)
- Atmospheric humidity (monthly average)

2. Emission data:

- Monitoring of surface water at representative points. The monitoring of surface water **should be carried out at two or more points**, including water upstream of the site and water downstream of the site.

  Samples will be taken in different seasons, preferably every six months. The parameters will vary according to the characteristics of the site to be remediated. In the case of mercury contamination, the parameters should include the concentration of mercury and of other heavy metals, anions, pH, conductivity, etc.

- Monitoring of groundwater. This will be carried out at one point, or more, situated upstream from the site's inlet, according to the groundwater flow direction, and at two points downstream from the site's outlet.

  The number of monitoring points could be increased on the basis of a hydrogeological survey of the area.

  The sampling frequency will be specific to each location and will be determined on the basis of the knowledge and assessment of the groundwater flow rate. The recommended parameters include pH, conductivity, heavy metals and anions.

- Monitoring of mercury vapor emissions and particulates with mercury content. A monitoring network should be established both within and outside the site to be remediated, to determine the environmental levels of mercury, and thus check the effectiveness of the remediation actions.

3. Soil sampling survey

The duration of the MP and the sampling and data collection frequency generally depends on the environmental authority.
The following table shows some of the main parameters to include in a MP for a remediation project at a mercury-contaminated site, during implementation of the remediation activities and once the project is finished.

MONITORING PLAN			
MONITORED MEDIUM	MONITORING FREQUENCY	LOCATION	MONITORING PARAMETERS
Surface water	Monthly, first two years	Water upstream of the **immediate** surroundings of the site to be remediated	Temperature pH Conductivity Dissolved oxygen Redox potential (Eh) Nitrites COD Ammonia Mercury
		Water downstream of the **immediate** surroundings of the site to be remediated	
	Six-monthly, remaining years	Water upstream of the area **near** the site to be remediated	Temperature pH Conductivity Heavy metals: mercury.
		Water downstream of the area **near** the site to be remediated	Temperature pH Conductivity Heavy metals: mercury
	Annual	Water upstream of an area **further** from the site to be remediated	Temperature pH Conductivity Mercury
		Water downstream of an area **further** from the site to be remediated	
Groundwater	Monthly, first 2 years	Drilling around the site to be remediated	Mercury
	Six-monthly, remaining years	Drilling around the site to be remediated	Mercury
	Annual	Wells and springs around the site to be remediated	pH, conductivity, $HCO3^-$, $SO4^{2-}$, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, $NO3^-$, $NO2^-$, $NH4^+$, mercury
Monitoring of meteorological data	Monthly	Site and surroundings	Direction, speed and frequency of prevailing wind
Monitoring of the mercury level in air	Monthly, first 2 years Quarterly remaining years	Site and surroundings	Level of mercury in the air
Monitoring of the mercury level in suspended matter	Monthly, first 2 years Quarterly remaining years	Site and surroundings	Level of mercury in particles in suspension

ANNEX : CASE STUDIES

1. Reconditioning of the Almadén mines.
2. Decontamination of the Flix dam in the Ebro River.
3. Environmentally safe decommission of a mercury cell chlor-alkali plant
4. Stabilization of soils contaminated with heavy metals using low-grade magnesium oxide

LEGAL DISCLAIMER: These case studies are a non-exhaustive compilation of recent projects undertaken for mercury decontamination, and provided only for informative purposes, without implying necessarily neither a certification nor an approval by UNEP/MAP of all the procedures employed in each of the sites and of the levels of contamination that may remain in them.

CASE STUDY 1: RECONDITIONING OF THE "CERCO DE SAN TEODORO" SLAG HEAP. MINAS DE ALMADÉN (CIUDAD REAL, SPAIN).

Background

Minas de Almadén y Arrayanes, S.A. (MAYASA) is a public company belonging to *Sociedad Estatal de Participaciones Industriales* (SEPI), which manages the mercury mines in Almadén (Ciudad Real).

Mining began in Almadén over 2,000 years ago, with production accounting for a third of historical world production.

The Almadén mining and metallurgy complex is found in the areas known as "Cerco de San Teodoro", near the urban area and the road to Córdoba. The site includes historic mines and those in operation until July 2003.

Minas de Almadén undertook in 2005 the most important environmental project in its history: the reconditioning of the "Cerco de San Teodoro" slag heap.

CERCO SAN TEODORO SLAG HEAP. MAY 2005. Photo by Paisajes Españoles

For centuries the “Cerco de San Teodoro” slag heap has been the dump site for both sterile tailings from mining operations and slag from metallurgy processes, reaching 3.5 million tonnes and covering an area of 10 hectares.

ACTION

In deciding which rehabilitation model to follow, a number of studies were made of the slag heap and the surrounding area. A summary of these studies concluded that the **materials dumped on the slag heap are hazardous due to their mercury content** and that the permeability of the underlying substrate is low, with no discernible lithological changes or fractures that may constitute preferential drainage paths.

Bearing these considerations in mind it was decided to undertake ***reconditioning of the slag heap with in-situ encapsulation*** **to guarantee waterproofing of the upper part of the heap, preventing refilling and therefore minimising the effects on groundwater and surface water, as well as reducing dispersion of the material dumped on the heap that may affect the surrounding soils**.

The reconditioning of the Cerco de San Teodoro slag heap was undertaken from 2005 to 2008 and cost close to 9 million euros.

In addition to the aforementioned environmental tasks, the reconditioning of the Cerco de San Teodoro slag heap has turned the mining and metallurgy complex into a social and cultural space open to the public: the Almadén Mining Park (www.parqueminerodealmaden.es).

METHODOLOGY USED

The slag heap lies within the easternmost part of the urban area and is a topographic high compared to the surrounding relief; the foot is well defined, limited to the south by the Córdoba road, to the west by other property, and to the north by the path to the Virgen del Castillo.

The materials are piled in a slag heap outside the Cerco de San Teodoro that extends south-east and north-west, surrounding the mining site, and in a second heap inside the Cerco in the south-westernmost area.

The studies characterising the slag heap and surrounding area yielded the following data:

COMPONENT MATERIALS

- Old metallurgy waste
- Current metallurgy waste
- Mining waste
- Other

ENVIRONMENTAL EFFECTS

- Hydrological risk
- Atmospheric risk
- Land use
- Effects on plant and animal life, geophysical processes–morphology and landscape-, and infiltration

The following action plan was drawn up to meet the established objectives:

A) slag heap conformation

The aim of this stage was the remodelling of the slag heap to improve stability and integrate it into the surrounding area. To do so, material was moved from one part of the heap to another to reduce the slope of the sides, enabling the subsequent laying of a geosynthetic pack to seal the heap.

REMODELLING OF THE CERCO DE SAN TEODORO SLAG HEAP MARCH 2006. Photo by Paisajes Españoles

B) sealing of the slag heap

The aim was to stop water entering the heap, and thus prevent the formation of leachates, the dispersion of materials through physical and thermal insulation and prevent mercury evaporation over the entire surface of the heap. A geosynthetic pack made up of 5 layers was installed.

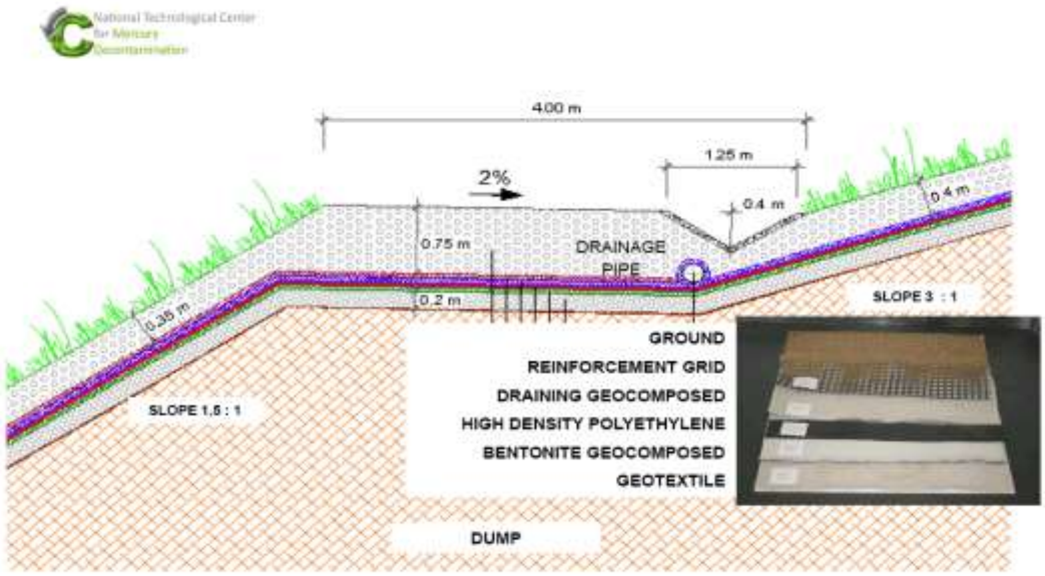
The seal package comprises: a geotextile layer, a bentonite blanket layer, a layer of high-density polyethylene, another of drainage geocomposite, and finally a layer of reinforcement geogrid, or geocells, depending on the steepness of the sides after remodelling.

CERCO DE SAN TEODORO SLAG HEAP MARCH 2007

The geosynthetics have different functions:

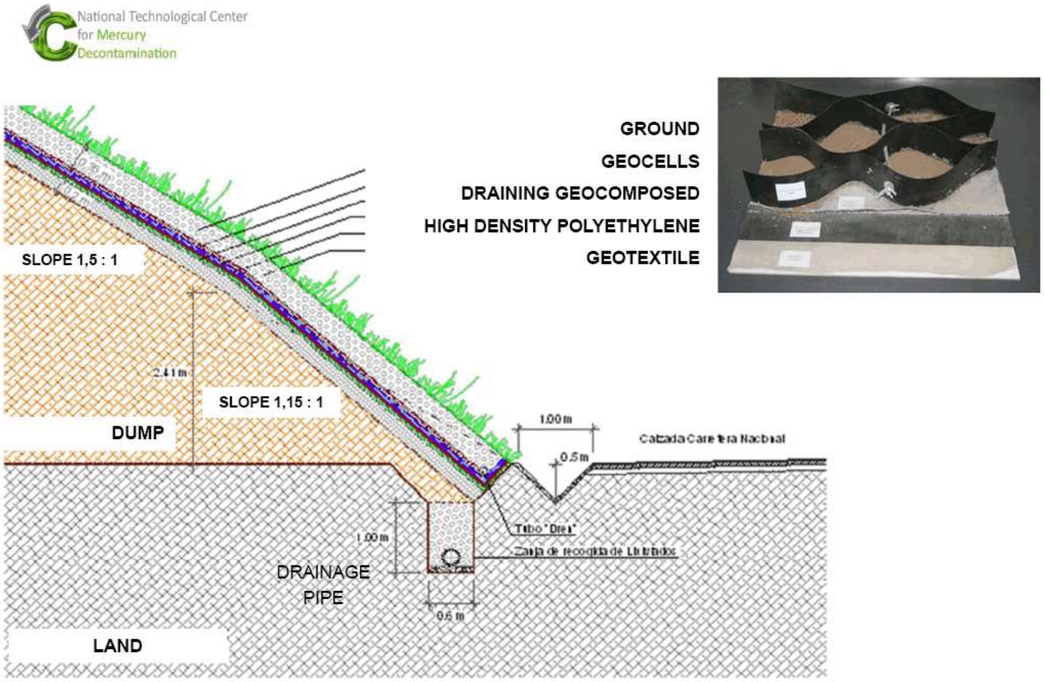
- GEOTEXTILE: The geotextile layer prevents piercing.
- BENTONITE BLANKET: This waterproofs the surface, reducing leachate formation and gas migration.
- HIGH-DENSITY POLYETHYLENE: The main component of the geosynthetic pack, as it guarantees that sealed area is totally impermeable.
- DRAINAGE GEOCOMPOSITE: This conveys water, separating and filtering the soil on which the geocomposite is laid.
- FLEXIBLE REINFORCEMENT GEOGIRD 80 kN/m: Installing this layer improves the stability of the earth on the surface of most the slopes on the heat.
- GEOCELLS: Drainage geocells are made of strips of high-density polyethylene, laid to stabilise the earth on the steepest slope.

The diagrams below show the distribution of the geosynthetic pack, according to slope.



SEALING SURFACE SCHEME

LOW INCLINATION SLOPE



SEALING SURFACE SCHEME

HIGH INCLINATION SLOPE

C) installation of a water collection, circulation and discharge system

This stage of the remediation aims to prevent erosion that may affect the stability of the slag heap. A water collection, circulation and discharge system was installed, through the construction of ditches, drainpipes and perimeter channels that collect runoff and prevent future erosion, which would affect the stability of the slopes.

D) restoration of plant cover

This action aims to recover plant life on the restored surface and integrate the slag heap into its surroundings. To do this, 50 cm of earth was added to the whole surface, a total of 180,000 m^3, followed by the mechanical hydroseeding of a 16-ha area to aid the regeneration of plant cover.

CERCO SAN TEODORO SLAG HEAP JANUARY 2008. Photo by Paisajes Españoles

EVALUATION OF RESULTS AND CONCLUSIONS

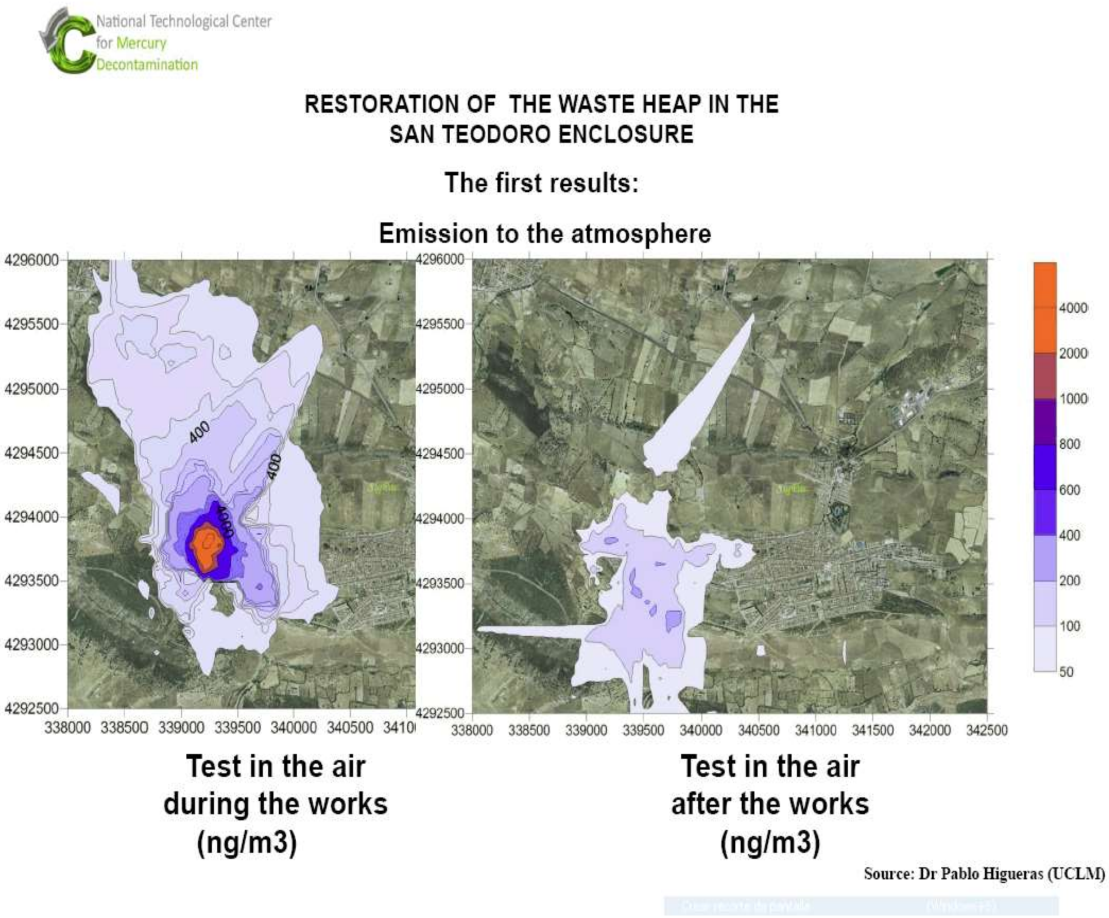
Since the reconditioning work was completed in 2008, the most obvious results observed have been:

- Integration of the slag heap into the landscape.
- Elimination of waste dispersal in the immediate area.
- Acceptable levels of mercury evaporation into the atmosphere.

- Leachate formation is almost zero, with no addition to nearby streams or groundwater.

Quality control during the course of the works, along with the significant environmental aspects identified for the project, was undertaken according to the Environmental Monitoring Plan (EMP) designed for the reconditioning project.

Currently, the post-completion monitoring established in the EMP continues. To date, the most reliable result observed is the drop in mercury levels in the air, as can be seen in the figures below from the study of air emissions undertaken during and after the reconditioning works.



RESTORATION OF THE WASTE HEAP IN THE
SAN TEODORO ENCLOSURE

The first results:

Emission to the atmosphere

Test in the air
during the works
(ng/m3)

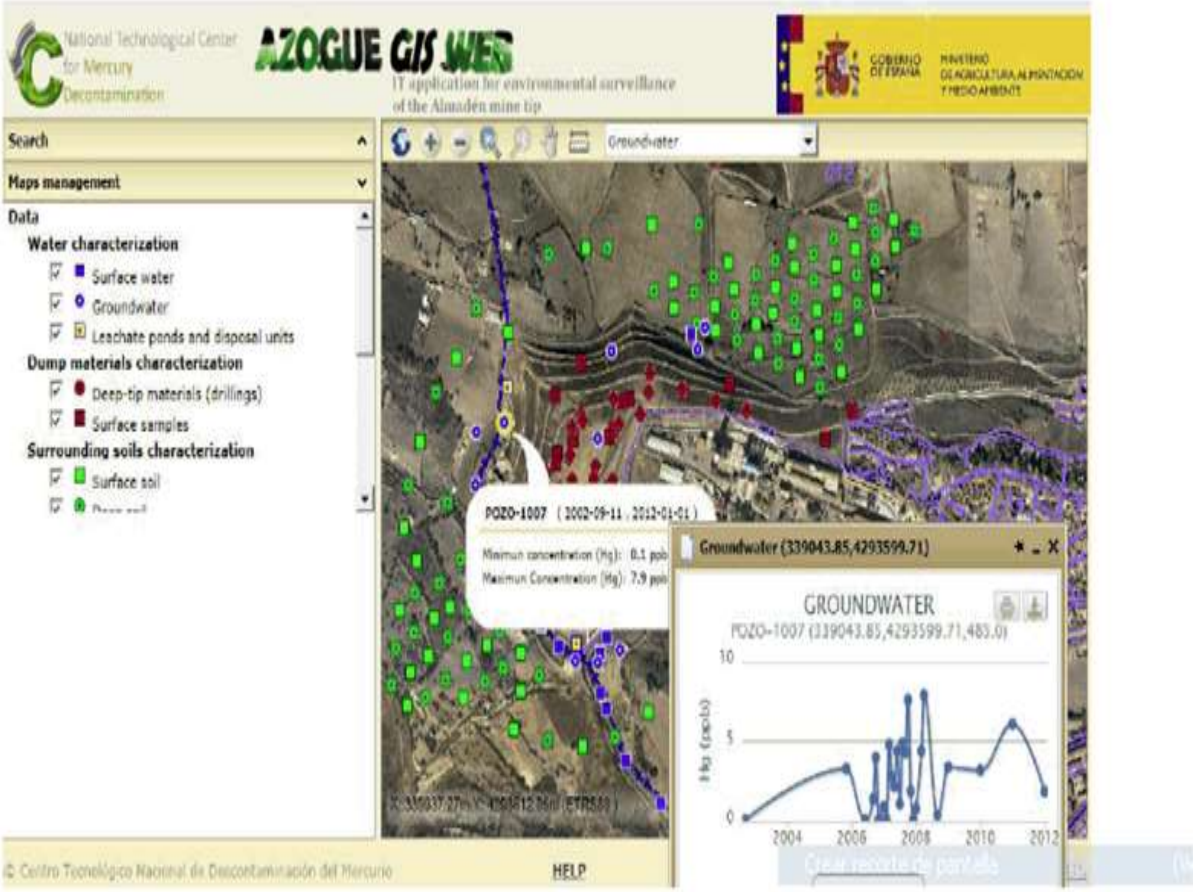
Test in the air
after the works
(ng/m3)

Source: Dr Pablo Higueras (UCLM)

In regard to water quality, although in some surface waters a notable improvement was observed, some more time is needed before more significant results are obtained.

The development of the analytical data on these waters can be followed on the website of the "Centro Tecnológico Nacional para la Descontaminación de Mercurio (CTNDM):

http://www.ctndm.es/proyectos/1-in.php where the data obtained is dumped monthly under the reconditioning Environmental Monitoring Plan, which includes the gathering of monthly samples at a number of points in surface and groundwater around the slag heap.



Software application for the environmental monitoring of the Almadén mine slag heap

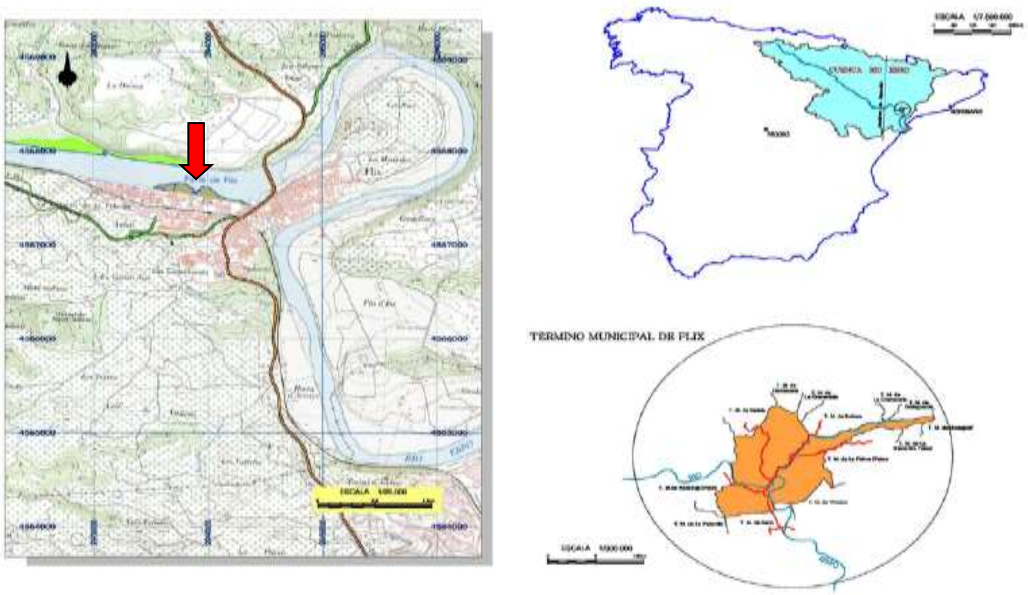
http://www.ctndm.es/proyectos/1-in.php

CASE STUDY 2: DECONTAMINATION OF THE FLIX DAM IN THE EBRO RIVER (Tarragona, Spain)

Authors: Marc Pujols, Project Manager, and Gracia Ballesteros, Deputy Director of Engineering and Construction. **ACUAMED.**

SUMMARY

The Flix dam, located in the lower stretch of the Ebro, retains in its basin some six hundred thousands cubic meters of sludge mainly dumped by a chemical plant located on the right bank. This sludge was the residual product of the plant's operations, and is composed of both chemicals and inert components. There are three main groups of contaminants: organochlorines (with persistent organic pollutants such as DDT and PCBs), heavy metals (mainly mercury) and radionuclides.



Location of the polluted site in the riverside of the Ebro

The concentration of the contaminants in the mud is relatively high, and they can be potentially mobilized; in fact, such transmission has actually occurred—as shown in the register of specific episodes in which the limits of tolerance of aggressive components contained in the ecosystem have been exceeded.

In light of this situation, the Spanish Ministry of Environment decided to start a process of designing, analysing, developing, comparing and finally choosing the means by which to correct and prevent, or mitigate, the transmission of these toxic elements into the environment.

As a result, the state company Aguas de las Cuencas Mediterraneas, S. A. (ACUAMED) was entrusted with the project of the elimination of the chemical pollution of the reservoir at Flix.

BACKGROUND

The accumulation of historical dumping can lead to situations that make the ecosystems vulnerable due to natural phenomena - floods, winds or sudden temperature changes. Just such a scenario is the situation in the Flix reservoir.

The production of chemical products on the banks of the river began in the late nineteenth century, and since then, the kind of substances produced have been large and varied, in accordance with technological advances and demand.

The initial processes were based on chlorine and caustic soda, obtained from the raw material of common salt, through an electrolytic process using mercury. More recently, apatite has been introduced in huge amounts as raw material in order to produce di-calcium phosphate. This apatite naturally contains a percentage of radionuclides, which, during the production process, are physically dumped. In addition to this, also to be considered is the fact that some of the contaminants found in the mud also come from the natural drag occurring upstream of the factory.

In addition, the River Ebro's morphology has substantially changed over the past century. Every time that a dam is built on the river, the immediate consequence is that the pool produced in the water increases sedimentation, and therefore reservoirs have a propensity for clogging. The Flix reservoir is no exception. The erosive force and natural drag of the River Ebro as it passed through this area was reduced following construction of the dam. Until then, most of what was dumped from the factory had been washed away downstream, but after construction of the dam, the vast majority of the dumped materials remained in the reservoir basin.

Aerial view, 1970

Aerial view, 1985

In light of all of this preliminary data, a search for solutions has been undertaken, in order to avoid either continuous or periodic risk of contamination.

WASTE GENERATING PROCESSES

The materials that make up the bank of the reservoir beside the factory mostly come from factory activity. The processes that produced or caused the majority of the materials deposited or that have settled in the bank are:

a) **Combustion of coal.**
b) **Dissolution of salt.**
c) **Trichloroethylene.**
d) **Perchloroethylene and carbon tetrachloride.**
e) **Dicalcium phosphate.**

POTENTIALLY POLLUTING PROCESSES

As previously mentioned, the contaminants belong to three main groups: heavy metals (mainly mercury), organochlorines and radionuclides (from the mineral used in the phosphate process).

Given the variety of processes carried out at the factory, in addition to those already mentioned, there may be others arising from chlorination processes, like DDT (1945-1975), PCBs (1959-1987), Hexachlorbenzene, and diverse reaction by-products.

SOLUTIONS CONSIDERED

Studies carried out have established that possible solutions can be classified into two groups depending on whether the waste is finally kept in the reservoir (in-situ solutions) or, conversely, collected and placed at another point (ex-situ solutions).

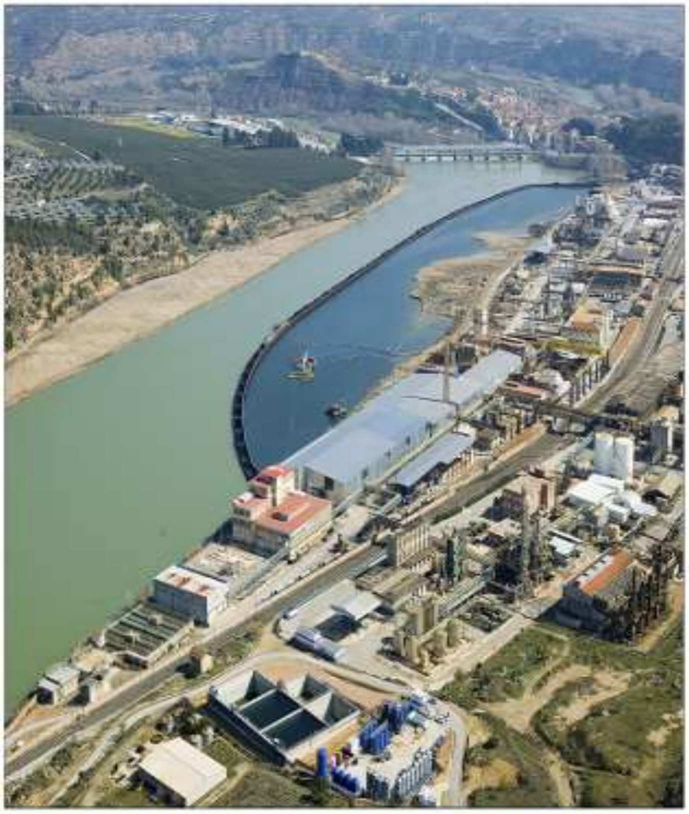
The key elements that define the optimal solution within each group are:

- In-situ solution: the creation of a working area, making up of waste, waste treatment and protection from river erosion.

- Ex-situ solution: creating a working site, removal of waste, treatment, transport to a dumping area and the dumping area itself.

ADOPTED RESOLUTION

The Monitoring Commission formed by various government bodies, including the Hydrographic Confederation of the Ebro, the Spanish Ministry of the Environment, the Government of Catalonia, the Flix municipality, the Spanish National Research Council, the Consortium for the Protection of the Ebro Delta (CEPIDE) and the project promoter (ACUAMED), after studying all the responses received from more than 80 organisations consulted to study the alternatives, including that of 'no action', decided that the ex-situ solution was the most environmentally safe alternative, since it actually reduced the level of pollutants and provided more guarantees.[10]



View of the site with the on-going decontamination works (2012)

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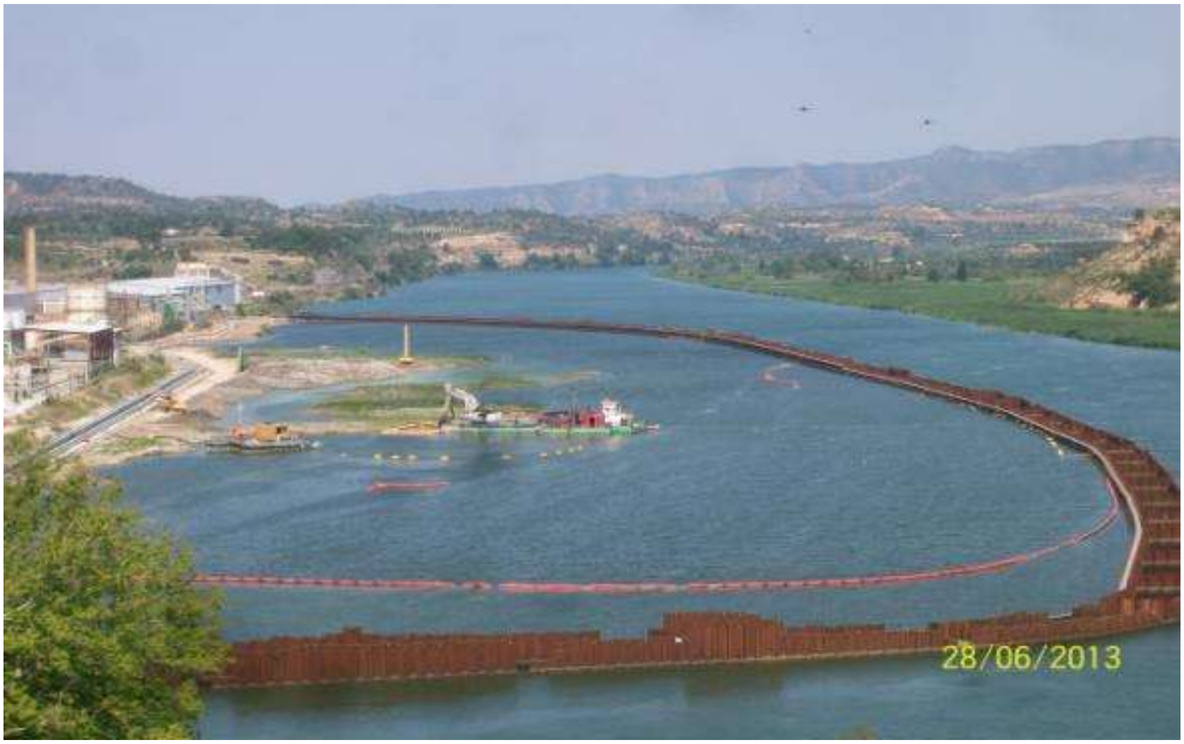
[10] BOE (Spanish Official Gazette), RESOLUTION of 25 October 2006, of the General Secretariat for Pollution Prevention and Climate Change, formulating an environmental impact statement on the assessment of the project Removal of Chemical Pollution from Flix Reservoir (Tarragona).

When designing and planning activities, a series of corrective measures to minimise the impact on wildlife were considered, because a nature reserve was located upstream nearby, with flooded grasslands and wildlife as diverse as the golden eagle, imperial heron and the otter.



Dredging activities inside the sheet piling

PRELIMINARY WORKS

- Construction of a **double wall of sheet piling 1300 m in length**, enclosing a working area on the right bank of the reservoir to isolate the contaminated river sludge, which must be executed prior to manipulation of the significantly contaminated mud. The main aim is to create a protected area (still water), independent from the Ebro's flowing water, so that during the performance (during the works inside the reservoir) the river can flow through a channel at the left bank of the reservoir. Should an incident occur during the process, the working area will remain confined and pollution won't be sent downstream.

- Construction of a **secant pile retaining wall 1100 m in length** on the shoreline of the right bank of the reservoir, to avoid the risk of landslip of the bank due to the removal of the waste, while preventing subsurface flow from the factory into the river.

- Construction of an **interceptor sewer for the existing waste drains** at the factory.

- Construction, within the factory compound, of **various industrial buildings to house the treatment facility for the extracted material and water**, as well as the collection centres.

- Construction of **seven wells for the supply of water to the towns situated downstream**. Its use is exclusively reserved in case of emergency.

- **Adequacy and waterproofing of a Class II landfill** (type of landfill enginereed for wastes that are neither toxic nor inert) in el “Racó de la Pubilla” (at a distance of 6 kilometers away from the river), following demanding criteria above and beyond that required by current legislation.

Conditioning works in the “Racó de la Pubilla” Landfill

One of the wells constructed for drinking water supply to downstream towns in case of emergency

DEPOLLUTION WORKS

After building the site, the removal of waste can proceed.The removal of the submerged fraction of mud will be done using suction ecological dredges, which will work surrounded by floating plastic curtains. This will minimize the disturbance of contaminants and will create a depression in the dredge area, where the water will be easily kept. This is complemented by the provision of a small pump that can operate when the dredger stops. To prevent the disturbance of contaminants, the dredging should be necessarily low.

Low disturbance dredging

Once removed, the material must be subjected to a treatment, the aim of which is to achieve waste conditions that enable it to be admitted for final containment in the dumping area provided.

The treatment consists of:

- **Soil size classification**, using sieves and hydrocyclones, followed by the **drying** of all the extracted material, with settling tanks and press filters.

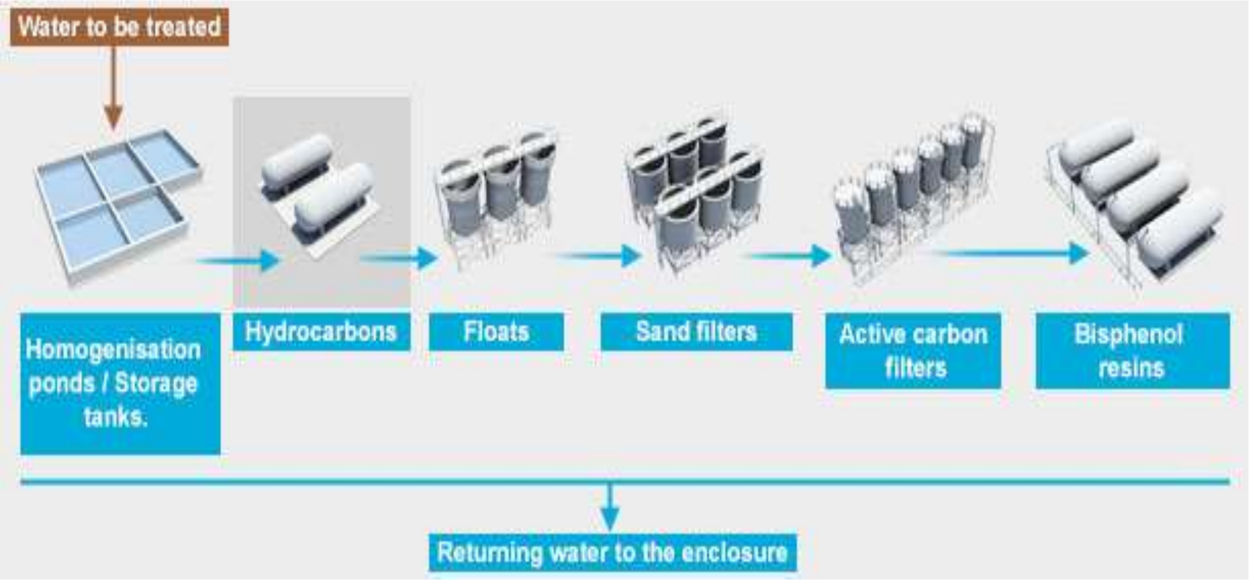
- The solid fraction will be classified depending on its contaminant concentrations, sending clean fractions directly to the filling area, and dealing specifically with those fractions that would be rejected at the dumping area. After studying all the possibilities, the chosen treatments (alternative or sequentially) are:

  - **Thermal desorption** (vs. organic compounds): The material is introduced into the desorption oven at less than 350°C to avoid evaporating the mercury. The gases coming from the desorption oven pass to a thermal oxidation oven where they are heated again, this time to 1100°C. After this, the temperature is cooled quickly to less than 200°C to prevent the formation of dioxins. The resulting gas from the thermal oxidation oven passes through a fabric filter to collect the particles in suspension.

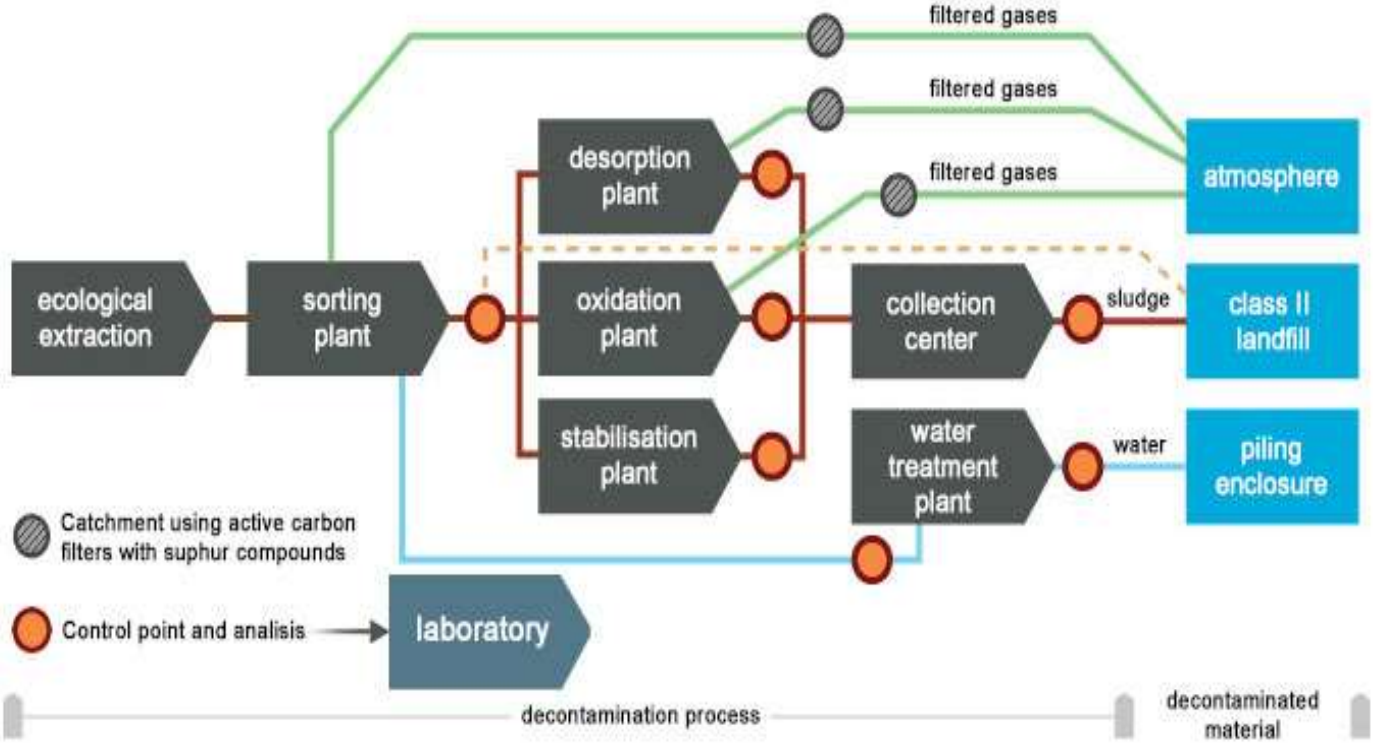
  - **Oxidation:** If the principal contaminants from the dehydrated sludge are volatile compounds in moderate concentrations, it is oxidized in the mixing tank by the addition of reagent and water. After mixing, the material passes to the reaction tanks. Two hours later, the result is an inert compound that is insoluble in water and ready to be taken to the landfill site.

  - **Stabilization** (vs. heavy metals): If the dredged sludge has high concentrations of mercury and other heavy metals, it is processed in the stabilization plant. Passing through some hoppers, the sludge is inertized with cement and specific additives to stabilize the mercury and prevent its presence in the possible leaching of the sludge.

- **Water** is sent to a **treatment plant** (WWTP), the capacity of which is around one hundred litres per second.



The diagram below highlights the crucial importance of the contamination controls at the end of each process, before approving the continuation in the chain of decontamination. Strict security guidelines are also followed during the handling of materials, to prevent any impact on people or the environment.



After the treatment, the material will be transported by trucks to the “Racó de la Pubilla” class II landfill (type of landfill designed for residues that are neither toxics nor inerts.)

DISMANTALING WORKS

The works are due to be finished by the end of 2015, and it will imply the following actions:

- Closure of the landfill site.
- Dismantling of the sheet pile wall.
- Dismantling of the surface water inceptors and repositioning of the landfill to the reservoir for the rainwater drains.
- Removal of the mobile and mechanical elements from the treatment plant.
- Dismantling of the plant building and fixed elements contained within.
- Reinforcement via coarse rubble slope against the pile wall along the full extension of where the extraction of material has taken place next to the secant pile protection wall.

SECURITY MEASURES

As already pointed out, the security measures include the floating plastic curtains and the double wall of sheet piling, as well as an intensive daily quality control of the water, upstream and downstream, both outside and inside the enclosure area.

Daily water quality control points

These tests, as well as the analysis of the dredged material, are carried out in the ‘on site’ laboratory, which includes the following equipment:

- Gas chromatography coupled with mass spectroscopy.
- Ion chromatography with conductivity detection.
- Atomic fluorescence.
- Visible and ultraviolet molecular absorption spectrophotometry.
- Plasma induced spectroscopy emission.
- Selective electrode system.
- Alpha radiation meters with zinc sulphur detectors.
- Beta radiation meter using a detector proportional to the gas flow.
- Gamma radiation meters using sodium iodide and germanium detector.

"On site" Laboratory

INFORMATION TO THE PUBLIC

A website has been devoted to inform the public with the details and news of the project.

Flix decontamination

The health and safety of people, water and ecosystems are the priorities of this project whose goal is to counteract over a century of chemical waste dumping into the Flix dam.

This dumping has resulted in a build-up of one million tonnes of polluting sludge and constitutes a threat to the Ebro's riverbed all the way to its mouth.

The state-owned company "Aguas de las Cuencas Mediterráneas, S.A." (Acuamed) is leading this decontamination project — the only one of its kind in the world — with a view to extracting, treating and removing this sludge and reclaiming the Ebro river and its ecosystem for the 800,000 people living in the Tarragona province.

Acuamed is firmly devoted to giving this project full transparency with an educational view to help society discover all the health, environmental and socioeconomic benefits it brings to Flix and the entire Ribera de Ebro county.

www.decontaminationflix.com/

COST OF THE PROJECT

The total cost estimated is around 192 M€, of which 70% is co-financed by European Union fundings, with the following breakdown of major items:

Treatment plant	50 M€
Conditioning of dumping area	38 M€
Sheet pile wall	21 M€
Pile wall	15 M€
Dredging	12 M€
Other	56 M€
Total	**192 M€**

CASE STUDY 3: ENVIRONMENTALLY SAFE DECOMMISSION OF A MERCURY CELL CHLOR-ALKALI PLANT

Author: Antonio Caprino. Electrolysis Production Manager. SOLVAY IBERICA, MARTORELL.

The decommission of a mercury-cell chlor-alkali plant is potentially one of the processes most likely to involve major release of mercury into the environment. It involves a series of steps that require thorough and carefully planning. The amount and composition of the waste generated may vary greatly, from protective equipment of workers like gloves to slag, production equipment, containers, rubble….

Below are the steps to be followed in the decommissioning of a mercury-cell chlor-alkali plant, with special emphasis on the precautions to be taken to ensure human health and safety and to prevent environmental contamination, based on Euro Chlor leaflets on decommissioning and on Solvay's experience in this field.

1. Introduction

In the 20th century, mercury electrolysis was commonly used in chlorine production worldwide; however, the use of mercury and the advent of new technologies mean that this technique is now largely obsolete. Indeed, no electrolysis plant using this technique has been built since the 1960s.

Given the challenge facing the sector in regard to the change in technology, Euro Chlor (an organisation that groups together most European chlorine manufacturers) undertook voluntarily to cease mercury-based chlorine production in Europe by 2020. In the Mediterranean Region no mercury-based plants shall remain in operation in 2020[11].

At global level a similar process is being followed: in 2002 there were 92 mercury-based plants, while by 2011 only 53 remained. UNEP reached an agreement in 2013 (Minamata Convention on Mercury), under which mercury-cell chlor-alkali plants will cease to operate between 2025 and 2035 in those countries that ratify the convention.

Given this situation, it seems appropriate to compile a document of good practices to be followed during the decommissioning of such plants.

2. The case of Solvay

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[11] Legal requirement of the Regional Plan of the Barcelona Convention for the reduction of inputs of Mercury. UNEP MAP, 2012.

Solvay is a world leading producer of chlorine with 13 plants producing over 2 Mt of chlorine a year. Four of these plants still use mercury cell technology. Between 2006 and 2011 there were 3 conversions made from Hg to membrane cells:

2006 in Rosignano, Italy
2007 in Bussi, Italy
2009 in Santo André, Brazil
Two changeovers will be completed in 2013: Lillo (Belgium), and Tavaux (France).

Based on these experiences, an explanation is given of how the decommissioning of a mercury cell plant is managed during the technology change process. The reference documents will be cited, along with the team in charge of the process and a breakdown of the operations to be carried out at local level, all based on the latest cases at Rosignano and Santo André. Finally, the main lessons learned from these processes are summarised in a list of good practices to be considered.

2.1 Managing the decommissioning process

2.1.1 Reference documents

- Euro Chlor Env Prot 3, ***Guidelines for Decommissioning of Mercury Chlor-Alkali Plants***.

- Euro Chlor Env Prot 19, ***Guidelines for the preparation for permanent storage of metallic mercury above ground or in underground mines***.

- Local documents such as: SHD (Syndicat des Halogènes et Dérivés) France - ‘**Protocol for decommissioning of a mercury cathode electrolysis unit’** ,

- Company’s own documents (Internal procedures, Schedules, action plans…)

2.1.2 Organisation

In order to undertake the required decommissioning processes it was decided to put together a team to define how these processes should be managed at the various Group plants.

The team was made up of process experts and SHE (Safety, Health and Environment) experts who defined the process and its scope, and created a technical database on the mercury-contaminated equipment and the recommended treatment.

The team also included experts in procurement to ensure good economic management during the investment period.

2.1.3 Phases of the operating process

2.1.3.1 Phase 1: preparation and planning

An estimate must be made of the contaminated waste to be treated, including the anticipated amount and concentration of mercury.
Likewise, it must be decided which equipment is to continue to operate during the decommissioning process to prevent workers from being exposed to mercury and contamination of the environment. This is normally gas scrubbing and wastewater treatment installations.

Based on experience, the amount of contaminated material to be treated varies between 1000 and 6000 t per plant (excluding buildings), a non-comprehensive list is given below by way of example:

- Carbon steel and other metals such as copper and aluminium
- Mercury
- Graphite and activated carbon
- Polyester reinforced and non-reinforced PVC, polyester resins, other plastics
- Coverings, e.g. ebonite, neoprene and butyl
- Joints made from diverse materials
- Sand and clay
- Electrical equipment
- Concrete, brick, rubble
- others

This list is used to define the treatment of each type of waste or whether it is to be sent to landfill. The treatment of each waste type is decided according to the description in the database prepared by the central team and the stipulations of each country’s legislation.

One important point to be borne in mind is that, at the beginning of the process, suitable metal containers must be made available to store the metallic mercury from the electrolysers temporarily.

Next, a call for bids can be made amongst contractors and a detailed plan of the process drawn up. This plan should include informing the authorities that all aspects of waste have been considered, including treatment, environmental control during the decommissioning process and all those concerning the protection of the personnel involved.

Finally, the number of workers required must be defined, both on the pay roll and freelancers, protective equipment, biomonitoring and environmental control.

2.1.3.2 Phase 2: Operations

This in turn is divided into three stages.

Stage one, called ‘Basic Health and Safety Provisions’ comprises the following operations:
- Emptying installations containing metallic Hg and process fluids.
- Thorough cleaning and confinement of the various contaminated cells, and, if necessary, covering them with water, to prevent emissions of Hg into the atmosphere.
- Dismantling of uncontaminated equipment (e.g. anodes, cell panels, etc.).

Such work must be undertaken by qualified personnel, usually the same involved when the plant was in operation.

In **stage two** the mercury-contaminated equipment is dismantled and undergoes appropriate treatment according to the establish plan. Only the equipment that must remain operable for reasons of SHE is not dismantled. This work can be undertaken by contractors if there is not enough permanent staff.

Finally, in **stage three,** the remaining equipment is dismantled (e.g. control gear, treatment units, etc.). This work is mostly done by contractors.

3. Case study photos

Below are some case study photos that illustrate the steps described.

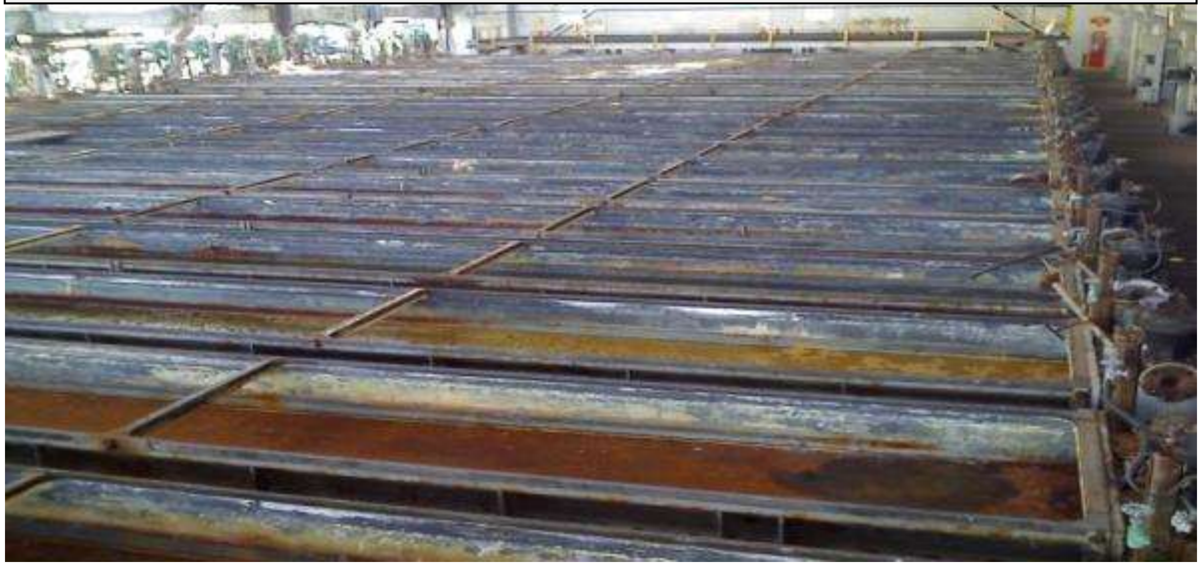
Cell confinement (connected to the air treatment unit)

Working area for safe handling of contaminated equipment connected to the Hg effluent treatment unit, regularly washed down with water

Floor of cell room regularly washed down

First stage of operations

End of first dismantling stage



4. Good practices learned

The decommissioning of a mercury-cell chlor-alkali plant must be managed as a specific project :

1. By a full-time team, enthusiastic and committed to the project, able to come up with innovative solutions that improve on current procedures. Personnel must be qualified and experienced, particularly those in charge of emptying circuits and dismantling contaminated cells in stage one.

2. The project must be carefully planned following available documentation and according to the specificities of each plant.

3. A number of things must be defined in the initial phase:

   a. How to shut down the cell room (all at once or in sections)
   b. Which cells should remain operative for SHE reasons.
   c. Listing contaminated cells and waste types with the corresponding treatment, which will serve when informing the authorities and drawing up requests for bids from contractors.

4. The protection of workers and the environment is a crucial aspect. Prior to the start of the work, the protective equipment to be used, the cells which are to remain operative to ensure minimum exposure, monitoring of the environment and water and biomonitoring must all be determined.

5. Finally, to ensure the success of the process, it is essential to implement progress indicators for the control and monitoring of the project.

5- Safe treatment of waste from the decommissioning of a chlor-alkali plant

The table below shows some recommended forms of treatment for waste containing mercury in the chlor-alkali industry, according to the BAT reference document.[12]

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[12] European Commission (2001): Integrated Pollution Prevention and Control (IPPC) - *Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing industry*.

Type of waste	Characteristic	Typical amounts (g/t Cl_2)	Hg content before treatment (g/kg)	Treatment	Final Hg mercury (mg/kg)
Brine sludge	Inorganic waste	Up to 20 000, depending on the quality of the salt	<0.150	Landfill following stabilisation	
Sludge from effluent treatment	Activated carbon	50-400	10-50	Distillation/landfill following stabilisation	Hg recovered / <10 in waste
Carbon sludge from caustic filtration	Activated carbon	20-50	150-500	Distillation/landfill following stabilisation	Hg recovered / 20-200 in waste
Gas emission filters	Activated carbon	10-20	100-200	Chemical treatment Landfill following stabilisation	Hg recovered / 20-200 in waste
Sludge from storage tanks, sinks, etc.		May contain large quantities	High Hg content in general	Distillation	Hg recovered
Rubber coating	Variable		Variable	Acid bath, cryogenic and/or washing Incineration	300
Metal-coated materials	Surface contamination		In general, <0.1%	Heat, cutting and washing or cryogenic	
Steel and iron parts from building		Variable amounts	Inhomogeneous In general, <0.1%	Acid bath/sold as waste	<5-10
Concrete and other construction waste		Variable amounts	Inhomogeneous/ In general, <0.1%	Landfill as hazardous waste or other waste according to content	>10 /<10

The table below shows the typical waste materials generated following the decommissioning of a chlor-alkali plant and their possible treatments for mercury recovery [13]

Typical material contamination			**Possible treatment**			
Material	**Typical percentage of Hg w/w**	**Physical state**	**Physical/mechanical treatment**	**Washing with water**	**Chemical washing**	**Retorting**
Sludge from storage tanks and sinks	10 - 30	Wet solid	▨	▨		▨
Sludge from sedimentation tanks, drains, etc.	2 - 80	Wet solid	▨	▨		▨
Sulphurised or iodised charcoal from hydrogen purification	10 – 20	Dry solid	▨		▨	
Carbon from soda filters	Over 40	Wet solid	▨	▨		▨
Graphite from decomposers	2	Porous solid	▨	▨	▨	▨
Rubber/packaging	Variable	Variable	▨	▨	▨	
Brick/concrete	0.01 – 0.1	Dry solid	▨	▨	▨	▨
Hg cell components (anodes, side walls, pipes…)	Variable	IC	▨	▨	▨	
Steel (cells, decomposers, scrap metal, H_2 condensers, pumps, pipes…)	0.001 – 1	SSC	▨	▨	▨	▨
Plastic equipment	<0.1	SSC		▨		
Copper conductors	0.04	SSC	▨			▨ (For flexible sheets)
Cell seal (concrete layers)	0.01		▨			
Asphalt	1 - 20	IC	▨	▨		
Concrete and subsoil	Variable	IC	▨	▨		▨
Wood	Variable		▨	▨		
Floor	Variable	IC	▨	▨		
Thermal insulation	0.03		No treatment prior to dumping			
Retort waste	< 0.1 – 0.1	Porous dry solid				
Wooden floors	0.05 – 0.08	IC				

IC: Inhomogeneous contamination / SSC: Solid with surface contamination

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[13] *Decommissioning of Mercury Chlor-Alkali Plants*. 5th Edition. September 2009, Euro Chlor

CASE STUDY 4: STABILIZATION OF SOILS CONTAMINATED WITH HEAVY METALS USING LOW-GRADE MAGNESIUM OXIDE

Author: José María Chimenos. University of Barcelona (UB)

The stabilization treatment with a pH-buffering chemical is an option to consider when the best alternative considered is to remove a contaminated soil with heavy metals from its emplacement, without a process of decontamination, and move it to a suitable landfill or safety cell.

This process of chemical stabilization minimizes heavy metals solubility. Lime or a mix of cement and lime are the usual buffering agent for many kinds of waste, but with the high pH values obtained with lime - a strong alkali - , the leachate water collected in the landfill may contain high concentrations of heavy metals, due to the redissolving of the previously formed metal hydroxides.

The most common heavy metal hydroxides reach their minimum solubility at a pH between 8 and 10. In the chemical stabilization of soils polluted with heavy metals it should be used an alkaline product with solubility equilibrium at that pH interval, and with a competitive price compared to lime.

Magnesium hydroxide, $Mg(OH)_2$, can be the most appropriate candidate, as it has minimum environmental impact, low solubility and pH equilibrium on contact with water close to 9.5. However, natural magnesium hydroxide (Brucite) is scarcely reactive, and the hydroxide on the market costs ten times the price of calcium oxide or hydroxide. More affordable is the low-grade magnesium oxide (MgO), which can be used as a stabilizing agent and is obtained from the calcination of the mineral Magnesite.

If mercury is present in the soil, it has to be carefully considered the possibility of formation of methylmercury, or its complexation with organic matter, such as humic acid. In this case, the stabilizing agent wouldn't be effective.

Here below is a description of some cases of stabilization of soils contaminated with heavy metals using low-grade MgO.

1- In 1998, Inabonos S.A. (a Roullier Group company) undertook the cleaning and decontamination of a 74,408m^2 plot in a former emplacement in Lodosa (Navarra, Spain), by moving contaminated soil to a safety cell, with the objective to build a new housing development. The process causing the contamination was the production of sulphuric acid from pyrite –iron sulfide-, a mineral with a high content of heavy metalls. The waste generated in the process contained iron oxides and heavy metals such as lead, zinc, arsenic, copper, mercury, cobalt, cadmium, chrome, nickel, tin, selenium, tellurium, and antimony and could be found up to a depth of 2.5 meters. Mercury concentration reached a peak of 1.7 g/Kg in the first half meter of depth.

120,000 m^3 of contaminated soil were extracted from the site, transported to a safety cell and stabilised. Stabilization was a gradual process, alternating layers of earth, approximately 0.5 m thick, with layers of hydrate - obtained from the calcination of natural magnesite and produced and marketed by the company Magnesitas Navarras S.A.-.This layer acted as a filter bed for the percolates from upper layers. The percentage of stabilizer added was about 5-6% by weight of the contaminated soil dumped in the safety cell. After dumping and stabilization, the safety cell was closed. Thus, leachates collected in the troughs of the safety cell could be discharged into natural watercourses without undergoing prior treatment, except those effluents with a high sulphate content.

2- On a coastal city nearby Barcelona, the ex situ stabilization of 12.5 hectares containing ashes from pyrite roasting along with pyrite mineral with high sulphur concentration of a former inorganic fertiliser factory was undertaken using 10% low-grade magnesium oxide. The final objective of this treatment was to move the stabilized soil to a Class II controlled landfill.

3- On a Spanish coastal city, a pre-pilot study was undertaken of in-situ stabilization with magnesium oxide of soil contaminated by the uncontrolled dumping of a former fertiliser factory. The area treated covered 200 m^2 and was 2 m deep. The stabilizing agents were added by injection and the contaminated soil homogenized using a rotovator. The results obtained show that the leachates from the samples stabilized with low-grade magnesium oxide enable a pH of between 9.5 and 10.5 , which is the optimal interval to minimise the solubility of heavy metals.