Block 4

DEALING WITH CHLOR ALKALI AND MERCURY:
SYNERGY BETWEEN MINAMATA AND STOCKHOLM CONVENTION: PRACTICAL CASES


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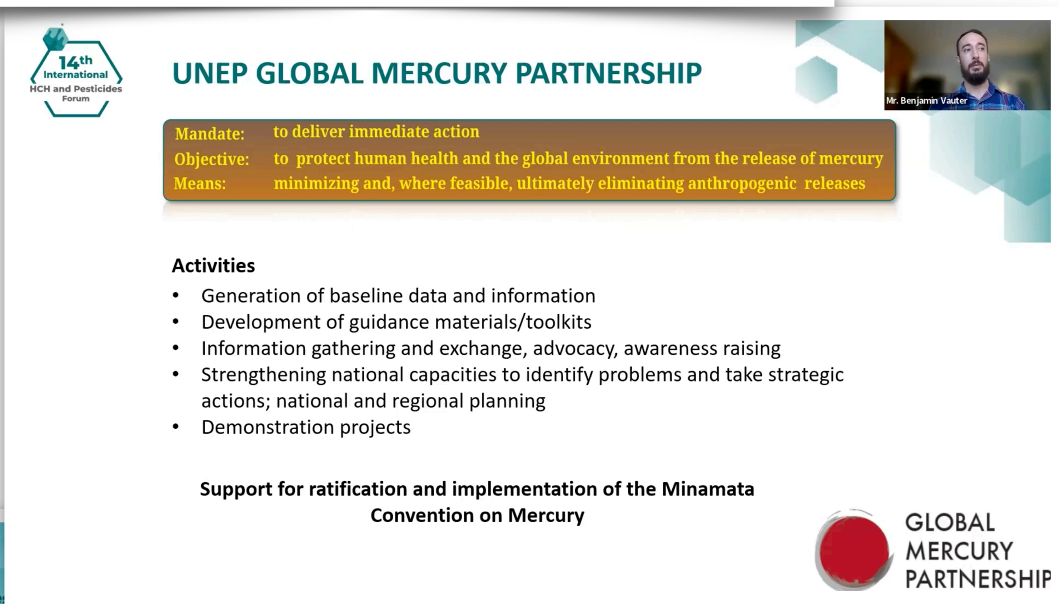
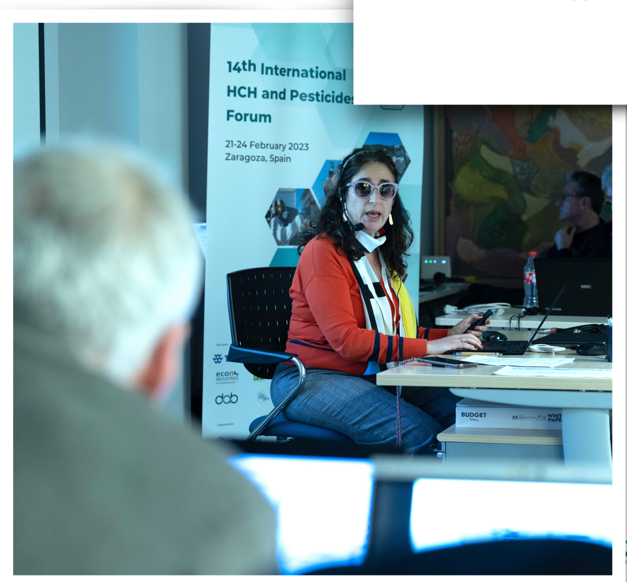

14th International HCH and Pesticides Forum
UNEP GLOBAL MERCURY PARTNERSHIP
Mr. Benjamin Vauter
Mandate: to deliver immediate action
Objective: to protect human health and the global environment from the release of mercury
Means: minimizing and, where feasible, ultimately eliminating anthropogenic releases
Activities
• Generation of baseline data and information
• Development of guidance materials/toolkits
• Information gathering and exchange, advocacy, awareness raising
• Strengthening national capacities to identify problems and take strategic actions; national and regional planning
• Demonstration projects
Support for ratification and implementation of the Minamata Convention on Mercury
GLOBAL MERCURY PARTNERSHIP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MINAMATA CONVENTION AND THE UNEP GLOBAL MERCURY PARTNERSHIP: MERCURY MANAGEMENT IN THE CHLOR-ALKALI SECTOR

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Abstract

The Minamata Convention on Mercury aims to reduce and where feasible eliminate mercury from products and processes around the globe. Having entered into force in 2017, the Minamata Convention includes a phase-out date for mercury cell chlor-alkali facilities by 2025. The Convention also requires each Party to take measures to ensure that mercury waste from these facilities is disposed of in ways that do not lead to recovery, recycling, reclamation, direct reuse, or alternative uses of mercury. Supporting these goals of the Minamata Convention, the UNEP Global Mercury Partnership's Chlor-Alkali Partnership Area, co-led by the US EPA and UNIDO, provides technical, and educational information to chlor-alkali production facility partners, governments, and other stakeholders. It promotes commercially competitive and environmentally responsible solutions for eliminating mercury use in chlor-alkali production.

This presentation by the Global Mercury Partnership's Chlor-Alkali Partnership Area will explain the role of the Convention and the Partnership in reducing mercury use and releases from the chlor-alkali, progress in these efforts, and perceived challenges and opportunities moving forward.

Keywords

Chlor-alkali, mercury waste, Minamata Convention, Global Mercury Partnership's Chlor-Alkali Partnership Area

RELEVANCE OF MERCURY CONTAMINATED SITES FOR GLOBAL MERCURY RELEASE AND IMPLEMENTATION SYNERGY OF THE MINAMATA & STOCKHOLM CONVENTION

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Abstract

Mercury contaminated sites considerably contribute to environmental pollution and release of mercury today and will become the most important emission source in future. Major releases stem from (former) mining sites of Hg and sites where mercury has been used in manufacturing of products (e.g., pesticides, medical devices, thermometers, light bulbs). Also, sites of gold/precious metal mining including artisanal gold mining (AGM) as well as sites of non-ferrous metals processing can be contaminated with mercury and have associated releases. Furthermore, mercury storage/disposal sites, mercury recycling sites and sites where mercury pesticides have been used can be contaminated and continuously release mercury. Last not least sites of former mercury use in industry (chlor-alkali sites; acetaldehyde; vinyl acetate; certain PVC) can be highly contaminated with mercury with current and future release and need systematic assessment and appropriate securing and remediation.

Chlor-alkali production sites can also be contaminated with PCDD/Fs and other unintentionally POPs listed in the Stockholm Convention with large legacies from the former use of graphite electrodes from 1890 to 1980s and in some developing countries longer. Additionally, a range of chlor-alkali sites were also production sites of chlorinated POPs (e.g. lindane/HCHs, PCP, DDT) partly with large contaminated sites

from POP production and disposal. Therefore for chlor-alkali site assessment there is a strong synergy for Minamata and Stockholm Convention implementation. Therefore when assessing chlor-alkali production sites, the technologies used in the past need to be assessed including the management of wastes. In addition, the organochlorine/POPs production portfolio at these sites needs to be assessed including the disposal practice.

The current study gives a short overview on mercury contaminated sites and highlights the need of a synergistic approach to assess mercury and POPs pollution for certain sites for a synergistic implementation of Minamata and Stockholm Convention where appropriate.

Keywords

Mercury contaminated sites, Minamata Convention, POPs, synergistic implementation

MERCURY CONTAMINATION AS A LEGACY OF CHEMICAL PRODUCTION IN THE CEE REGION

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Summary

The Minamata Convention was adopted in 2013 to protect the environment and human health from mercury. Mercury has been known as a pollutant for decades, and the effects on human health associated with its presence in the environment are well known. This toxic metal bioaccumulates particularly in aquatic environments, and through the food chain and, especially through fish and seafood, enters the human body. Even before the Minamata Convention, a threshold by WHO (0.5 mg/kg wet weight) for mercury concentrations in fish was established which should not be exceeded for human consumption. The results of our study show that this concentration is commonly exceeded in fish from the vicinity of former and operating factories using mercury in various processes, chlor-alkali plants in particular. Fish from these areas poses a serious health risk. It also shows that the mercury problem is of global concern due to its transportation from hotspots to distance of tens of kilometres in aquatic environment. Remediation of these sites is also complicated due to the presence of other contaminants such as e.g. POPs.

Keywords

chlor-alkali, contamination, mercury, Minamata Convention, chemical industry, remediation, contaminated sites

1. Introduction

Mercury is a substance of global concern due to its long-range transport, persistence, ability to bioaccumulate, and toxicity. The Minamata Convention was adopted in 2013 to reduce mercury transport globally. The chemical industry in the region of Central and Eastern Europe (CEE) left many heavily contaminated sites and polluting factories that are subject to the treaty provisions. This study evaluates mercury contamination in the vicinity of such hot spots.

Impacts of mercury on human health and the environment

Mercury has been well known as an environmental pollutant for several decades. The way mercury affects organism depends on its chemical form and route of exposure. The pathways and fate of mercury in aquatic environments are important because it is in waters, sediments, and wetland soils that inorganic mercury is converted to methylmercury, which concentrates in animals at the top of a food chain, including humans. Once mercury enters a human organism, it acts as a neurotoxin, or negatively impacts the immune system. The majority of human exposure to mercury is from the consumption of fish and marine foods. Thus, the most studies of mercury contamination focus on aquatic ecosystems and mercury levels in fish.

Mercury in chemical industry

There are several manufacturing processes intentionally involving mercury that are recognized by the Minamata Convention on Mercury. These processes are mercury-based chlor-alkali production; sodium and potassium methylate or ethylate production using mercury cell electrolysis; vinyl chloride monomer, acetaldehyde, and polyurethane production using mercury as a catalyst. These applications of mercury in the chemical industry are addressed by Article 5: Manufacturing processes in which mercury or mercury compound are used. Some uses of mercury in chemical industry are to be phased-out while others are to be restricted.

2. Materials and methods

In this study, we present eight case studies focused on contamination with mercury at sites contaminated due to former or recent chemical factories using mercury in the CEE and CIS countries. Geographical locations of the sites are shown in Figure 1. Some of these sites were remediated already however most of them remain to some extend contaminated. This description is based on previous larger report (Mach et al. 2016). Particular attention is paid to fish contamination at these sites. Levels of mercury in fish were measured in previous studies.

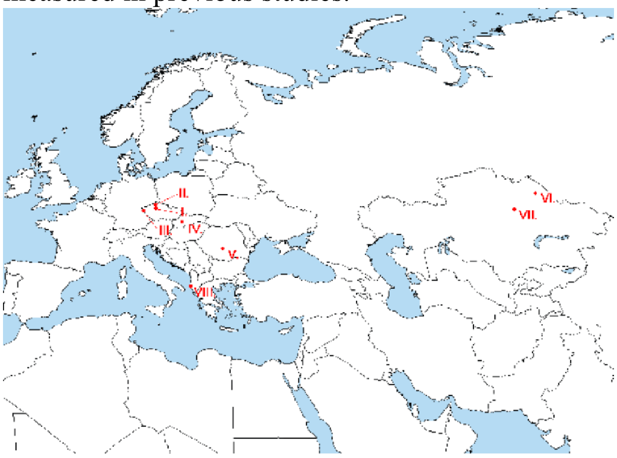

FIGURE1. GEOGRAPHICAL LOCATIONS OF THE CASE STUDIES' SITES

3 Case studies

3. 1 Spolana Neratovice, Czech Republic

Spolana Neratovice is the largest chemical factory in the Czech Republic with a chlor-alkali production plant and plant for manufacturing PVC plastic, located close to the Labe River. There were used graphite electrodes in the old amalgam electrolysis plant. Mercury contamination was observed not only in the Labe River but also in nearby quarry lake Mlékojedy. Angling has a long history in the city of Neratovice and a local group of Czech Fishing Union continued to encourage fish population for angling in the Labe River and Mlékojedy quarry lake despite mercury contamination. Contamination of surrounding environment was very well documented by the study focused on mercury oak bark (see Figure 2 and Table 1).

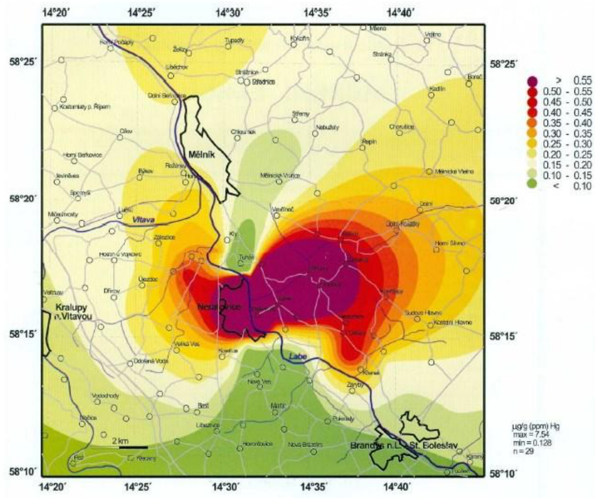

FIGURE 2. CONTAMINATION OF SPOLANA NERATOVICE SURROUNDING ENVIRONMENT

3.2 Spolchemie, Czech Republic

Spolchemie is one of the oldest chemical factories in the Czech Republic and one of the two chlor-alkali production plants in the Czech Republic is a part of the Spolchemie chemical complex. Spolchemie is situated on the confluence of the River Labe and River Bílina. Mercury contamination was reported in soils at the area of Spolchemie), in sediments and biofilm of the River Bílina (Pokorný et al., 2011) (see Table 1) and in fish from both the River Labe and the River Bílina (see Figure 3).

3.3 Marktredwitz, Germany

Marktredwitz Chemical Factory was the oldest chemical production site in and in the world. Marktredwitz is located on the Kössein water stream in the watershed of the Ohře River with Skalka reservoir, which later flows into the Labe River. Despite the expensive decontamination after 200 years of operation of the factory and the discharge of mercury into the Kössein watershed, much pollution remains. Sediments from the Kössein water stream, Reslava and Ohre Rivers pose a secondary source of pollution (see Table 1), especially during floods when the decontaminated sediments enter the Skalka reservoir. Consumption of fish from the Skalka reservoir thus poses a health risk. The fish are contaminated mainly by methyl-mercury (Maršálek et al., 2005).

3.4 Fortischem, Slovakia

Fortischem a.s. is one of the Slovakia's key chemical manufacturing sites in Slovakia and has been identified as one of the "hotspots" near Nitra River. There is a mercury cell chlor-alkali production plant at the site. The first of two studies conducted by Greenpeace Czech Republic (2002) examined two waste-water discharges and related sediment (see Table 1).

3.5 Oltchim, Romania

Oltchim is one of the largest chemical factories in Romania and the largest chlor-alkali plant in Central and Eastern Europe located close to Babeni Reservoir on River Olt. Mercury contamination of surface sediments in the Babeni reservoir (see Table 1) is too high with respect to sediment quality guidelines and is one order of magnitude higher than the local background concentrations measured in sediments from the upstream Vâlcea reservoir (Bravo et al., 2009). An increase of mercury concentrations observed along the food chain lead to the highest values found in fish (Bravo et al., 2014), 92 % of studied fish exceeded the threshold of 0.5 mg/kg w. w. with most of the mercury in the form of methylmercury.

3.6 Khimprom, Kazakhstan

The Pavlodar Chemical Plant (Khimprom), is a former industrial factory that was designed as a dual-purpose production factory capable of manufacturing both agents of chemical warfare and civilian chemicals, including chlor-alkali plant which operated for 18 years and caused serious widespread contamination. The chlor-alkali plant is located 2 km south of Lake Balkyldak (15 km2) and 5 km east of the River Irtysh. The most contaminated lake was Lake Balkyldak. It is a waste-water settling pond without outlet (Ullrich et al., 2007) and in comparison with other aquatic ecosystems contaminated by mercury from chlor-alkali plant, Lake Balkyldak could be the most severely impacted lake ecosystem known to date and it is in need of remediation, since it represents a threat (Ullrich et al., 2007). Sediments from Lake Balkydak are heavily contaminated with mercury (see Table 1) (Ullrich et al., 2007) and it is used regularly by fishermen who catch fish both for their own consumption and for sale.

3.7 Karbid, Kazakhstan

The Plant of Synthetic Rubber or the "Karbid" is a chemical factory in central North Kazakhstan, which has been producing synthetic rubber while using mercury sulphate as a catalyst for almost 50 years. The entire industrial area is located on the west bank of the Samarkand Reservoir on the Nura River, near Temirtau in Karaganda Region. Even after decontamination of the site in 2013, high concentrations of mercury in sediments were detected at many sampling locations, with the highest being 174 mg/kg (Šír and Petrlík, 2015), even 70 km from the source (See Table1).

3.8 Vlora, Albania

North of Vlora in Albania is the site of a former chemical manufacturing complex consisting of a chlor-alkali plant and plants for the production of VCM and PVC plastic, identified as "hot-spot" for mercury pollution in 2002 (Lazo and Reif, 2013), especially electrolysis and polymerisation plants. The former chemical factory is located near the Vlora Bay, a part of the Adriatic Sea. There is another area used as dump for disposal of contaminated sludge between the former chemical factory and the coast with concentrations from 0.33 to 156 mg/kg (Beqiraj, Cullaj and Kotorri, 2008). As a result of spreading contamination from the former chemical complex, high concentrations of mercury were found in sediments, seawater and biota in the area near the former factory (Lazo and Reif, 2013).

4. Results

Results of the analyses of mercury in fish in the vicinity, mostly downstream from the described factories/contaminated sites are summarized in graph at Figure 3.

Mercury analysis come either from the research by IPEN and Arnika in 2012 (Arnika Association and IPEN

Heavy Metals Working Group, 2013) or from other studies published in accessible literature (Andreji et al., 2005; Maršálek et al., 2005; Žlábek et al., 2005; Bravo et al., 2010; Corsi et al., 2011; Musil et al., 2015; Šír and Petrlík, 2015) between the years 2005 and 2015. Part of these results were also included and discussed in the global-scale assessment of mercury in fish (Evers et al., 2014; Buck et al., 2019).

Mercury levels were in the range of 0.5-3.41 mg/kg. The threshold of 0.5 mg/kg w.w. established by the WHO (WHO, 2004) was exceeded in all fish samples presented in this study but the sample downstream of Spolchemie which is discussed further below.

Mercury levels in fish were highly elevated in compared to the natural level of mercury, nevertheless directly downstream of Spolchemie mean mercury concentrations in fish did not exceed the threshold of 0.5 mg/kg w.w. established by the WHO (WHO, 2004), but Žlábek et al. (2005) found that mean mercury levels in common bream (Abramis brama) from the River Labe 20 km downstream from the Spolchemie exceeded WHO limit. Randak et al. (2009) found that the mean mercury concentration in chub (Leuciscus cephalus L.) caught downstream of the factory was 0.26 mg/kg w.w. A similar mean value of 0.28 mg/kg w.w. was found in the investigation by the Arnika Association and IPEN in 2012 in common bream muscle (Abramis brama2012 (Arnika Association and IPEN Heavy Metals Working Group, 2013). If the stricter US EPA (US EPA 2001) reference dose of 0.22 mg/kg is used, eating fish from the River Labe downstream from the confluence with the River Bílina poses a health risk.

The most considerable were mercury levels in fish also in Vlora, because the bay is important fishing area. The study made by the Arnika Association, Eden Center and IPEN in 2013 reported that a mean mercury concentration in mullet (Mullus surmuletus) was 0.617 mg/kg w.w. (Eden Center, Arnika Association, IPEN, 2013) and a majority of mullets exceeded current human health criteria for mercury established by the WHO (WHO, 2004) and was nearly three times higher than the EPA (US EPA, 2001) reference dose of 0.22 mg/kg. High levels of mercury have also been found in the red mullet muscle (Mullus barbatus) - 1.06 mg/kg d.m. (Corsi et al., 2011) or 0.14 – 3.39 ppm in small sharks (Galeus melastomus) of the Adriatic Sea (Storelli, Ceci and Marcotrigiano, 1998).

5 Discussion

In most cases fish caught downstream from described sites contaminated in result of long lasting use of mercury in chemical factories had levels of mercury which exceeded current human health criteria for mercury established by the WHO (WHO, 2004), see graph at Figure 3. This contamination can last even after major part of contamination is remediated as it was documented in fish caught downstream from Marktredwitz in the Czech dam near German borders. Remaining contamination in Nura River downstream from decontaminated area in Temirtau is a similar case. Problem is in remaining contamination in sediments which were not remediated.

TABLE 1. CASE STUDIES DETAILED INFORMATION

Chemical factory	locality	mg/kg	notes	reference
Spolchemie in Ústí nad Labem	River Bílina	32	6.7 mg/kg in biofilm	(Pokorný *et al.*, 2011)
Marktredwitz Chemical Factory	Kössein water stream	269	maximum, ethyl-mercury + methyl-mercury	
	River Reslava	435	highest concentration from 1983	
	Skalka Reservoir	12.9	456,000 m^3 of sediment	(Titl *et al.*, 2011)
Fortischem in Nováky	discharge to River Nitra	131	112 µg/l in wastewater	
Fortischem in Nováky	lagoon	197		(Labunská, 2002)
Oltchim in Râmnicu Vâlcea	Babeni Reservoir	0.8 - 6.6	5,8 mg/l in surface water	
Chemical Complex in Pavlodar	Lake Balkyldak	1500	*first 9 km	
Karbid in Temirtau	River Nura	150-240	in 25 km after discharge	

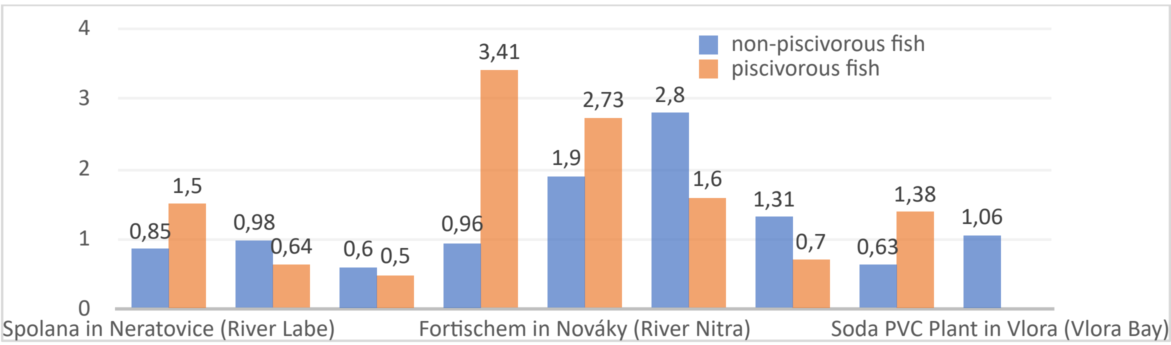

FIGURE 3: MEAN LEVELS OF MERCURY IN MUSCLE OF FISH ON CONTAMINATED SITES (MG/KG WET WEIGHT)

There was also observed simultaneous contamination with persistent organic pollutants (POPs) in some of here demonstrated cases. There is problem with contamination with polychlorinated dinbenzo-p-dioxins and dibenzofurans (PCDD/Fs) which were unintentional by-products mainly in residues from production of chlorine by using graphite electrodes in chlor-alkali plants (UNEP, 2013). High levels of PCBs were measured in sediments from Nura River (Petrlik et al., 2015). These may result form the use of chlorinated paraffins as flame retardants in rubber (UNEP,

2013) but most likely leaked from metallurgical plants located in Termitau as well.

There is also high contamination of water sediments and fish with other POPs such as hexachlorocyclohexanes (HCHs) and/or hexachlorobenzene (HCB) in the vicinity of Vlora in Albania or downstream from Spolchemie in Usti and Labem, Czech Republic. This was caused by production of pesticides in chlorine chemical factories in the past (Vlora, Spolana Neratovice, Spolchemie Usti and Labem and others) and/or by releases of HCB as unintentional by-product from production of chlorinated solvents (Spolchemie Usti nad Labem).

Described cases demonstrate how complex contamination inside the chemical factories as well as in the sediments outside of their former production areas can be.

IPEN developed basic guidance for identification, management and remediation of mercury contaminated sites in order to assist mainly to developing countries or countries with economies in transition in finding solutions for such sites as they are described in our study (Bell, 2016). Its previous version included basic technologies to address also POPs contaminated sites as well. IPEN document became basis for development of guidance adopted by the Conference of Parties (COP) to the Minamata Convention later on (Minamata Convention on Mercury, 2019). This document as well as Technical Guidelines for mercury waste (Basel Convention, 2015) does not suggest waste incineration as environmentally sound management for treatment of wastes containing mercury because of uncontrolled releases of mercury. This suggestion is fully reflected also in BAT/BEP Guidelines for waste incineration developed within framework of the Minamata Convention ('Guidance on best available techniques and best environmental practices (Minamata Convention on Mercury) - Waste Incineration Facilities', 2016). Indirect thermal desorption seems to be most suitable way for evaporation of both mercury and POPs from contaminated material from sites described in cases of contaminated sites originated from chemical production described in this study. POPs can be destroyed by non-combustion technologies in residues from remediation of the sites described in this study (Bell, 2020).

Some of the sites described in our study were already fully and/or partly remediated. Remediation of the sediments from the vicinity of Nura River downstream for Temirtau is described in one of previous studies. However high levels of mercury and PCBs in sediments and continuing contamination of fish downstream from the contaminated site were observed. Former pesticide factory in Marktredwitz was also remediated but high levels of mercury in sediments downstream remained as reservoir of continuing mercury pollution for river flowing into Skalka reservoir in the Czech Republic where methylation leads to high levels of mercury in fish.

Conclusions

Mercury contamination of fish downstream from contaminated sites with origin in the past chemical production and/or abandoned technologies represent serious risks for human health and represents also serious environmental threat to water ecosystems.

Contamination of former chemical plants areas and their vicinity is very complex and needs to be addressed by combination of remediation techniques. This problem was addressed in various guidance documents prepared within the framework of both Basel and Minamata Conventions, and in more details also in IPEN studies and guidance documents.

Acknowledgements

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References

Andreji, J. et al. (2005) 'Concentration of Selected Metals in Muscle of Various Fish Species', Journal of Environmental Science and Health, Part A, 40(4), pp. 899–912. Available at: https://doi.org/10.1081/ESE-200048297.

Arnika Association and IPEN Heavy Metals Working Group (2013) Chlor-alkali plants: Neratovice, Ústí nad Labem and Some Other Chemical Hot Spots in the Czech Republic. Arnika - Toxics and Waster Programme and IPEN, p. 9.

Basel Convention (2015) General technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants. Geneva.

Bell, L. (2016) 'Guidance on the identification, management and remediation of mercury-contaminated sites'. IPEN.

Bell, L. (2020) 'NON-Combustion Technology for POPs waste destruction: Replacing incineration with clean technology'. Gothenburg - Perth.

Beqiraj, A., Cullaj, A. and Kotorri, P. (2008) 'High-contaminated soil with mercury in Bay of Vlora (Albania) and its possible remediation'.

Bravo, A.G. et al. (2009) 'Historical record of mercury contamination in sediments from the Babeni Reservoir in the Olt River, Romania', Environmental Science and Pollution Research, 16(1), pp. 66–75. Available at: https://doi.org/10.1007/s11356-008-0057-5.

Bravo, A.G. et al. (2010) 'Mercury human exposure through fish consumption in a reservoir contaminated by a chlor-alkali plant: Babeni reservoir (Romania)', Environmental Science and

Pollution Research, 17(8), pp. 1422–1432. Available at: https://doi.org/10.1007/s11356-010-0328-9.
Bravo, A.G. et al. (2014) 'Extremely elevated methyl mercury levels in water, sediment and organisms in a Romanian reservoir affected by release of mercury from a chlor-alkali plant', Water Research, 49, pp. 391–405. Available at: https://doi.org/10.1016/j.watres.2013.10.024.
Buck, D.G. et al. (2019) 'A global-scale assessment of fish mercury concentrations and the identification of biological hotspots', Science of the total environment, 687, pp. 956–966.
Corsi, I. et al. (2011) 'Ecotoxicological Assessment of Vlora Bay (Albania) by a Biomonitoring Study Using an Integrated Approach of Sublethal Toxicological Effects and Contaminant Levels in Bioindicator Species', Journal of Coastal Research, (58), pp. 116–120. Available at: https://doi.org/10.2112/SI_58_11.
Eden Center, Arnika Association, IPEN (2013) 'Contaminated site: Vlora Mercury Hot Spot in Albania.' Arnika - Toxics and Waster Programme and IPEN.
Evers, D. et al. (2014) 'Global mercury hotspots: New evidence reveals mercury contamination regularly exceeds health advisory levels in humans and fish worldwide', BRI-IPEN Science Communications Series, 34, p. 2014.
Greenpeace Czech Republic (2002) Greenpeace evidences huge mercury contamination of the Spolana. Press release by Greenpeace Czech Republic from 16th of July 2002.
'Guidance on best available techniques and best environmental practices (Minamata Convention on Mercury) - Waste Incineration Facilities' (2016). Geneva, UNEP.
Labunská, I. (2002) 'The Nováky Chemical Plant (Novácké chemické závody) as a source of mercury and organochlorine contaminants to the Nitra River, Slovakia.' Greenpeace Research Laboratories.
Lazo, P. and Reif, J. (2013) 'Vlora, an Abandoned PVC Factory at the Mediterranean Coast: Mercury Pollution, Threat to Humans, and Treatment Options', Bioremediation of mercury: current research and industrial applications, pp. 67–80.
Maršálek, P. et al. (2005) 'Mercury and Methyl-mercury Contamination of Fish from the Skalka Reservoir: A Case Study.', Acta Veterinaria Brno, (74), pp. 427–434.
Minamata Convention on Mercury (2019) 'Guidance on the management of contaminated sites.' UNEP/MC/COP.3/8/Rev.1, Geneva, UNEP.
Musil, J. et al. (2015) 'Realisation of fish muscles analysis including their fish out from the River Labe and the Mlékojedy pond.' T. G. Masaryk Water Research Institute Praha.
Petrlik, J. et al. (2015) 'Contaminated sites and their management. Case studies: Kazakhstan and Armenia.' Arnika - Toxics and Waste Programme, AWHHE, CINEST, EcoMuseum.
Pokorný, D. et al. (2011) 'Report on Water Management in the Czech Republic in 2010.' Report of Department of State Administration of Water Management and River Basin Ministry of Agriculture of the Czech Republic and Department of Water Protection of the Czech Republic Ministry of the Environment of the Czech Republic.
Randak, T. et al. (2009) 'Effects of pollution on chub in the River Elbe, Czech Republic', Ecotoxicology and Environmental Safety, 72(3), pp. 737–746. Available at: https://doi.org/10.1016/j.ecoenv.2008.09.020.
Šír, M. and Petrlík, J. (2015) 'Results of environmental sampling in Kazakhstan: mercury, methylmercury, PCBs and OCPs contamination of the River Nura (Final report). Contaminated sites and their management. Case studies: Kazakhstan and Armenia.' Arnika - Toxics and Waste Programme.
Storelli, M., Ceci, E. and Marcotrigiano, G. (1998) 'Comparative study of heavy metal residues in some tissues of the fish Galeus melastomus caught along the Italian and Albanian coasts', Rapp. Comm. Int. Mer. Medit, 35, pp. 288–289.
Titl, F. et al. (2011) 'Mercury on the Tributary to the Skalka Dam. Assessment and Proposed Measures. A Feasibility Study.' Aquatest a. s.
Ullrich, S.M. et al. (2007) 'Mercury contamination in the vicinity of a derelict chlor-alkali plant. Part I: Sediment and water contamination of Lake Balkyldak and the River Irtysh', Science of The Total Environment, 381(1), pp. 1–16. Available at: https://doi.org/10.1016/j.scitotenv.2007.02.033.
UNEP (2013) 'Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport.' UNEP Chemicals Branch, Geneva, Switzerland.
US EPA (2001) 'Water Quality Criterion for the Protection of Human Health: Methyl- mercury.' Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency Washington, DC.
WHO (2004) 'Safety evaluation of certain food additives and contaminants Food Additive series 52'. World Health Organization, international programme on chemical safety. Available at: http://apps.who.int/iris/bitstream/handle/10665/43038/924166052X.pdf;jsessionid=6E5829865EEC24EE3D6D7580992C27AB?sequence=1.
Žlábek, V. et al. (2005) 'Mercury content in the muscle of fish from the Elbe River and its tributaries', Czech Journal of Animal Science, 50(11), pp. 528–534. Available at: https://doi.org/10.17221/4258-CJAS.

WHERE STOCKHOLM MEETS MINAMATA – MERCURY AND HCH ISSUES AT CHLOR-ALKALI FACILITIES

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Abstract

With few exceptions, hexachlorocyclohexane (HCH) has been produced at sites where mercury cell chlor-alkali plants were operational. The Stockholm Convention banned Lindane and all HCH isomers in 2009 and the Minamata convention has set the goal to phase out all mercury cell chlor-alkali facilities world-wide by 2025. This phase out gives renewed attention to the clean-up and remediation of these facilities where both HCH and Mercury are serious issues. Especially where both HCH production wastes and wastes from maintenance and renewal of the mercury cells have been dumped together with the presence of both HCH and mercury complicates disposal and destruction options. Hg concentrations for acceptance of soil for thermal treatment are in the order of 3 ppm depending on the facility and soil type. For High temperature incineration, maximum acceptance levels are in the order of 50 – 100 ppm. With mercury wastes containing in excess of 5000 ppm, care has to be taken to separate these wastes from the HCH production wastes. This article describes a set-up implemented at the OHIS remediation in North-Macedonia where, with the help of protocols and the X-ray fluorescence (XRF), the various wastes were successfully separated during remediation.

Keywords

Mercury, hexachlorocyclohexane, lindane, HCH, Minamata Convention, Stockholm Convention, XRF, chlor-alkali

Introduction, scope and main objectives

The Minamata convention has set the goal to phase out all mercury cells chlor-alkali facilities world-wide by 2025. This phase out gives renewed attention to the clean-up and remediation of these facilities where both HCH, which has been banned under the Stockholm Convention in 2009, and Mercury are serious issues.

Hexachlorocyclohexane (HCH) was one of the most extensively produced pesticides, industrially manufactured mainly after the Second World War[1]. When producing Lindane, technical HCH first needs to be created by photo chlorinating benzene, which yields a mixture of isomers. This reaction is carried out by dissolving chlorine. The chlorination process of benzene results in approximately 14 % γ-HCH and 86 % inactive isomers, with the latter consisting of approximately 65-70% α-, 7-10% β-, 7% δ-, 1-2% ε-HCH, and 1-2% other components.

Therefore, the production of one ton of technical HCH translates into a ratio of 140 kg gamma-HCH (Lindane) and 860 kg of inactive isomers. These inactive isomers are potential waste and predestined for disposal. The product is later washed to remove any untreated chlorine and traces of HCl that might have been formed during the process. Excessive benzene is stripped and returned to storage. The molten product from the bottom of the distillation still is run onto a flaker, which is a cooled metal belt where the product solidifies [2].

It is estimated that 382 000 t of technical HCH and 81 000 t of lindane were used in Europe alone from 1970 to 1996. This is equivalent to an estimated cumulative usage of 259 000 t α-HCH, 135 000 t γ-HCH and 20 000 t β-HCH[3]. With the exception of γ-HCH most of these products ended as wastes in the vicinity of their production facilities. The use of technical HCH and gamma-HCH peaked in Europe in the 1960 till 1970ties[4]. This period is also the hay-day of mercury cell Chlor-alkali sites, which was the dominant process for the production of Chlorine up until the 1970ties[5]. The need for a source of Chlorine made Chlor-alkali sites pre-eminently suitable for the production of Technical HCH and Lindane.

Historically chlor-alkali mercury cell facilities contributed to large mercury losses. As an example, the mercury consumption by Chlor-alkali facilities in the United States in 1990 was staggering 220 tons per year[6] for up to 35 facilities. Accounting for a yearly loss of 6.2 tons per facility per year. In Mexico, the three (3) most recent operating Chlor-alkali plants are still using the mercury cell technology, which together produce 147,000 tons of chlorine annually and have an annual mercury consumption of 5.7 tons per year[7].

UNEP estimates that contaminated sites release 8–33 metric tons of mercury per year to water and 70–95 metric tons of mercury to air [8]. The 2018 Global Mercury Assessment [9] recognizes contaminated sites as an anthropogenic source for which emissions cannot yet be reliably estimated, and also concludes that there is no detailed knowledge on the processes of secondary releases resulting from mercury initially released to terrestrial pathways.

FIGURE 1 FORMER MERCURY CELL FACILITY IN NORTH-MACEDONIA

Where contamination is present

Although current emissions have been reduced greatly, most Chlor-alkali facilities have been and are still sinks for mercury. Decades of mercury losses during production has not only been emitted directly through the air and water but mercury has accumulated in the mercury cell building, and other structures such as the sewer systems, piping and in soil and groundwater. The soil and groundwater contamination is due to both the deposition of atmospheric contaminant and the historical disposal of graphite sludges and other wastes on and around the sites [10]. Outside these sites, poorly performing wastewater treatment systems and disposal of sludges have contributed to the contamination of sediments in rivers and marine environments often impacting ecosystems far away from the sites themselves.

Investigations of former mercury cell buildings show mercury concentrations in concrete, mortar and masonry of these facilities in hundreds to thousands of mg/kg. Concentrations of up to 80.000 mg/kg have been reported for the concrete floors of the production facilities themselves [11]. Add to this the mercury that is found in the soil and groundwater underneath the buildings, in the sewers, and pipes, and it is clear that a substantial part of the historic mercury consumption by the Chlor-alkali industry has not been emitted through the air and via waste water. A large part of the residual mercury rather remains in the structure of the plants and the surrounding soil.

When it comes to HCH wastes, these materials have been dumped in large quantities in the surroundings of the sites. In many cases, the HCH were used to fill existing quarries (example; Wintzenheim France) or used for the heightening of roads and fields (O'Porrino Spain, Hengelo the Netherlands) or in (semi)permitted landfill sites (Bailin Spain, OHIS, North-Macedonia). The quantities of HCH wastes is in the thousands of tons at the most of these sites.

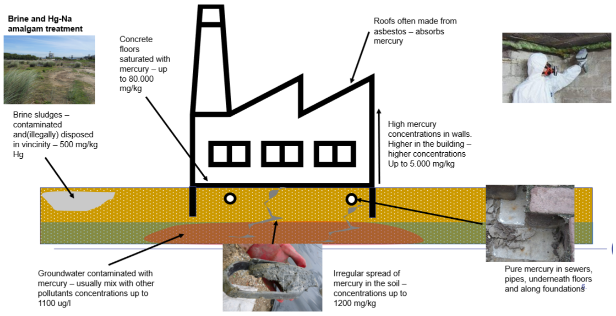

FIGURE 1: SCHEMATIC OVERVIEW OF THE PRESENCE OF MERCURY IN FORMER CHLOR-ALKALI FACILITIES

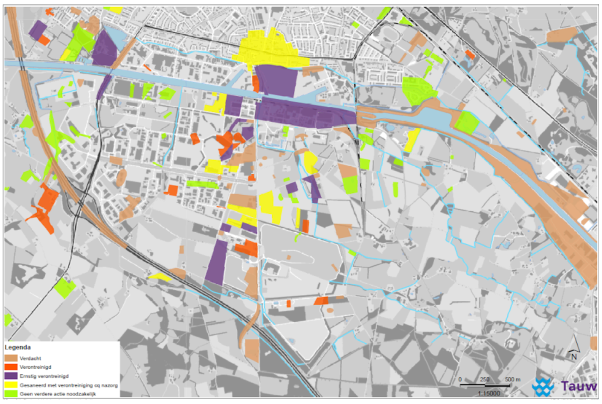

FIGURE 2: MAP WITH LOCATION OF HCH CONTAMINATED LAND AROUND A FORMER HCH PRODUCTION FACILITY IN HENGELO, THE NETHERLANDS

Orange sites are unconfirmed (possibly contaminated); red sites are confirmed (contaminated); purple sites area heavily contaminated (recently partially remediated or isolated); yellow sites have been remediated and/or aftercare measures are in place; for green sites no actions are necessary[12].

Remediation of HCH and Mercury contamination

Especially where both HCH productions wastes and wastes from maintenance and renewal of the mercury cells have been dumped together with the presence of both HCH and mercury complicates disposal and destruction options.

To achieve the required minimum Destruction Efficiency of 99.999 per cent [13], the most common destruction technology for HCH wastes is High Temperature Incineration. For heavily contaminated soil, a common method is thermal treatment. Both techniques have a proven track record. Both options have however limitations for the concentration of mercury they can handle.

Based on an internal inventory of facilities in the Netherlands, Belgium and Germany maximum Hg concentrations for acceptance of soil for thermal treatment are approximately 3 ppm depending on the soil type and/or treatment facility. For High temperature incineration, maximum acceptance levels are in the order of 50 – 100 ppm.

When mercury containing wastes, with concentrations in excess of 5000 ppm, are disposed together with HCH production wastes, the upmost care should be taken to separate the two wastes. This situation occurred at a former HCH production facility in Skopje, North Macedonia. Here, the basin used for disposal of HCH production was also used for disposal of brine sludge wastes and graphite anodes from the mercury cells. For this site, an excavation strategy was developed to minimize the mixing of different waste and soil flows (e.g., soil for thermal treatment, soil containing mercury above acceptance levels, "pure" HCH waste). As such, the general stepwise approach was to:

1. Assess for distinct visual properties (e.g., pure waste, anthropogenic materials, different coloring, different texture) both lateral and vertical
2. Analytical in-situ field investigation using the handheld X-ray fluorescence (XRF) analyzer on materials with similar visual properties
3. Determination of excavation strategy and relevant depots based on observations and measurements
4. Excavation based on the excavation strategy; the on-site supervisor will accomplish the excavation and might adjust plan based on observation during excavation
5. Batch testing of soil in depots using the handheld XRF to develop a database of XRF results
6. Batch testing of soil in depots for laboratory testing
7. Determination of final destination of depots based on laboratorial analyses

The proposed site investigation set-up (i.e., step 1 and 2) for determining the excavation strategy is given in more detail below. The on-site supervisor, in cooperation with the contractor, decided on the most appropriate set-up for the area based on "new" observations. This strategy was successful in preventing the mixture of mercury wastes with HCH wastes.

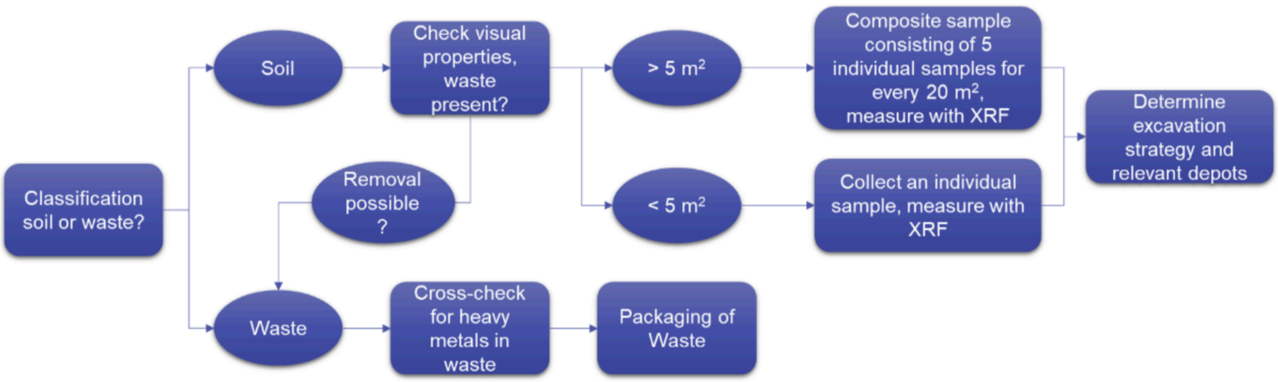

FIGURE 3: FLOW DIAGRAM FOR ASSESSMENT OF WASTE PROPERTIES

Conclusions

The presence of mercury wastes at former HCH production facilities is commonplace. Utmost care should be taken to separate HCH and mercury waste types as most disposal and destruction facilities for HCH wastes have mercury restrictions in place. When investigating an HCH site, mercury should be one of the main points of attention. The development of a detailed Conceptual Site Model, highlighting the sources, pathways and receptors and integration of site specific human health and ecological risk assessment is essential for the final cost-effective remediation of these facilities. During the remediation itself, protocols for the excavation and separation of the wastes can help with keeping wastes separate. The use of a handheld XRF analyzer is beneficial in establishing mercury concentrations.

Acknowledgements

We would like to thank the EU Commission in their support for the investigation of HCH sites throughout the EU. In addition, we would like to thank Mr. Aleksandar Mickovski for his support in the remediation and investigation of the HCH legacy from the OHIS facility in Skopje. Mr. Boudewijn Fokke and George Tsaimos of Polyeco are thanked for all their support and fruitful discussions during the remediation at the OHIS site. Last but not least we would like to thank Mr. John Vijgen for his relentless efforts to bring the HCH waste problem to the attention of the world.

References

1. Vijgen, J., Abhilash, P.C., Li, Y.F. et al. Hexachlorocyclohexane (HCH) as new Stockholm Convention POPs—a global perspective on the management of Lindane and its waste isomers. Environ Sci Pollut Res 18, 152–162 (2011)

2. De Bruijn J (1979) Reduction of chlordane, DDT, heptachlor, hexachlorobenzene and hexachlorocyclohexane isomers contained in effluents. Brussels, Commission of the European Communities (Report ENV/223/74-E Rev.2)

3. Knut Breivik, Jozef M. Pacyna, Jörg Münch, Use of α-, β- and γ-hexachlorocyclohexane in Europe, 1970–1996
4. Knut Breivik, Jozef M. Pacyna, Jörg Münch, Use of α-, β- and γ-hexachlorocyclohexane in Europe, 1970–1996, Science of The Total Environment, Volume 239, Issues 1–3, 1999, Pages 151-163,
5. O'Brien, Thomas, Bommaraju Tilak V., Hine, Fumio, Handbook of Chlor-Alkali Technology Volume I: Fundamentals, Springer Science 2005
6. Where Goes the Missing Mercury? As U.S. mercury controls tighten, attention focuses on mercury-cell chlor-alkali plants by Jeff Johnson March 15, 2004 | Chemical and Engineering news Volume 82, Issue 11
7. Acosta G., Inventario preliminar de emisiones atmosféricas de mercurio en México. Comisión para la Cooperación Ambiental (CCA) No. 3.2.1.04. 2001.
8. United Nations Environment Programme (UNEP) (2013). Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport. Geneva, UNEP Chemicals Branch. Available at http://wedocs.unep.org/handle/20.500.11822/7984
9. United Nations Environment Programme (UNEP) (2019). Global Mercury Assessment 2018. Geneva, UNEP Chemicals Branch. Available at https://wedocs.unep.org/bitstream/handle/20.500.11822/27579/GMA2018.pdf?sequence=1&isAllowed=y
10. Mihaiescu, Tania & Mihaiescu, Radu & ODAGIU, Antonia. (2012). Environmental Issues within the Chlor-Alkali Manufacturing Industry – Mercury Cell Process. Bulletin UASVM Cluj Agriculture. 69. Bulletin UASVM Agriculture 69(2)/2012 Print ISSN 1843-5246; Electronic ISSN 1843. 10.15835/buasvmcn-agr:8746.
11. OLD ENVIRONMENTAL BURDENS IN CHEMICAL PLANT OHIS, SKOPJE, Update risk assessment report, ENACON s.r.o, 13-11-2009
12. Consortium of HCH in EU, Inventory of sites that are potentially impacted by HCH in EU member states – List of sites in the Netherlands, reference R025-1272383CBN-V03-los-NL, d.d. December 13, 2021.
13. Basel Convention, General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants, UNEP/CHW.14/7/Add.1/Rev.1, June 20th 2019

MERCURY AND HCH WASTE TREATMENT FROM CHLOR-ALKALI PLANTS

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Summary

Currently, the demand for remediation of obsolete chlor-alkali plants that used elemental mercury during the manufacturing process has increased considerably, due to the emissions that these facilities cause to the environment.
During these remediation works, large quantities of contaminated waste with high concentrations of both mercury and HCH are obtained. Due to the hazardous nature of these wastes, it is necessary to treat them using the best available technologies for remediation and subsequent use of the decontaminated land, discarding landfill as an option.
With its VacuDry® technology, a low-temperature vacuum distillation process, econ industries offers the leading solution to recover resources from hazardous industrial wastes. VacuDry® units are available starting from 5 ton/day up to 250 tons/day and just require less than 20 % of the energy compared to other thermal treatment systems. The option for electrical heating can reduce the carbon footprint of the entire process to zero. In the VacuDry® process, contaminants are separated and concentrated in a closed process at temperatures of around 300 °C and low vacuum < 100 mbar abs. This treatment process aims to separate the recyclable soil components from the pollutants for reuse.
Finally, in the case of the mercury obtained in the remediation process, it has to be properly treated as stipulated in the Minamata Convention. Therefore, econ industries has developed a unique mercury stabilisation process, where the toxic mercury is converted into mercury sulphide, a non-toxic and stable compound for its safe final disposal.
Both technologies, the VacuDry® process as well as the mercury stabilisation, are available in skid-mounted, mobile design for on-site treatment. Transport and export of the mercury wastes is therefore no longer necessary."

Introduction

Due to the increasing number of chlor-alkali plants to be decommissioned, there will be a significant increment in the amount of hazardous waste contaminated with mercury and other polluting compounds such as HCH, etc. In order to avoid unforeseen risks during transport and to reduce the carbon footprint caused by long distances road transport, this waste will need to be treated locally using the best available technologies.
Taking into account the above, econ industries has developed the most efficient and cleanest solution to recover resources from hazardous industrial wastes, based on more than 20+ years of experience and more than 30 industrial waste recycling projects.
The following chapters explain in detail the various on-site waste treatment technologies and provide case studies adapted to the needs of the chlor-alkali sector.

Available on-site treatment technologies

Referring on-site treatment technologies for the chlor- alkali waste, econ industries offers a complete treatment solution; from extracting the mercury from the waste to the stabilisation of the recovered mercury in HgS.
The first treatment process and to extract the mercury from the original waste, is the VacuDry® unit (figure 1). This is a low-temperature vacuum distillation process which it is mainly used for soils and sludges contaminated with mercury and/or other pollutants (HCH compounds, hydrocarbons, etc.)
Once the mercury has been extracted, this must be disposed of in the safest manner in accordance with the authorities' regulations. For this reason, a Mobile Mercury Conversion Unit (MMCU – figure 2) is used with the aim to convert the toxic elemental mercury (Hg) into a non-toxic mercury compound, in this case, mercury sulphide (HgS) or cinnabar.

FIGURE 1: VACUDRY® PLANT

FIGURE 2: MOBILE MERCURY CONVERSION UNIT

VacuDry® technology

Thermal vacuum distillation offers a low-emission and energy-efficient technology for the treatment of contaminated soil and hazardous waste. In the VacuDry® process, contaminants are separated and concentrated in a closed process under the influence of heat and vacuum. This treatment process aims to separate the recyclable soil components from the pollutants and send them for recycling (figure 3). The amount of waste or pollutants that is subsequently recycled elsewhere or has to be disposed of should thus be as pure or as highly concentrated as possible. Ideally, only a few grams of pollutants remain for disposal from each ton of contaminated material.

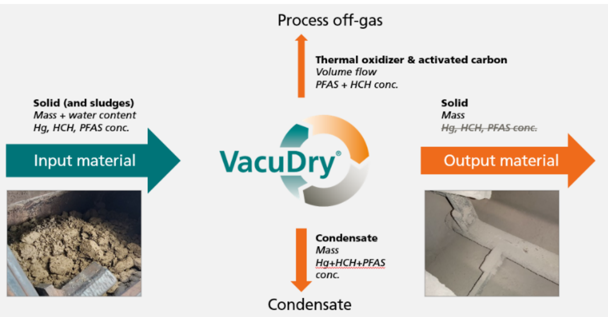

FIGURE 3: VACUDRY® CONCEPT

The core of the VacuDry® system is a single-shaft batch evaporator consisting of a horizontal reactor in which mixing elements (shovels) are arranged around a rotating shaft, which continuously homogenize the material during the treatment period and guarantee efficient heat transfer. Mixing enables short, energy-saving batch times as well as uniform cleaning results.

The bottom material inside the evaporator is indirectly heated by a double jacket. Synthetic thermal oil is used as heat transfer medium, which can withstand temperatures of up to 400 °C and is heated in a closed circuit by means of an electrically heated thermal oil system. In the subsequent condensation unit, a filter for removing entrained particles, a tube bundle condenser and a vacuum pump are connected to the evaporator for the gas phase. With the aid of indirect heating at the evaporator shell and the vacuum pump, the heating temperature is gradually increased and the pressure inside the evaporator is reduced to below 50 mbar absolute pressure. The low process pressure allows substances with a boiling point of up to 450 °C (at atmospheric pressure) to be evaporated. In addition, the long heat application in the batch process partly causes long-chain compounds to break up, which explains why higher-boiling compounds can also be evaporated.

The vaporized substances, like mercury, are liquefied at the condenser and can thus be collected. The remaining off-gas stream, including the non-condensable components, is then passed through the vacuum pump, passes through a thermal oxidiser, where the persistent compounds are heated up to 1,200 °C for more than two seconds for complete destruction, afterwards through a cooling and separator system and finally across an activated carbon filter before being discharged into the atmosphere.

With this design, the VacuDry® systems achieve the international and national emission standards, including the German TA-Luft, for example, when hydrocarbon and mercury waste is used.

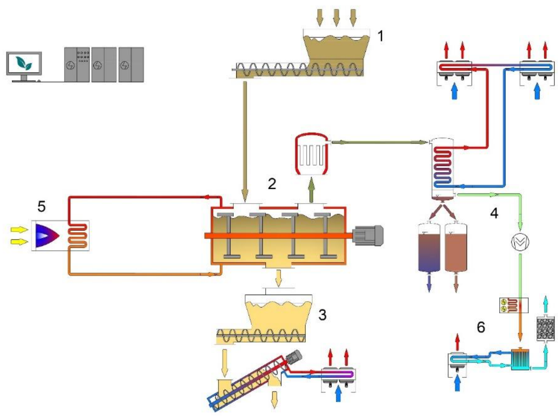

FIGURE 4: VACUDRY® PROCESS IN LARGE-SCALE APPLICATION. 1: INFEED, 2: VACUUM SINGLE-SHAFT BATCH EVAPORATOR WITH FILTER, 3: OUTFEED, 4: CONDENSATION UNIT WITH VACUUM PUMP, 5: THERMAL OIL UNIT, 6: WASTE GAS TREATMENT WITH THERMAL OXIDIZER AND ACTIVATED CARBON FILTER; SOURCE: ECON INDUSTRIES SERVICES GMBH.

VacuDry® TECHNOLOGY – Case studies (References)

In this chapter two real cases are presented where the VacuDry® technology was used to decontaminate soil contaminated with mercury and other hazardous substances.

Note: The technical requirements for treating the waste generated when decommissioning chlor-alkali plants, that used mercury in their production process, are perfectly adapted to the following cases.

On-site remediation of a mercury contaminated site (France)

70,000 tons of mercury and PAH contaminated soil and building rubble had to be cleaned in an industrial facility in the south of France. For the realization of this remediation work, an econ industries VacuDry® 12,000 was installed. After the treatment, the mercury free soils could be re-used on-site as a building material.

FIGURE 4: VACUDRY® TECHNOLOGY INSTALLED IN FRANCE

The initial composition of the contaminated soils and the treatment operating conditions during the remediation works were as follows:

TABLE 1. INPUT MATERIAL COMPOSITION AND OPERATING CONDITIONS

Composition (input material)	Water	Mercury	Solids (soil)
	6.1%	> 50 ppm	93.9%
Batch time	255 min	Min. pressure	50 mbar (abs)
Max. material temp.	350°C	Max. heating temp.	380°C

As shown in the table above, to achieve the target of < **1 ppm** mercury in the output material, the material was heated to a temperature of approximately 350°C at a pressure of 50 mbar (abs). The total duration of the process, including loading and unloading of the waste, was approximately 4 hours.

The appearance of the input material and the decontaminated soil (output material) are shown in the following pictures.

FIGURE 5: INPUT MATERIAL INSIDE EVAPORATOR

FIGURE 6: CLEANED SOIL AFTER TREATMENT

On-site remediation of a mercury contaminated area in India

In order to treat mercury contaminated soil derived from a former thermometer factory in India, econ industries designed and built a soil recycling facility. It was necessary to implement a technology that would allow for on-site, ex-situ remediation rather than transporting contaminated material over long distances. Due to further local transport restrictions that neither allowed skids to be larger than 20 ft. nor heavier than 20 tons, the solution was econ's semi-mobile VacuDry® 3 000 unit. This plant is currently in operation.

The initial composition of the contaminated soils and the treatment operating conditions during the remediation works were as follows:

TABLE 2: INPUT MATERIAL COMPOSITION AND OPERATING CONDITIONS

Composition (input material)	Water	Mercury	Solids (soil)
	17.5%	> 80 ppm	82.5%
Batch time	255 min	Min. pressure	50 mbar (abs)
Max. material temp.	350°C	Max. heating temp.	380°C

FIGURE 7: VACUDRY® TECHNOLOGY INSTALLED IN INDIA

As shown in the table above, to achieve the target of **< 1 ppm** mercury in the output material, the material was heated to a temperature of approximately 350°C at a pressure of 50 mbar (abs). The total duration of the process, including loading and unloading of the waste, was approximately 5 hours.

The appearance of the input material (Fig. 8) and the decontaminated soil or output material (figure 9) are shown in the following pictures.

FIGURE 8: INPUT MATERIAL INSIDE EVAPORATOR

Mobile Mercury Conversion Unit - (MMCU)

Strict legal requirements and corporate responsibility require a traceable disposal solution for the recovered mercury from the Chlor-alkali plants decommissioning and other origins.

Therefore, econ industries has developed an on-site mercury conversion process, where the highly toxic elemental mercury is transformed into a non-toxic mercury compound named mercury sulphide or cinnabar.

IMAGE 9: CLEANED SOIL AFTER TREATMENT

The unit operates according to the mercury sulphide formation reaction. Elemental mercury is mixed with solid sulphur in a stoichiometric ratio to form HgS. This reaction takes place in a liquid phase and under an inert atmosphere, avoiding material oxidation and potential hazards. The continuous and intensive mixing during the process ensures a complete reaction to form or obtain mercury sulphide (red cinnabar), which allows for its safe and final disposal once it has been packaged according to the acceptance criteria of the disposal site.

FIGURE 10: MERCURY CONVERSION PROCESS

MMCU technology – real cases (References)

econ industries has stabilised more than 500t of elemental mercury (Hg), from the chlor-alkali industry, to mercury sulphide (HgS) for safe final disposal. Specifically, 400 tonnes of mercury were stabilised in a chlor-alkali plant in England and another 130 tonnes were converted to HgS in Poland.

Conclusions (on-site Chlor-alkali waste treatment using econ technology)

Taking into account the detailed information on the technologies and case studies presented above, econ industries offers a proven on-site treatment solution for the treatment of decommissioning waste and the stabilisation of the recovered mercury for its safe final disposal.

VacuDry® technology ensures a high degree of decontamination of the solid waste (>95%), allowing it to be reused as backfill material and

reducing large volumes of hazardous waste going to landfill.
As the technology can be installed directly on-site, this considerably reduces logistics costs and avoids unforeseen risks during the mobilisation of waste from site to site.
Due to the advanced technology and the use of renewable energy supply the system has a very low carbon footprint compared with other kind of technologies.
The system fully complies with the requirements laid down for the regulatory authorities.

FIGURE 11: ON-SITE MOBILE MERCURY CONVERSION INSTALLED AT A CLIENT SITE

BATREC: TREATMENT OF MERCURY AND MERCURY WASTES: MERCURY STABILIZATION AND SAFE DISPOSAL

Castellnou, Angels

BATREC Industrie AG, Wimmis, Switzerland

BATREC, Recycling solutions

BATREC, a subsidiary company of the Veolia group, part of Sarp Industries, is a leading specialist in the treatment and recycling of industrial hazardous wastes, particularly those containing Mercury.

Mercury treatment

Mercury is present in many industries including oil & gas and non-ferrous metal industry. Parties that have ratified the **Minamata Convention** are committed to taking action to eliminate Mercury from its use in both everyday products and industries (e.g. chlor-alkali units or mines).

BATREC has developed a **patented solution to stabilize metallic mercury** (Hg) to mercury sulfide (HgS) for a permanent and safe disposal in a salt mine. **HgS** is the safe, most stable and most non-soluble non-toxic mercury compound. In addition, the BATREC process is a wet process and thus not prone to gaseous mercury emissions, improving operational safety.

BATREC offers in addition **other treatment technologies** according to the different types of waste:

- **Reactivation unit with a thermal treatment step** for the decontamination of mercury absorbents, allowing these products to be returned into industrial processes.
- **Distillation unit** for Mercury waste (any type of waste contaminated with mercury: lamps. Thermometers, button batteries), to recover the Hg in metallic form, followed by a stabilization of liquid mercury.

Sludges, residual material, soils, from old-industrial sites are processed at our facility to extract Hg in several stages. At the end of the process, the recovered Hg is stabilized.

BATREC contributes to the progressive global removal of mercury by treating **all types of mercury waste**, rendering them safe in an environmentally sound way in compliance with international legislation.

Legislation

The MINAMATA CONVENTION is an international treaty developed with the backing of the United Nations Environment Program to protect human health and the environment from the harmful effects of mercury.

150 countries agreed on:

- the reduction and phase out of mercury use in a number of products and processes.
- implementing control measures on environmental emissions.

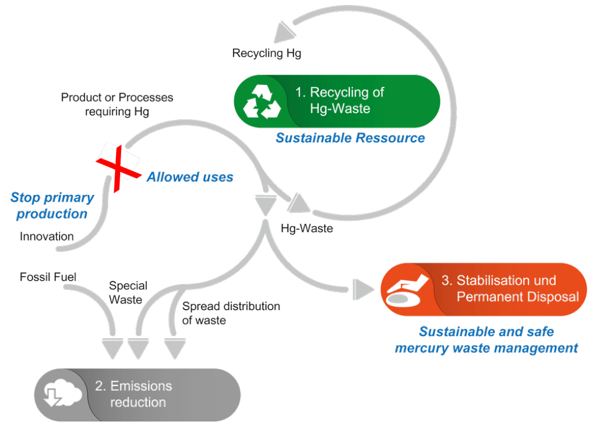

FIGURE 1: AROUND MINAMATA

Treatment technologies: mercury stabilisation. Stabilisation process

The safest solution to dispose of liquid mercury is to transform it into HgS (cinnabar) and then to send it for final disposal at a licensed, deep underground storage facility .The transformation of Hg into HgS is considered to be the best solution since HgS is the only nontoxic mercury compound. HgS is also the most stable mercury compound and the most insoluble mercury compound.

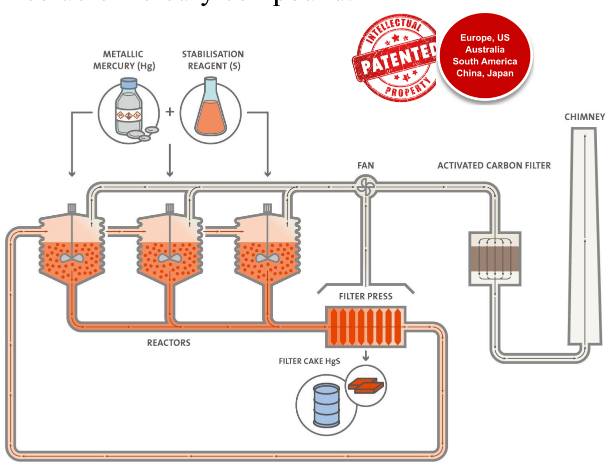

FIGURE 2: PROCESS FLOW SHEET - HG STABILIZATION

The HgS is produced by mixing the liquid Mercury into a polysulfide solution in a wet chemical reaction. The active sulphur of the polysulfide solution reacts with the metallic Mercury to become HgS according to the following chemical reaction:

$$Hg_{(l)} + S^{2-} \rightarrow HgS_{(s)}$$

FIGURE 3: HG DROPS - HGS

The benefits of using a wet chemical process over a dry powder process are that it mitigates the chances of HgO (mercuric oxide) forming without the need for an inert gas environment and without the explosion risks associated with processing dry powders.
The wet chemistry also allows the temperature of the reaction to be controlled (60-70°C) meaning that it is considered a low temperature and therefore low energy process. The reaction is controlled through a combination of dosing rate manipulation and the use of a heating/cooling jacket to ensure rapid and thorough creation of HgS. As the mercury added is always covered by the polysulphide solution in the reactor, there is little opportunity for volatilisation of the elemental mercury, and therefore the off-gas stream is safer and easier to handle and clean. It should be noted that the chemistry must be carefully controlled to stop unwanted toxic compounds forming.
Finally, the fully reacted solution is pumped through a filter press to create two streams. The filtrate (liquid) is the polysulphide solution, which can be recharged with sulphur and reused in the process several hundred times before it becomes spent. The spent polysulphide is used as a waste water treatment product elsewhere in the plant, meaning that there are no waste products from the process other than the HgS.
The filter cake is the HgS. The conversion rate of Hg to HgS is >99.999% with a remaining metallic mercury concentration in the final product of <100 ppm. Typically, the remaining HgS compound contains 86% mercury and 14% sulphur by mass, meaning that the mercury content per unit mass is higher than alternative stabilisation methods, saving on disposal costs. The filter cake has a moisture content of <5%, remaining damp enough that any handling or sampling can be done with minimal risk of dust. The filter cake typically contains <1% unreacted sulphur.

FIGURE 4: HGS PRODUCED WITH THE BATREC STABILISATION PROCESS

Traceability, analysis and final disposal

Before the HgS is sent from BATREC to salt mine, the HgS will be sampled and ana an independent sampling company in provide the clients and authorities with a transparent and independent mass balance of the process. This extensive sampling and analytical characterisation of the material is done in order to ensure and guarantee that all the liquid Mercury delivered to BATREC is fully stabilised, transformed into HgS and finally transferred to the salt mine as mandated.
The salt mine is chosen as a final disposal site due to its unique geology. The storage caverns are ~500m below ground and surrounded by rock salt. The salt absorbs any moisture meaning that there is a dry atmosphere. Also, the nature of salt is that it flows over a geological timescale, releasing stresses in the formation and ensuring that stress fractures do not occur.

Mercury waste: Other treatment technologies

Today the poisonous, liquid metal mercury is still used in several applications. We find mercury in hospitals (thermometers), in laboratories (analyzers), in waste gas cleaning systems (crematoria), as road and sports field lighting (metal-vapor lamps), in dental laboratories (amalgam) or in button cells.

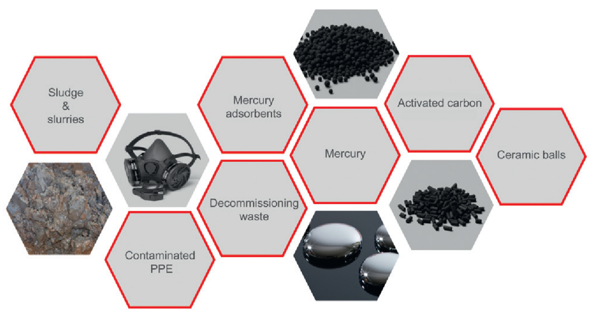

FIGURE 5: TYPE OF WASTE STREAMS

BATREC offers in addition **other treatment technologies** according to the different types of waste:

- **Distillation unit** for Mercury waste (any type of waste contaminated with mercury: lamps.

Thermometers, button batteries), to recover the Hg in metallic form, followed by a stabilization of liquid mercury.

By heating to over 360°C, the mercury contained in the waste vaporizes, and condenses again as pure mercury in a condensation column.

The condensation unit is followed by an activated carbon filter, which removes the remaining traces of mercury from the exhaust-gas stream. Distillation is conducted as a batch process, and guarantees low-emission operation – for the safety of the employees and the environment.

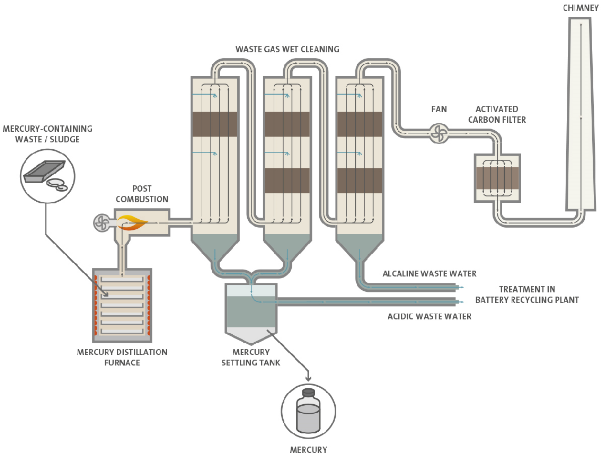

FIGURE 6: HG DISTILLATION PROCESS

- **Reactivation unit with a thermal treatment step** for the decontamination of mercury absorbents, allowing these products to be returned into industrial processes. Soils and sludges contaminated with soil, or PPE (see figure 5) are processed through this unit.

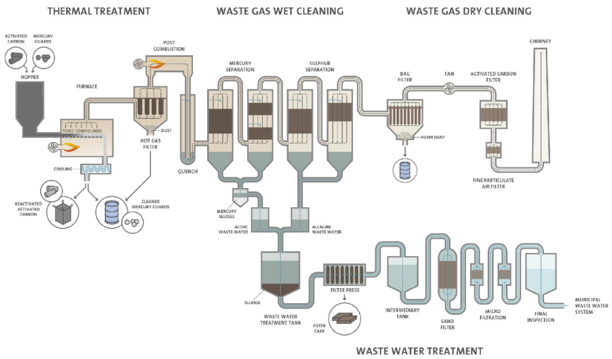

FIGURE 7: PROCESS FLOWSHEET

Sludges, residual material, soils, from old-industrial sites are processed at our facility to extract Hg in several stages. At the end of the process, the recovered Hg is stabilized.

Conclusion

BATREC is a company based in Wimmis, Switzerland, specialised in hazardous waste treatment/recovery. Services offered by BATREC include the recycling of batteries, treatment/ recovery of hazardous wastes containing mercury, the reactivation of activated carbon and the decontamination of mercury guards for customers from all over the world. BATREC turns waste into a resource and so ensures a closed materials cycle. As a Swiss company, BATREC applies the highest environmental and safety standards.

BATREC contributes to the progressive global removal of mercury by treating **all types of mercury waste**, rendering them safe in an environmentally sound way in compliance with international legislation.

BATREC: HG DECONTAMINATION: CASE STUDIES IN SPAIN AND ABROAD, INCLUDING MERCURY BASED CHLOR-ALKALI PLANT DECOMMISSIONING

Castellnou, Angels

BATREC Industrie AG, Wimmis, Switzerland

BATREC, Recycling solutions

BATREC, a subsidiary company of the Veolia group, part of Sarp Industries, is a leading specialist in the treatment and recycling of industrial hazardous wastes, particularly those containing Mercury.

Global evolution of environmental legislation

- Parties that have ratified the **Minamata Convention** are committed to taking action to eliminate Mercury from its use in both everyday products and industries (e.g. chlor-alkali units or mines).
- US Export Ban. Mercury Export Ban Act 2008
- EU Export Ban Regulation (EC) N° 2017/852.
  - Article 11 "… mercury and mercury compounds, whether in pure or in mixtures, from any of the following large sources … shall not lead to any form or reclamation of mercury."
  - Article 13 (3) "Prior to being permanently disposed of, mercury waste shall undergo conversion …"
- The safe long-term storage of mercury is regulated by existing EU waste legislation (Directives 2008/98/EC & 1999/31/EC and Decision 2003/33/EC). This ensures that only those sites with the necessary permits for the storage of hazardous waste can be used.

The legislation creates a demand for safe, sustainable treatment through stabilization, together with a reassurance that the Mercury does not re-enter the market. It concerns mainly customers from: Chlol-Alkali industry. Natural gas production. Nonferrous mining industry (e.g. gold mining). Nonferrous metallurgy (Cu- & Zn-smelters).

Today, the use of mercury-based chlor-alkali production has been phased out since 2017 and this technology is no longer used in Europe.

BATREC contributes to the progressive global removal of mercury by treating all types of mercury waste, rendering them safe in an environmentally sound way in compliance with international legislation.

Mercury treatment

BATREC has developed a **patented solution to stabilize metallic mercury** (Hg) to mercury sulfide (HgS) for a permanent and safe disposal in a salt mine. **HgS** is the safe, most stable and most non-soluble non-toxic mercury compound. In addition, the BATREC process is a wet process and thus not prone to gaseous mercury emissions, improving operational safety.

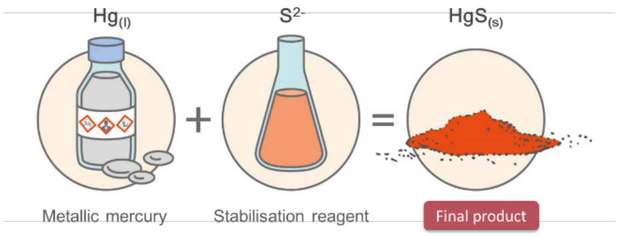

FIGURE 1: $HG_{(L)} + S^{2-} \rightarrow HGS_{(S)}$

Traceability is key: Basel Convention – when needed, **Mass Balance Reports** according to national and international regulations.

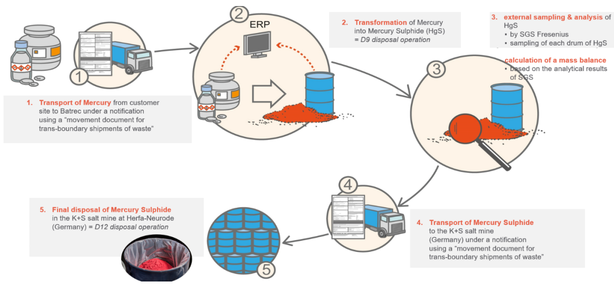

FIGURE 2: TRACEABILITY: TRANSPORT, STABILISATION, SAMPLING AND ANALYSIS, FINAL DISPOSAL

Projects accomplished in Chlor-Alkali Industry and Gold Mines:

- Decommissioning of European Hg based Chlor-Alkali plants.
- More than 1'800 T as of 2016 (Spain, Belgium, France, Italy, Hungary, Slovakia, Czech Republic, Switzerland).
- **Industrial gold mines.** Continuous production worldwide.

More than 500 T as of 2016 (Latam Region).

Two Case Studies are provided with a detailed examination within a real-world context, where BATREC offers a turnkey solution.

- transfrontier shipment formalities according to **Basel Convention** on the control of transboundary movements of hazardous waste;

- **local operations** (e.g on-site supervision for packing, labelling, shipping into maritime containers, health and safety protocol);
- road and maritime transport according to **ADR/ IMDG** regulations
- **Mercury stabilisation** through the patented BATREC process to HgS, safe transport and permanent disposal of the HgS in the salt mine.
- **full traceability chain** is ensured from the on-site to the final disposal in the salt mine – including the provision of a final report tracking the waste.

FIGURE 3. SAFE STORAGE OF HG IN A STORAGE FACILITY BEFORE SHIPMENT

CASE STUDY – SPAIN, CHLOR-ALKALI

- **Administrative handling:** preparation of the Basel Convention transboundary notification package and support on the reception of the consents from all competent authorities of the countries involved. National and international paperwork.
- **Local operations:** support on the correct labelling and storage according to the local and ADR regulations.
- **International transport:** global coordination of transport involved parties, according to the deliveries planning schedule.
- **Waste treatment:** transformation of more than 700 tons of liquid mercury into mercury sulfide (HgS) including final disposal in a salt mine using the appropriate technology and the necessary permits.
- **Reporting:** provision of the necessary detailed in compliance with Articles 12 and 14 of the Regulation (EU) 2017/852 of the European Parliament and of the Council


FIGURE 4. TRANSPORT OF HG FROM PRODUCER TO BATREC

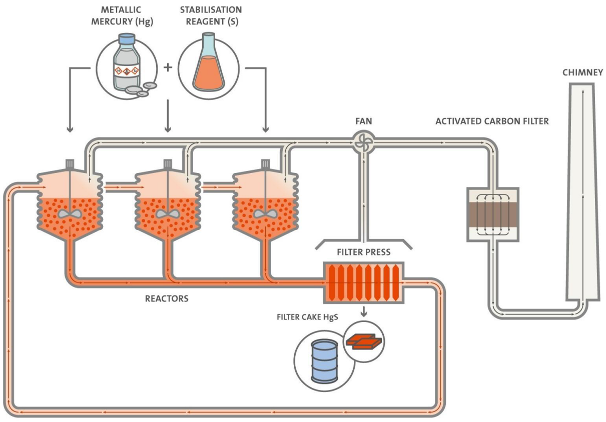

FIGURE 5: PROCESS FLOW SHEET - HG STABILISATION

Case study - mining industry

BATREC offers to the mining industries its door-to-door services consisting of on-site supervision for packing, labelling, loading into maritime containers and international transport, following Basel Convention for Transboundary movement of waste, prior to Hg stabilization and final disposal. More than 500 T have been shipped from several countries.

- **On-site supervision**: Supervision Works at the Mine and Stuffing of Maritime Containers
  - Inspection of Hg containers.
- Labelling.
- Maritime Container Stuffing
- Basel Convention and IMDG and ADR paperwork

- **Health and Safety.** BATREC-VEOLIA provided training following occupational health protocol.
- **Full traceability**: local VEOLIA teams ensured the proper traceability of each mercury container thanks to a dedicated labelling system.
- **National and International transport**: supply and coordination of the road and maritime carriers from the mine to Wimmis.

- **Export/import customs clearance management**. Includes handling of the route risk study including full time custody of the convoy from the mine to the local port. Road transport in Europe.

Conclusion

BATREC is a leading specialist in the treatment and recycling of industrial hazardous wastes, particularly those containing Mercury.
Two Case Studies (Chlor-Alkali in Spain and Mine Industry in America) with a detailed examination within a real-world context, are provided, where BATREC offers a turnkey solution.

ARTISANAL SMALL SCALE GOLD MINING (ASGM) PROJECT INDONESIA

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Summary

Indonesia is the third largest contributor of the global mercury pollution by ASGM. The NEXUS3 Foundation - TAUW bv consortium and partners were granted by the TAUW Foundation for a ASGM pilot remediation project. The pilot intends to apply sustainable remediation techniques. PT Amman Mineral, one of the project partners, donated a mercury analyser. The pilot has four phases: (1) inception, including site investigations of ASGM sites and selection of a pilot remediation site (2) a tier 3 risk assessment, (3) the remediation and monitoring and (4) outreach and the development of a toolkit to remediate ASGM sites. This abstract summarizes the findings of the inception and the tier 3 risk assessment.

Eleven ASGM sites were preliminary assessed. The Kayu Putih site at Lombok and the Taliwang, at West Sumbawa were selected for a detailed site assessment.

The detailed site assessments concluded that the soil and groundwater are contaminated by mercury. The primary source is the ASGM, using mercury. The secondary sources are the sedimentation ponds, the diffuse contaminated topsoil around the rod-mills, the groundwater and the sludge in the domestic shallow wells. The mercury concentrations in the groundwater samples the are above the Dutch intervention value but just above, equal and below the EU/WHO drink water limits. For both sites the pathways are direct contact with the contaminated topsoil and the water from the shallow wells used in the households and kitchen gardens. The tier 3 risk assessment concluded that human health risks cannot be excluded at these sites.

From the two sites that were detailed assessed, the Taliwang site is selected as the pilot remediation site because all on-site ASGM activities have stopped and therefore recontamination with mercury is excluded. This site comprises of a family house with a shop, a shallow well, a garden with the remains of a platform that supported the ASGM rod-mill and a backfilled sedimentation pond. All ASGM installations were removed two years before.

The selected remediation techniques are: excavation of the mercury contaminated soil. immobilization of mercury by mixing the soil with Biochar and containment in an off-site depot by planted Vetiver Grass. As the groundwater has mercury levels around the drinking water norm over a large area and the people are not drinking this water, a groundwater remediation is not justifiable.

In the villages where ASGM is still practiced remediation is not justifiable instead, the awareness should be raised with a focus on the phasing out the use mercury in ASGM. Only when the use of mercury has stopped, remediation should be considered. Based on the experiences with pilot project a toolkit will be developed to remediate ASGM site where the mercury is not anymore used.

Keywords

Artisanal Small scale Gold Mining, mercury contamination, soil remediation immobilization and containment, awareness raising, toolkit to remediate ASGM site

Introduction

Artisanal and Small-Scale Gold Mining, referred to as ASGM, is responsible for the bulk of manmade mercury emission on earth. Indonesia is the third largest contributor of the global mercury pollution. This is mainly caused by mercury used to extract gold from ore in ASGM. Due to exposure to mercury during this ASGM process, including the atmospheric deposited mercury from the burning and evaporated mercury and transfer of mercury through impacted soils , health and environmental problems occur.

ASGM at Lombok and Sumbawa

Gold ore is manually mined in hills and mountains on Lombok and Sumbawa. These mines are mostly small shaft mines. The ore from these mines is carried to villages in small bags and (manually) crushed before processing (milling and amalgamation) in rod-mills.

On average, a special made platform at a family compound to process ore, has one to eight rod-mills. The rod-mills are rotating drums with a lid on the side, of around 100 litters, secured on small concrete supports. . Together with the ore, water and mercury are added to these drums for the gold mercury amalgamation. 20 - 40 kg crushed ore is fed into the rod-mill. Water and mercury are added and after around five hours milling, it is assumed that the ore is fine enough for the gold mercury amalgamation. From literature and the few information obtained, the amounts of mercury used vary between 0.3 kg and 1 kg of mercury to 20 kg ore. After milling the content of the rod-mill, process water, milled ore, the amalgam, and the excess of mercury, are drained from the rod-mill drum and separated by gravitation using water. The edges of the build platforms with the installed rod-mills are higher to prevent spilling and to facilitate drainage of the process water with the tailings. The processed ore and water from the drum are poured in a basin, the amalgam and the excess of mercury settle at the bottom of the basin. Excess of water with the tailings are poured on the platform and drained from the platform in a small settlement pit, constructed in the rod-mill platform to reclaim the coarse tailings. From this small pit the tailings, containing the finer particulars (sludge), are drained to mostly an unlined sedimentation pond to drain the process water from the tailings. The tailings are drained and dried as the process water freely infiltrates in the subsoil.

At the last stage of separation, the excess of mercury and the amalgam in the basin are drained and filtered using a strong fabric cloth to separate the mercury from the amalgam by squeezing. The gold is retrieved by burning the amalgam. The burning is done at the family compounds and/or at (specialised) gold-shops mostly located in these villages. Finally, the drained/dried tailings from the sedimentation pond are bagged and sold to a cyanidation plant. Noteworthy is that last year's more cyanidation plants in West Sumbawa and West Lombok to process these tailings were constructed.

The whole ASGM process from milling, to reclaiming the excess of mercury and finally separating the amalgam, uses a lot of water. Therefore, the majority of the rod-mill locations have an open shallow well close by, to provide process water. The water from these wells is besides process water for ASGM, also used in households for cooking, sanitation, watering livestock and irrigation of the kitchen gardens. Occasionally well water is used as drinking water, but the majority of households use bottled drinking water.

Introduction to the pilot-project

The NEXUS3 Foundation - TAUW bv consortium and the Department of Soil Science of the Agriculture Faculty of the University of Mataram Lombok and PT Amman Mineral (a large mining company at Sumbawa) as project partners were granted by the TAUW Foundation for a ASGM pilot remediation project. The pilot intends to apply sustainable remediation techniques This article reports the findings of the site investigation phase and the tier 3 risk assessment and preparation of the pilot remediation.

ASGM site assessment results

Eleven villages where ASGM was/is practiced were preliminary assessed as part of the project. The ASGM practises in these villages at Lombok and Sumbawa are comparable and are resulting in similar sources, source-receptor-pathways and receptors pattern. A representative cross section of the initial conceptual site model of a village practicing ASGM at multiple family compounds at West Lombok and West Sumbawa is given in Figure 1.

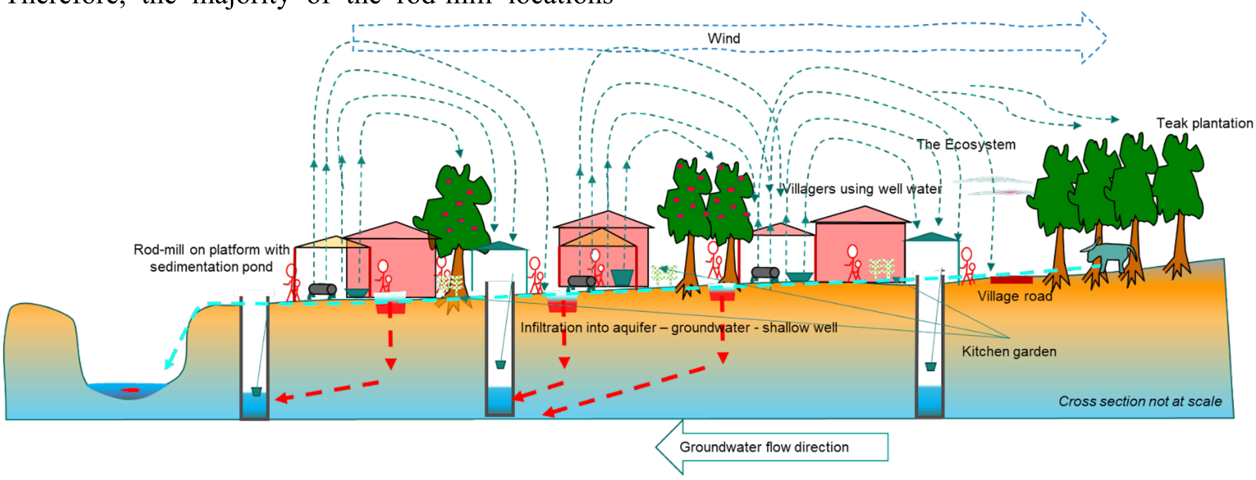

FIGURE 1. REPRESENTATIVE CROSS SECTION OF THE INITIAL CONCEPTUAL SITE MODEL OF A VILLAGE PRACTICING ASGM AT MULTIPLE FAMILY COMPOUNDS AT WEST LOMBOK AND WEST SUMBAWA

Based on the initial conceptual site models and tier 1 risk assessments of these eleven sites, two sites were seceded for a detailed site assessment. The selected sites are the Kayu Putih site at West Lombok and the Taliwang at West Sumbawa.

Kayu Putih has around 17 family compounds and about 70 people are living in this community. Nearly all are or were involved in ASGM. Kayu Putih borders to the west the main road with left and right a trench to drain surface runoff water, and to the north and west a tree (teak) plantation is situated. A few hundred meters east of the site is a foot slope of a hill situated, and to the south and (south)west is a small meandering stream. This small stream enters a river and subsequently flows into the Lombok Strait, around 1 km North of Kayu Putih. The Lombok Strait connects the Bali Sea to the Indian Ocean.

The terrain slopes in general to the northwest and the groundwater flow direction is assumed to be also northwest. The southern area of the site surface drains towards the small stream. The runoff in the northern part drains through the unpaved road between Kayu Putih and the teak plantation to end up in the trench that runs parallel to Jalan Raya Pelangan. The western part of the site drains directly to this trench.

The second site is a family compound with a house annex shop, and a kitchen garden in the centre of the small town, Kuang of the Taliwang regency in West Sumbawa. Two years ago, ASGM was completely stopped, the rod-mill was removed and the sedimentation pond was backfilled.

The site is approximately 500 m south of a large meandering river. The town including the selected site are subjected to flooding in the rainy season. The terrain slopes slightly to the south, runoff is therefore directed towards the south, the groundwater flow direction is interpreted towards the north. One well is situated on-site and multiple wells are within a distance of 50 m.

Sources

The detailed site assessments concluded that the primary source was the ASGM, using mercury. The main secondary sources are the sedimentation ponds, the diffuse contaminated topsoil around the rod-mills, the subsoil at the sedimentation ponds, the groundwater and the sludge in the domestic shallow wells. The general topsoil quality in the village was only slightly impacted (see Figure 2).

FIGURE 2. RESULTS OF THE SITE ASSESSMENT

The highest concentrations are measured in the sedimentation ponds which were actively or recently used at the time of the sampling.

Elevated levels of mercury were found in all sampled domestic (shallow) groundwater wells, the detected mercury concentrations are above the Dutch intervention value but just above, equal and below the EU/WHO drink water limits.

Based on the results, it is concluded that the mercury contamination of the soil and groundwater is occurring. The primary source of the mercury contamination is the ASGM using gold mercury amalgamation. The secondary point sources are the sediments in the sediment ponds and the domestic wells and the soil below the sedimentation ponds. The secondary diffuse sources are the topsoil around the rod-mills and the groundwater. The atmospheric deposition does contribute to the deterioration of the soil and groundwater quality.

Receptors

The receptors that are most at risk are the villagers, including their family members, involved in ASGM. The exposure is mainly due to the burning of amalgam in the family compounds where people live close to each other. The villagers not involved in ASGM (women and children) are also exposed and at risk. In addition, the villagers are also eating vegetables from plots where the soil is contaminated with mercury and use the water with mercury from their wells in their household. The surrounding ecosystem is also a receptor, especially the aquatic ecosystem in the nearby, creeks, rivers and finally the sea receiving the contaminated sediments.

Source-receptor-pathways

The major source-receptor-pathways are the inhalation of mercury vapour during the burning of the amalgam. Other pathways are ASGM processes where direct contact with the mercury and contaminated soil occur. The spreading of the mercury by ASGM process water is a pathway towards the sedimentation pond and the surrounding soil including the subsoil. From all these pathways, and from the from the mercury gold amalgamation process mercury vapour emits and is deposited in the surrounding community and faraway from the site, providing a diffuse mercury source. This may explain the elevated levels of mercury in all groundwater wells and the topsoil baseline samples.

The ASGM village visited are practicing subsistence farming and consume food products from kitchen gardens, receiving atmospheric mercury deposition and animal products from the livestock roaming around in these ASGM villages. The food these villagers consume is therefore also a major pathway for human exposure. This is especially true for villagers eating form a single plot of land (so called single food basket). In this case the food products from their kitchen gardens and animal products from their own livestock are all exposed to mercury from the amalgamation process, the mercury contaminated soil, groundwater and the atmospheric mercury depositions.

The Tier 3 risk assessment

The Taliwang site is an abandoned mercury contaminated site where ASGM no longer takes place. It is exemplary of a site where the residual mercury contamination still affects the community. Recontamination of this site is excluded as ASGM activities have stopped and the installations, except for the rod-mill platforms, have been removed.

To justify and direct the sustainable management of this site, a tier 3 human health risk assessment was carried out. To assess the risks for residential land-use, including all relevant exposure pathways the RBCA (Risk-based Corrective Action Toolkit for Chemical Releases), version 2.6, GSI Environmental Inc, 2011, was used. To assess the risk for the consumption of livestock products (dairy and meat), in case these are herded on site the RAIS (Risk calculator of The Risk Assessment Information System) was used. The used parameter values for the human health risk calculations are presented in the Table 1.

TABLE 1 RISK WORST CASE AND ASSUMPTIONS

Parameter	Value	Remarks
Organic matter	2,5%	Worst case
Clay fraction	20%	Worst case
Land use	Residence with kitchen garden	
Surface soil exposure pathways	Residential receptors on & off-site (10 m) All routes: • Direct ingestion • Dermal contact • Inhalation • Ingestion vegetable above & below ground	Ingestion of livestock products (dairy & meat) cannot be assessed in RBCA. Therefore, RAIS used
Air exposure pathway	Residential receptors on & off-site (10 m) All routes ambient outdoor air & indoor air: • Affected soils, volatilization to ambient outdoor air & enclosed space • Affected soils leaching to groundwater & volatilization to enclosed space • Affected groundwater volatilization to ambient outdoor air & enclosed space • Affected surface soils particulates volatilization to ambient outdoor air	Model runs have been performed with (A) and without (B) 'Affected groundwater – volatilization to ambient outdoor air and enclosed space'. This is done because in the investigation the levels of mercury in groundwater are low (highest 0,9 ug/l)
Groundwater exposure pathway	All routes: • Groundwater ingestion • Surface water impact	Model runs have been performed with (A) & without (B) these routes, because residents mainly use bottled water for drinking water.
Exposure factors - Default values for residential receptor except		
Water ingestion rate	0,1 L/d	Residents use mainly bottled water
Site-specific Soil Parameters		
Depth to water-bearing unit	1 m	Measured during field campaign 12 Apr 2022; 0.5 m below ground level. However, in RBCA a minimal level of 1 m can only be selected
Depth to top of affected soil	0 m	
Depth to base of affected soil	0.5 m	Same as groundwater level

Based on the tier 3 human health risk assessment it is concluded that human health risks cannot be excluded at the site. The most critical exposure routes are in order of magnitude:

- Consumption of vegetables grown on-site
- Consumption of meat from livestock feeding on-site
- Groundwater exposure (in case of using groundwater as drinking water)
- Indoor air exposure
- Soil exposure (mainly soil and vegetable ingestion)

Based on the tier 3 outcome it is concluded that remediation is necessary to avoid on-site human exposure to the mercury.

Preparation of the remediation

To select the best remedial option for the Taliwang site a remediation assessment is carried out. The best option is the one that reduces as much as possible the environmental risks (human, ecological and migration) with the best environmental merits not entailing excessive costs. To outcome of the remediation assessment using a multi criteria decision analyses is that the best remedial approach is ex-situ immobilization and containment.

Anticipated actions are the demolition of the platform, the rubble will be crushed, the contaminated sediment from the domestic well will be removed and the contaminated soil will be excavated. All will be mixed with Biochar to immobilize the mercury. The soil mixed with the Biochar will be contained in depot with a maximum height of 2 meter and planted Vetiver Grass. The Vetiver Gras with a root system up to 2 meters maximum can absorb mercury and protect the depot from erosion.

Currently three green waste products as possible feed for the production of Biochar are being bench tested. The green waste products are (1) coconut peels, (2) corncobs and (3) rice husk. The bench scale testing will result in the recipe of Biochar with the highest absorption capacity.

As the groundwater in all the sampled domestic wells has mercury levels around the drinking water norm and the people are not drinking this water, a groundwater remediation is not justifiable. It is very likely that the mercury groundwater contamination is regional issue.

In the villages where ASGM is still practiced remediation is not justifiable, instead, awareness should be raised with a focus on the phasing out the use mercury in ASGM. Only when the use of mercury has stopped, remediation should be considered. Based on the experiences with the pilot project at the Taliwang site, a toolkit will be developed to remediate ASGM site where the mercury is not anymore used.

References

1. WHO Guidelines for Drinking-Water Quality, 4th ed.; WHO: Geneva, Switzerland; Available online: https://www.who.int/publications/i/item/9789241549950

2. Wet Bodembescherming S, T en I waarden https://wetten.overheid.nl/BWBR0033592/2013-07-01

3. EPA, 1991 https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

REMEDIATION OF MERCURY CONTAMINATED SITES. THE CASE OF "CERCO SAN TEODORO" ALMADEN DUMP AND THE OLD MERCURY METALLURGY FACILITIES OF THE CERCO DE ALMADENEJOS

Conde Ana I., Carrasco, F. Javier

Minas de Almadén y Arrayanes, S.A., S.ME, San Teodoro, s/n. Almadén. Spain, Mercury Technological Centre

Hg is a constitutive element of the earth that exists naturally in the environment in a variety of ways, the most frequent being cinnabar ore (HgS). Hg has been a highly valued metal since time immemorial for its special characteristics. However, the evidence of the damage it causes to the environment and to humans has made it subject to regulation by international organisations, undertaking measures to control their production, emission, uses and management of their waste in order to protect human health and the environment, such as Strategy Concerning Mercury (EC, 2005), at a global level, the Minamata Convention (UNEP, 2017).

Almadén, is the area with the largest mercury deposit in the world. Almadén and MAYASA, the state-owned company that has exploited and marketed these resources since time immemorial, are closely and historically linked to the mining-metallurgical activity of Hg production and marketing. Due to the health and environmental problems caused by Hg, the evolution of social sensitivity and the subsequent regulations, Almadén's cinnabar extraction ceased in 2001, its metallurgical activity in 2003 and its Hg trading activity in March 2011 as per Regulation 1102/2008. Once all Hg related activities ceased, MAYASA carried out the environmental restoration of its facilities, with the objective of minimising the environmental effects of 2,000 years of mining and metallurgical operations.

Of all environmental remediation activities developed by MAYASA along the last years, the San Teodoro waste heap restoration is far away the most important.

This heap was for centuries the deposit for both sterile from the mining, and slag of the metallurgical processes, reaching a size of 3.5 million tons and occupying an area of 10 hectares.

The environmental studies of the waste heap and its surrounding have conducted to a restoration model: the "in situ" encapsulation to ensure the waterproofing preventing water recharge and to minimize the effects on both groundwater and surface water, to reduce the dispersion of the material deposited on the tip that could affect the surrounding soils, and the emissions of mercury.

The restoration work was done during the years 2005 to 2008, and an environmental monitoring program was included in the design that allows to check the degree of achievement of the target set by performing the restoration works. Among others to restore the vegetation of the surface and the landscape integration of the heap, were set.

The current situation of the dip permits to check the high degree of achievement reached, as the restored surface has not been recovered only on the aesthetic and landscape integration, but has also reached a very high degree of re-vegetation.

After the completion of the restoration work of the dump, the values of mercury in surface water and groundwater show that the encapsulation of the dump has allowed the recovery of the area and its surroundings because both surface water and groundwater fulfill the legal limits of mercury in water.

MAYASA, through the MERCURY TECNOLOGICAL CENTRE, following its policy of remediation of the Almadén and its surrounding area has worked on possible solutions for the enclave "Cerco de Almadenejos", located 12km from Almaden (Ciudad Real) Spain.

The site is a historic metallurgical site operational in the 18th-19th centuries, and has the remains of the old Hg extraction furnaces and storage buildings. The studies of the site show that the enclosure acts as a gaseous Hg emitting source, constituting a contamination point and a potential danger for the area. The Mercury Techological Centre of MAYASA are working in the proposal *"Demonstration of new process of decontamination on mercury contaminated sites improving soil management and land use",* whose main objective to demonstrate an innovative and environmentally technology for the decontamination of mercury contaminated soil, by means of its *in situ stabilization*, being sustainable, cost effective and allowing an integral solution when dealing with mercury contaminated soil in areas with special restrictions, regarding decontamination processes due to geographical locations and/or historical and cultural features as in the Cerco of Almadenejos.

The project will combine well-known soil remediation technologies with the new product (not tested yet in the EU) to produce a robust, efficient and environmentally friendly solution to resolve mercury soil contamination. Therefore, the following specific objectives are envisaged for the project:

- Provide a real scale demonstration of the capabilities of a new solution by implementing it on an existing contaminated site (3 Ha, in the Cerco de Almadenejos).

- Assess the technical, environmental, and economic feasibility of the new technology to issue relevant protocols and methodologies on this kind of soil decontamination process regarding results dissemination at EU level.
- Pave the way for future innovative applications of this technology to a wider range of site conditions and contaminant types.
- Deliver a new use for the site, by the restoration and optimisation of environmental conditions having a positive impact on the population's human health and the surrounding area.
- Achieve a sensible impact on key players: authorities, industry, and the media.
- Provide decision makers and regulators with new rationales and goals for inclusion in future soil remediation protocols.

Expected results

As a direct product of the actions contemplated in the project the main results that can be obtained are summarised below:

• A complete characterisation of the selected area, and the best remediation strategy will be defined for the reduction of Hg levels in the Cerco de Almadenejos.

• The decontamination will be carried out minimising the use of reagents with respect to the amount used in more conventional procedures, with the aim of reducing the final ratio of reagents required to soil.

The project will contribute significantly to reduction of Hg contamination in the Cerco de Almadenejos by reducing Hg dispositions in soil, based on previous experiences, field tests were carried out, on a pilot scale in the project developed in Boroo (Mongolia), and laboratory tests have been made with soil samples of the Cerco de Almadenejos, using different doses of the reagent and with different maturation time, both results have been able to achieve up to 80% reduction in the concentration of mercury in the soil eluate

Furthermore, the project will increase environmental quality in the Cerco de Almadenejos and its surrounding area due to the soil stabilisation treated by physical and thermal insulation as it will decrease the resuspension of dust downwind and mercury evaporation from the soil.

The results will demonstrate, on a real scale, that it is possible to decontaminate soils contaminated with Hg by means of chemical stabilisation "in situ" compared to other "ex situ" remediation technologies that are more expensive, less environmentally friendly and technically less viable mainly, in this case, due to the special characteristics of the site with a large volume of soil with a high Hg content to be treated.