5.1. SOIL EXCAVATION AND OFF-SITE DISPOSAL

Although soil excavation and off-site disposal is a long-established remediation approach for impacted sites, the unique properties of Hg mean that excavation methodologies need to be refined and the off-site disposal options are more limited and costly.

Soil Excavation

Excavation of Hg-impacted soils needs to be performed in a controlled manner, so as to: 1) optimise soil volumes needing off-site disposal (the primary cost for this remediation approach); and 2) minimise the risk of increasing impacted soil volumes, primarily by avoiding coalescence and downward migration of elemental Hg.

Full-time supervision of excavation works by trained personnel is advised, as this enables visual inspection and soil monitoring (using field instruments – see Section 4) to optimise waste volumes by effective segregation of clean and impacted soils. On-site instruments also support the mitigation of Health & Safety risks and validation of the base and sides of the excavations prior to confirmatory laboratory analysis.

Source: ERM

Supervising staff should identify Hg-impregnated structures (slabs, walls, foundations), which have the potential to re-contaminate surrounding soils if left in place, and maintain the integrity of low permeability horizons (e.g. clay layers) to prevent downward migration of elemental Hg. They should also direct excavation efforts to impacted horizons and preferential Hg-migration pathways (e.g. cracks/fissures, granular backfill, rootlets), thereby minimizing excavated volumes and the remediation time and costs.

Although labour-intensive, manual removal of elemental Hg (e.g. using hand tools, syringes, suction pumps), when discovered during excavation, is typically cost-effective, as the pure Hg represents significant mass and it will reduce the costs of soil treatment and disposal.

The characteristics of Hg and the issues described above inevitably lead to longer excavation times than for soils impacted by other pollutants. However, if these best practice measures are employed, the volumes of soil requiring treatment and off-site disposal can be materially reduced, leading to lower remediation costs.

Source: ERM

As excavation forms the basis for all ex-situ technologies, the careful control of excavation and minimisation of waste volumes are equally applicable during the early phases of both soil stabilisation and thermal remediation projects discussed in subsequent sections.

A well thought out project plan is essential to ensure that the excavation works proceed in an orderly manner. The need for robust Health & Safety controls, including appropriate PPE, air monitoring and regular medical testing (including baseline tests) is also an important aspect during the works, and specific plans should be prepared to identify risks and implement appropriate mitigation measures.

On-site treatment before off-site disposal

If granular soils are present (e.g. alluvial deposits), soil sorting (e.g. by griddle bucket, hydrocyclone or mechanical screener) can materially reduce soil volumes requiring off-site disposal, as Hg is typically concentrated in the finer soil fraction. Air capture and treatment should be considered to minimise Hg-impacted air emissions from the treatment. Mechanical screening of Hg-impacted soils during remediation of the acetaldehyde site in France (see Case Study 4) reduced volumes of waste soil requiring off-site disposal by circa 60%.

Source: ERM

To ensure acceptance at some off-site disposal facilities, other forms of pre-treatment can be necessary prior to consignment of the waste materials. As described further in Sections 5.2 and 5.3, several treatment technologies have been patented, trialled or taken to full implementation for this purpose. The majority of these technologies aim to solidify/stabilize the materials by converting elemental Hg and Hg compounds into stable sulphide-rich forms of Hg.

Off-site treatment/recovery and disposal facilities

As mentioned previously, off-site disposal represents the main cost associated with this remediation approach, typically ranging from 250-500 €/T, or potentially higher for heavily-impacted materials.

If limit values for Hg relating to leach testing can be achieved, then landfilling within an appropriate class landfill is an applicable disposal route. During the remediation works performed in 2014 (Case Study 4), the Bellegarde Landfill operated by SITA FD was permitted to accept pre-stabilised Hg-impacted soils with leachable Hg of up to 0.2 mg/l, which corresponded to circa 5 000 mg/kg total Hg at the site in question. These soils were stabilised at the Bellegarde site prior to disposal to a specific landfill cell.

Other treatment and disposal options available within Europe for more heavily-impacted materials are summarized in the table on the next page.

Company	Location	Description	Comments	Web Address/ Contact Information
Offsite Disposal				
SITA FD	Bellegarde, France	Hazardous waste landfill	Accept soil/debris. No liquid metallic Hg and no radioactive waste. Hg thresholds of 5 000 mg/kg total and 2 mg/kg leachable. Other threshold values on TOC and metals also apply.	+33 04 66 01 13 83
Minosus (Veolia Environmental Services)	Cheshire, UK	Underground disposal in industrial salt mine	Accept soil/debris, but cannot accept liquids (including liquid metallic Hg), sludges, gases or radioactive waste. Waste must be non-flammable, non-explosive, non-volatile, non-odorous, non-deliquescent, non-radioactive and non-reactive upon exposure to air, salt or moisture within the mine. Total Organic Carbon (TOC) threshold of 3% and the facility conducts biodegradability testing prior to acceptance.	http://veolia.co.uk/
Umwelt, Entsorgung und Verwertung GmbH (UEV)	Heilbronn, Germany	Underground disposal in former salt mine	Accept soil, debris, but cannot accept liquids or waste with significant free moisture. No liquid metallic Hg and radioactive waste is generally refused.	http://www.uev.de/
K+S Entsorgung, GmbH	Hessen, Germany	Underground disposal in former salt mine	Accept soil/debris, but cannot accept liquids or waste with free moisture (including Hg droplets). No liquid metallic Hg and no radioactive waste. Hg threshold of 5% Hg by weight. Materials would be refused if methyl-Hg is potentially present.	http://www.ks-entsorgung.com/
Glückauf Sondershausen Entwicklungs- und Sicherungsgesellschaft mbH (GSES)	Sondershausen, Germany	Underground disposal in former salt mine	Accept soil, debris, but cannot accept liquids or waste with significant free moisture. No liquid metallic Hg and radioactive waste is generally excluded.	http://gses.de/
Miljøteknikk Terrateam AS	Mo i Rana, Norway	Underground disposal in rock caverns of former steel works	Facility has a permit to receive 70,000 metric tons of inorganic hazardous waste per year. The waste must be stabilised/solidified before placement into the rock cavern. Maximum allowed leaching of 0.01 mg Hg/l based on the US TCLP63 test.	http://www.terrateam.no/
NOAH	Langøya Island, Norway	Stabilisation with lime and gypsum and disposal below sea level in former limestone quarry	Accept high-concentration waste (> 1000 mg/kg Hg), but not liquid metallic Hg. Upper TOC limit of 1% for high-concentration waste and 5% for less-contaminated waste. NICOLE expresses concern about the hydrological and hydrogeological setting of this facility (photo below).	http://www.noah.no/
Offsite Treatment				
Nordische Quecksilber Rückgewinnung GmbH (NQR)/Remondis	Dorsten, Germany	High-capacity thermal desorption/ recovery	Former DELA facility recently acquired by Remondis and is undergoing re-startup/permitting. Previously able to accept large volumes of waste (e.g. commercial products, soil, debris and free elemental Hg). Dioxins possibly an issue and testing required.	http://www.remondis-industrie-service.de/ris/loesungen/nqr-mercury/
Hg Industries (Aurea)	Voivres-lès-le-Mans, France	Batch thermal desorption/ recovery	Former MBM facility. Typically handles shipments of 20-25 tons (max) high-concentration waste (e.g. commercial products, soil, debris, and liquid metallic Hg).	+33 679 013 625
BATREC Industries (Veolia Environmental Services)	Switzerland	Batch thermal desorption/ recovery	Typically handles shipments of 1-50 ton high-concentration (> 10,000 mg/kg) waste (e.g. batteries, soil, debris, and free elemental Hg).	+33 637031265
Gesellschaft für Metallrecycling mbH (GMR GmbH)	Leipzig, Germany	Batch thermal desorption/ recovery as well as an immobilisation process with geopolymers	Typically handles small batches of slurries, sludges and other residues containing natural radioactivity and/or Hg as well as free elemental Hg.	http://www.gmr-leipzig.de/
Ophram Laboratoire	Saint Fons, France	Batch thermal treatment/ Hg recycling	Specializes in the recycling and refining of pure metallic Hg. Supplies high-purity Hg in sealed ampoules to microelectronics and optronics sector for semiconductor production.	http://www.ophram.com/

Table 3. Treatment and Disposal Facilities for Highly-Impacted Mercury Contaminated Waste

SOURCE: K+S ENTSORGUNG, GMBH, HESSEN, GERMANY

Special packaging and handling requirements are required for most of the disposal facilities listed above, including the use of sealed drums, bulk bags or steel containers.

Given the high cost and relatively low throughput of several of the batch thermal treatment and recovery facilities listed in Table 3, they are typically only used for recovered free metallic Hg and/or the most highly-impacted soils and waste that cannot be accepted in other storage or treatment facilities. At the time of publication of this booklet, the former high-capacity DELA thermal desorption facility in Dorsten, Germany, had been acquired by Remondis and undergoing permitting/start-up as Nordische Quecksilber Rückgewinnung GmbH (NQR). Once operational, it is anticipated that this facility will likely offer a lower-cost, higher-capacity treatment option for highly-impacted Hg wastes.

Cross-Border Waste Shipments

Another important consideration with respect to waste handling is compliance with export requirements during cross-border shipment of wastes to their final disposal site. Chlor-alkali producers have a legal responsibility under EC Directive 1102/2008 to report the amount of >95 % pure Hg recovered during the decommissioning of chlor-alkali plantsv. To arrange export and comply with the EU Waste Directive 2008/98/EC , the consignee must apply to the competent authority of the country where the waste is produced and obtain consent from the relevant exporting and importing countries and pay any fees. In 2007, close to 700 000 T of waste (coded as 170503-Contaminated soil and stones) was transported across EU borders, with the biggest recipient being Germany .

Due Diligence of Disposal / Treatment Facilities

Appropriate due diligence is recommended when considering off-site treatment and disposal facilities. Key questions to answer include:

- Is the facility fully permitted to accept your waste materials?
- Does the operator of the facility assume full responsibility for the waste?
- If cross-border transfer is required, does it comply with EU Directives?
- For long-term storage solutions, how geologically secure is the facility?
- For treatment facilities, what does the facility do with the recovered Hg?

5.2. SOIL WASHING

Soil washing techniques utilise physical and/or chemical processes to reduce the Hg content in solid materials (soil, sediment or sludge). There are three commonly-used approaches to soil washing. The most common is particle-size beneficiation. This is based on the premise that contamination is associated with surface area. Fine-grained materials have the greatest surface area and therefore the highest concentration of contaminants. Separation of the fines from the coarser fractions (which generally have lower contaminant levels) can significantly decrease the volume of soil requiring treatment and/or disposal. The second approach often used for Hg-impacted soils, especially materials impacted with elemental Hg (Hg^0), is density separation. The density of elemental Hg is 13.5 g/cm^3 compared to the density of soil, which is generally about 2 to 3 g/cm^3. This density difference provides a basis for separating elemental Hg from soil and reducing the overall mass of material requiring treatment/disposal. The third approach comprises chemical leaching of Hg from the soil. For this approach, liquid solutions such as nitric acid, hydrochloric acid and potassium iodide/iodine are used to remove Hg from the solid matrix.

Comprehensive information regarding the origin of the Hg impacts will provide a good basis for understanding the species of Hg likely present at a site. However, it is important to consider that the physicochemical nature of the contamination can change slowly over time due to various phenomena like oxidation, complexation, methylation, adsorption, etc. The Hg species present and the physicochemical nature of the soil will strongly effect the efficiency of a treatment process such as soil washing[28,29,30,31].

Summary of Recent Soil Washing Projects

Conventional physical separation techniques are the most typically applied in Europe and North America, comprising steps such as screening, sieving, hydrocycloning, attrition scrubbing, froth flotation, magnetic separation, etc[28]. These techniques can be relatively simple, and therefore cost-efficient, as proven by the extensive track record in the last 25 years. Physicochemical soil washing techniques, including chemical extraction, entails (simplified) hydrometallurgical methods, generally making them more complex, lower in throughput and currently more expensive[29,32,33]. This is reflected in the scarce number of projects and their small size, often at pilot scale only.

The existence of competitive solutions, such as controlled landfilling (up to concentrations of 5,000 mg/kg Hg in Europe) and specific thermal treatment techniques, impose a financial boundary condition on the applicability of soil washing for Hg-impacted soils. Practically this means that conventional soil washing techniques are typically applied primarily for the removal of elemental Hg, for which bespoke washing plants have been designed.

In 1993, approximately 10,000 m^3 of coarse sandy soil impacted with various metals including Hg was treated by washing (consisting of screening, hydrocycloning, attrition scrubbing and froth flotation) at the King of Prussia superfund site (New Jersey, USA). Throughput of the plant was 25 T an hour. Although it is described in the project report for this site[33] that Hg concentrations could be reduced from 100 mg/kg to 1 mg/kg, the report does not provide any actual performance data regarding Hg.

During the remediation of a former chlor-alkali plant operated by Nexus in British Columbia, Canada, approximately 24,000 T of soil were reportedly treated by washing between 1999 and 2003. The soil washing plant had a capacity of 14 T an hour, and reduced the Hg concentration down to 40 mg/kg. The initial concentrations were not specified. The process used at this site was reportedly the basis for the Orica Botany transformation project in Australia[33].

A former chlor-alkali plant near Syracuse was identified as one of the primary sources of contamination to the Onondaga lake (New York State, USA). Concentrations of elemental Hg up to 19,000 mg/kg were found in soil at this site. In 2003, about 8,500 T of soil were treated by soil washing, which reportedly removed about 7 T of Hg. However, no technical data regarding the soil washing plant or the soil composition were published.

During the remediation of the former EKA chlor-alkali site in Bengtsfors, Sweden, in 2007, large volumes of Hg-impacted gravels were found. These were treated on-site by simple drum washing of the fraction >20 mm, with a throughput of 100 T an hour. The re-use target was 5 ppm. Although the undersized fraction was potentially washable, the environmental permit did not allow on-site washing and the undersize had to be landfilled. The recycled oversize fraction made up about 70 % of the total soil volume[31].

In 2010, 13,000 T of sandy soil were washed off-site in a treatment centre in Antwerp. The soil came from a former felt production site in Lokeren, Belgium, and was impacted by Hg, mainly in the form of Hg nitrate. Initial Hg levels of up to 50 mg/kg were washed to below 5 mg/kg. As expected, the removal efficiency of highly water soluble Hg nitrate salt was high.

After some years of laboratory scale and pilot testing, a bespoke soil washing plant (simple screening, drum washing) was built for the Orica project (Botany Bay, Australia)[34]. The plant was erected in a hall with air extraction and monitoring. The former chlor-alkali site was heavily impacted with Hg (80 to 15,000 mg/kg Hg). The plant had to stop operations after only a few months of production in 2011. The specific reasons for stopping the plant were not published, but issues with Hg vapour emissions and poor performance are mentioned. Only 2,900 T of soil were treated, 1,350 T re-used, and 1.2 T of Hg removed. The treatment target level was 70 mg/kg.

A former chlor-alkali site operated in the Netherlands contained 60,000 T of impacted sandy soil, with Hg levels up to 1,200 mg/kg[34]. Extensive laboratory research showed that reductions in Total Hg concentrations between 70 and 80% could be achieved through soil washing. Although the re-use target was set at a relatively-low 7 mg/kg total Hg, it was decided to carry out on-site soil washing with the aim of recycling as much soil as possible. In total, 20,000 T of soil were washed. Although the lab-scale removal rates were achieved in the full-scale process, only 3,000 T of the washed soil met the 7 mg/kg target.


Source: DEC (subsidiary of DEME Environmental Contractors)

During the bidding process for the remediation of an Hg-impacted site in France, lab-scale soil washing tests were conducted by DEC (part of DEME Group). The site soil consisted mainly of gravel (55 %) and sand (35 %), with 10 % fine materials. Initial concentrations were generally in the order of 100 to 10 000 mg/kg, with some visible Hg droplets. During the test, the gravel was effectively separated and washed to below the established re-use levels (28 mg/kg). However, cleaning the sand fraction was more difficult. The operator opted for a dry gravel sorting process, with sand and fine materials considered as residue and landfilled off-site. Laboratory tests carried out on soils from several sources, mainly chlor-alkali facilities[29,30,35], typically show that medium to high concentrations of elemental Hg (100 to 10,000 mg/kg) in sand could be effectively reduced to below 50 mg/kg. Further decreases require intensive conventional soil washing steps (e.g. attrition scrubbing or froth flotation) and/or alternative techniques (ultrasonic scrubbing or chemical complexation). Characterisation of the residual Hg after physical washing by visual inspection or microscopy and by sequential leaching tests showed that microscopic Hg droplets were absorbed within fissures of the sand grains, and some Hg oxides were still present.

Conclusions

Physical soil washing can materially reduce Hg concentrations in soil, with the gravel fraction effectively cleaned to relatively-low concentrations. The sand fraction, however, is generally much more difficult to treat, and requires intensive techniques (e.g. scrubbing, flotation, chemical cleaning) in order to reach concentrations of 10–20 mg/kg total Hg. As with any soil washing, the fines (clay + silt fraction) should be below about 30 % of the total soil mass.

A disadvantage of soil washing is that the residue of fines (filter cake) can be very concentrated in Hg, making it difficult and expensive to transport and dispose off-site.

For Hg impacted sites, two types of soil washing applications can be considered: firstly reducing elemental Hg concentrations to moderate levels, for example below 1 000 mg/kg in Europe to allow landfilling. Secondly, more intensive soil washing can reduce Hg concentrations to lower levels (10-50 mg/kg), which is often sufficient to comply with site-specific risk-based standards.

5.3. STABILISATION / SOLIDIFICATION

Stabilisation/solidification (S/S) is a frequently-used technology for the treatment of Hg-impacted soil and waste[28]. A wide range of Hg-impacted material can be treated by various S/S processes, including soils, sludge, liquid wastes, industrial waste and elemental Hg. Stabilization/solidification can be applied either in situ or ex situ, although it is most commonly implemented ex situ.

Stabilization/solidification is a well-established remediation technology in the USA, Japan and several European countries. It originates from the construction, mining and nuclear waste industries and was later applied to soil remediation. The uptake of S/S as a remediation technique in Europe was relatively slow compared to other technologies prior to enactment of the EU Landfill Directive, mainly due to the lack of technical guidance, performance uncertainties, previous poor practice and potential residual liabilities . In the UK, for example, this changed following the publication of guidance from the Environment Agency in 2004 supporting a risk-based framework for the management of land contamination.

Application of S/S to impacted soils and wastes is supported by a body of scientific evidence gathered over several decades, and Hg-specific techniques and innovations are continuing to be developed. Stabilization/solidification can be used on its own or combined with other management approaches as part of a remedial strategy. However, the different species of Hg can, under certain conditions, display complex behaviour presenting potential challenges to the use of S/S.

A significant proportion of the available literature is focused on the S/S or pre-treatment of Hg-containing waste (including hazardous and radioactive waste) for landfill disposal, rather than re-use on site. Although this research merits consideration, the review provided herein focusses on S/S treatment of Hg-impacted soils.

Stabilization/solidification relies on the reaction between a binder and/or reagent with soil/waste to reduce contaminant mobility. These techniques do not reduce the contaminant concentration, but instead reduces its mobility through chemical or physical changes. The key S/S processes currently used for Hg-impacted soils include:

- **Stabilisation** – involving the addition of reagents to an impacted soil to chemically fix the soluble species, producing a more chemically stable, less soluble material.
- **Solidification** – involving the addition of binders to a impacted soil to change its physical nature in order to contain or encapsulate contaminants into a solid and robust low-permeability matrix.
- **Amalgamation** – considered a sub-set of the S/S techniques, and involving the dissolution of Hg in other metals (e.g. copper or zinc) and solidification to form a non-liquid, semi-solid alloy called an amalgam. The technique is also commonly used to supplement more traditional cement-based S/S techniques[39,40]. Hg stabilisation with sulphur or sulphur polymer cement (SPC) is also sometimes referred to as amalgamation[41]. However, combining Hg with sulphur results in Hg sulphide, a stable ionic compound, not an amalgam or alloy[42].

Bench-scale testing followed by pilot-scale application are important elements of the design process, thereby providing confidence in full-scale operation.


SOURCE: ANCHOR QEA, LLC

Stabilisation / Solidification Techniques

A range of ex-situ and in-situ techniques have been successfully applied for S/S of Hg-impacted soils, although ex-situ methods are more commonly used[38]. Mobile plant and reagent delivery systems can be configured to meet most site conditions and deliver the right mix of binders and reagents. However, several S/S reactions can partially volatilise Hg and so require adequate control measures and associated health and safety precautions.

Compared to in-situ S/S techniques, ex-situ techniques can be more onerous on-site with several material handling stages needed, but can provide higher production rates, better quality control over binder delivery and mixing and improved verification of the stabilised material. This is especially important to ensure complete encapsulation in the S/S material of elemental Hg, which is dense and can be difficult to mix.

Physical pre-treatment, including processing and screening, can be an effective first step prior to ex-situ stabilisation, so as to prepare a homogenised medium and optimise mixing, and to concentrate the Hg compounds given their affinity for the finer soil fractions. Wet screening is not recommended prior to S/S, as the dense Hg droplets can behave as a separate liquid phase[43].

Recovery of elemental Hg prior to S/S application can be advisable to reduce contaminant loading, especially when on-site re-use/retention of the treated material is planned. Breaking up larger Hg globules to provide a larger surface area to react with the binder/reagent is another key pre-treatment step. Some technologies include a mechanical system for breaking the elemental Hg into fine spherical particles (prills)[44]. As described below, a suitable reagent (e.g. sodium sulphide) can also be initially added to produce either Hg oxides or Hg sulphides and once mixed sufficiently, the cement is added[45].

In-situ stabilisation is well established in geotechnical applications, for which specialised injection/mixing equipment have been developed. However, in-situ mixing or injection is less established for environmental application, as homogenous treatment can be difficult to ensure and validate[44]. These techniques are most often used to stabilise sludge lagoons, deeper soil contamination or soil under infrastructures. It can produce a “monolith” in the ground, which needs to be carefully designed to avoid localised flooding and to minimise constraints for future site-use. This approach continues to be developed, as demonstrated by some case studies presented in NICOLE’s Summary Report[9] and the US EPA[28], including the use of innovative nanoparticles.


In situ stabilisation of sediment and soils impacted with Hg and PAHs in a former effluent treatment pond using binder agents.
Source: ARCADIS

Treatment rates for S/S vary significantly based on the form of Hg present, and the number of processes and reagents used. However, rates of 300 to 600 m^3 per day should be achievable. Rates where chemical processes such as amalgamation are undertaken may be considerably lower.

Binders and Reagents

Several binders and reagents can be used in the S/S of Hg-impacted soils and waste (US EPA[28]). The most commonly used include Portland Cement, enhanced by additional binders such as ground granulated blast furnace slag (GGBFS), pulverised fly ash (PFA), asphalt or bitumen[44]. Elemental sulphur and various sulphide additives have also been used successfully[43,67,69].

Some elemental Hg and organic Hg compounds can prove difficult to stabilise and additional chemical or physical pre-treatment is needed to ensure effective S/S. Common stabilizing agents include elemental sulphur, sodium sulphate, reactivated carbon, or ferric-lignin derivatives prior to solidification.[45,46,47]. Other additives containing sulphur such as GGBFS have also been successfully applied. With adequate blending, such additives have been shown to successfully convert the Hg compounds into less soluble forms, such as mercuric sulphide (cinnabar and metacinnabar)[68].

The two main chemical S/S approaches applied to soils or wastes containing elemental Hg are: 1) conversion of the elemental Hg to Hg sulphide; and 2) amalgamation. Some techniques combine both and include the use of a cement-based mix enhanced with GGBFS and copper powder[40,41].

The ratio of binders/reagents to soil will depend on detected concentrations and the soil's chemical composition (i.e. Hg species, but also other contaminants or naturally-occurring substances that could interfere with the S/S process). The choice of binder/reagent should be site-specific, and subject to bench tests and pilot trials. Several case studies relating to laboratory and site-scale applications are provided by the US EPA[28] and GRS[40].

The choice of binder/reagent and the dosage used will lead to variable stability of the materials treated and also influence the curing time, compressive strength, costs and treatment process applied on-site[28].

Influencing Factors and Considerations

Key factors commonly affecting the effectiveness of S/S include good characterisation of the materials to be treated, selection of the best binder and reagent, effective contact between the contaminants and binder/reagent, good physical and chemical consistency of feedstock, appropriate mixing equipment and binder delivery, control over external factors (e.g. temperature and humidity) and the control of other inhibitive substances.

The applicability of S/S to treat Hg-impacted soils depends on the Hg species present, its mobility and concentrations, together with the soil pH and moisture content[48]. The presence of more than one Hg species may complicate the process and reduce the effectiveness unless characterised and designed appropriately. Typically, the solubility of Hg increases in more acidic conditions, although some studies suggest that some soluble Hg compounds (e.g. Hg sulphate) may form at higher pH[49].

Certain non-Hg compounds in the soil may also interact with the S/S reagents, thus affecting their performance. For example, high concentrations of chloride may render phosphate additives ineffective[50]. For certain binders to be effective, the treated material needs to have a specific moisture content and therefore material may need to be pre-treated to adjust the moisture.

Typical doses for binders are 5 to 15 % of the Hg-containing soils by weight. However, doses where high levels of elemental Hg are present can be higher.

Performance

The performance of S/S in soils is often linked to meeting risk-based remedial targets associated with leachability testing and also physical strength tests if the S/S material is to be re-used on-site. However, there is little precedence of S/S-treated Hg-impacted soils being re-used on-site (unless in-situ techniques have been applied) and as such the strength testing requirements may be of less importance. The leachate performance of ex-situ S/S-treated Hg-impacted soils is regularly linked to meeting landfill acceptance levels.

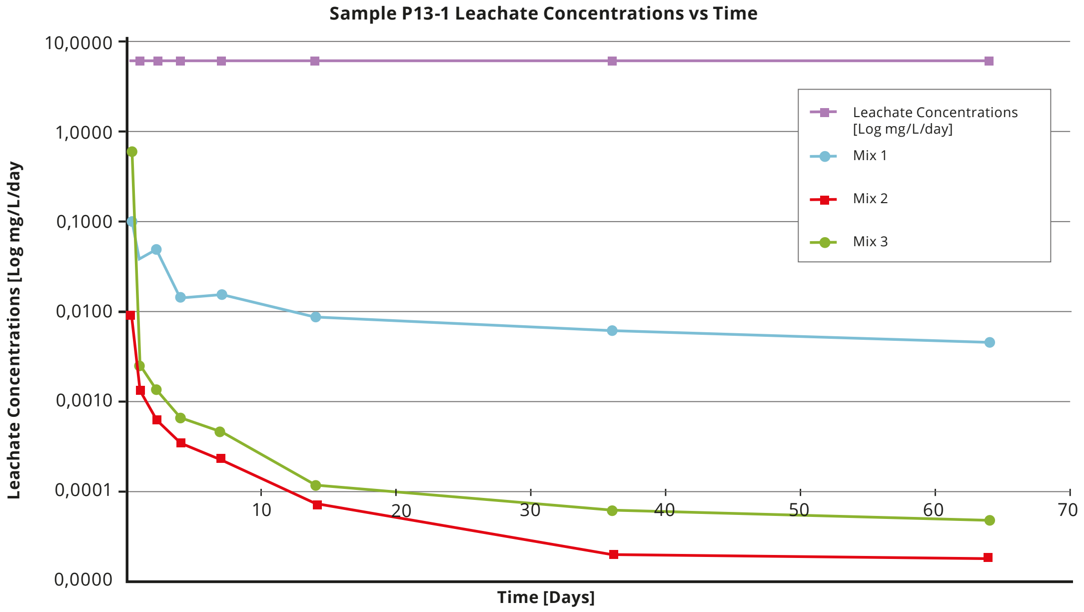
Successful S/S pre-treatment of Hg-impacted soils in the US and Canada are reported to regularly meet the associated non-hazardous landfill leachability acceptance criteria of 0.025 mg/l and 0.2 mg/l, respectively. For comparison, the European Waste Acceptance Criteria (WAC) leaching limits using BSEN 12457-3:2002 at a cumulative liquid:solid ratio of 10 for granular wastes for inert, non-hazardous and hazardous landfills are 0.001 mg/l, 0.02 mg/l and 0.2 mg/l, respectively[38].

Various bench and site trial case studies[28, 40] show that Hg concentrations in soil of 1,000 to 4,000 mg/kg can be successfully treated by S/S, achieving leachable concentrations between 0.002 mg/l and 0.0139 mg/l (using the Toxicity Characteristic Leaching Procedure test). Celtic (wholly-owned subsidiary of EnGlobe) have performed in-house tests that found that material with up to 200 mg/kg total Hg is readily stabilised and could be re-used on-site.

The Mercury Amalgamation Stabilization/Solidification white paper prepared by the Oak Ridge National Laboratory[41] provides a comprehensive discussion of the impact of elemental Hg spikes (up to 10,000 mg/kg) on leachate and the performance of various slag-cement based binders and reagents.

Long-Term Performance

A limitation in the published literature is an apparent lack of appropriate long-term data on the chemical behaviour of Hg-impacted soils treated by S/S, particularly where the material has been in contact with water. In-situ techniques that create monoliths in the ground



Source: Celtic (subsidiary of EnGlobe)

may meet their agreed leachability remedial targets, but consideration of the long-term performance of the S/S material remains to be tested. There is a significant amount of performance data for other S/S materials, which suggest that Hg-containing materials should be stable in the long-term. However, this is an area requiring further research in real environments.

The current understanding of long-term performance is generally based on predictive models focused on leaching mechanisms and have been applied to Hg wastes, stored either in landfill cells or dedicated storage facilities. However, these models are still being developed and refined. They are becoming more sophisticated to consider the complexity of contaminated soils and numerous site-specific factors that could affect the long term performance of the S/S process.

The credibility of S/S treatment of Hg-impacted soils, as with all remediation technologies, is dependent on thorough design (including interpretation of site or re-use conditions), bench or pilot trials, optimised on-site application and verification reporting to demonstrate clear lines of evidence based on the works undertaken. In particular, confidence in the long-term performance and the use of credible verification processes are essential when used as part of a risk-based remediation strategy.

CASE STUDY 5:
PULP AND TISSUE MILL, WASHINGTON STATE, USA

A FORMER PULP AND TISSUE MILL OPERATED FROM 1926 TO 2007, INCLUDING A FORMER CHLOR-ALKALI PLANT. THE SITE IS SITUATED ADJACENT TO A MARINE SHORELINE IN A POPULATED AREA, AND IS PLANNED FOR MIXED-USE REDEVELOPMENT. IN THE CHLOR-ALKALI PORTION OF THE SITE, THE REMEDIAL INVESTIGATION IDENTIFIED SHALLOW GROUNDWATER AND FILL SOILS THAT WERE IMPACTED WITH HG, AS WELL AS A COMPARATIVELY SMALL VOLUME OF HIGHLY-IMPACTED VADOSE ZONE SOIL CONTAINING FREE-PHASE HG IN LOCATIONS WHERE ELEMENTAL HG WAS PREVIOUSLY HANDLED.

Source: Anchor QEA, LLC

Key learnings

- Supported by laboratory treatability testing, on-site stabilization and off-site landfill disposal was selected as the far more cost-effective option relative to off-site thermal treatment for managing the highly-impacted soils containing free-phase Hg.
- Bench-scale testing evaluated the effectiveness of S/S with Portland cement, Portland cement with elemental sulphur, and Portland cement with ferrous sulphate, including an evaluation of Hg vapour release due to heat generation during stabilization (cement hydration). The results supported the selection and development of an optimized S/S protocol using Portland cement with elemental sulphur for full-scale application[66].

CASE STUDY 5:
PULP AND TISSUE MILL, WASHINGTON STATE, USA

- Full-scale application of S/S using Portland cement with elemental sulphur achieved the required treatment standards for off-site landfill disposal without exception (166 individual treatment batches).

- Subsurface impacts from caustic solutions resulted in geochemical conditions favoring either elevated Hg concentrations in groundwater or soil (but typically not both), as Hg mobility in groundwater increases at high pH while soil adsorption and uptake decreases. In down-gradient areas where the groundwater pH values decrease towards neutral, dissolved Hg concentrations also decline but soil concentrations increase.

- Further bench-scale testing evaluated amendments for their Hg removal efficiency from high pH groundwater, increased uptake capacity of amended soil, and long-term stability of the sequestered Hg. Long-term effectiveness was tested by subjecting treated Hg-loaded soils to leaching under both aerobic and anaerobic conditions. Overall, ferrous sulfate and GAC were found to be the most effective amendments for remediation of site groundwater, while a Portland cement-ferrous sulfate mixture was the preferred amendment for minimizing leaching from site soils[28,70,71,72].

- Based on the bench-scale testing results, full-scale implementation in the near future is anticipated to include a combination of approaches including in situ injection/soil mixing and reactive barriers to address Hg in groundwater and soil across the site.

Source: Anchor QEA, LLC

Source: Anchor QEA, LLC

5.4 THERMAL TREATMENT

Mercury's chemical properties (see Table 4 below) allow the application of various thermal technologies for the effective treatment of Hg-impacted soil and other solid wastes. Experience over the last decade has shown that thermal treatment is often the most cost-effective method for removing Hg from solid waste, especially for fine-grained materials such as silty and loamy soils. Common co-contaminants, such as PAHs, PCBs, dioxins, furans, TPH and organo-lead compounds, can also be effectively removed and/or destroyed within properly designed thermal treatment units.

Table 4. Chemical Properties of Hg

Melting Point	- 38.8 °C
Boiling Point	357.1 °C (225 °C at 50 mbar)
Vapour Pressure	0.00163 mbar at 20 °C

A number of ex-situ thermal technologies have been developed and tested in recent years for the treatment of Hg-containing solid wastes, with varying levels of success:

- Heated screw conveyors/continuous mixers;
- Vacuum retorts;
- Vacuum thermal desorption (indirectly heated batch vacuum mixers); and
- Rotary kilns (direct-fired or indirectly heated).

The last two technologies (vacuum thermal desorption and rotary kilns) have been proven effective and economically viable for the treatment of Hg-containing soil and solid waste. Thermal desorption is also being developed for the remediation of impacted soils in-situ, with recent studies indicating successful treatment of both in-situ soil and biopiles.

Ex-situ Thermal Treatment - Vacuum Thermal Desorption (Batch Vacuum Mixers)

At the core of the batch vacuum mixer is an evaporation chamber, which uses heat and a controlled vacuum to volatilise contaminants with boiling points below 450°C (at atmospheric pressure). The system is typically heated by circulating synthetic thermal oil in an external heating jacket and through a rotating central shaft, which also mixes the waste during treatment (Figure 2).

Batch vacuum mixer with solidification unit for treated material.
Source: ECON Industries GmbH

The treatment process is conducted in stages to allow entrained water and target contaminants to be recovered separately. In the initial stage, operating temperatures of c.150°C and a low vacuum (c.800 mbar absolute) are applied for water removal. Following evacuation of the water vapour, the operating temperature is increased to c.370°C and the pressure lowered to c.50 mbar (absolute) for the removal of Hg and other co-contaminants.

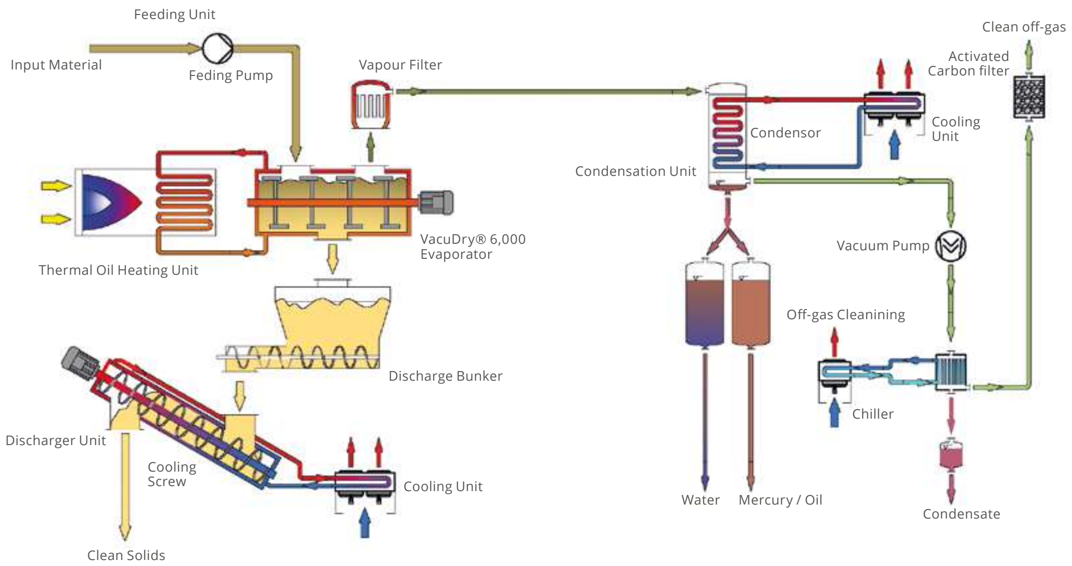
The resulting vapour stream is filtered to remove entrained particulates, and then run through a condensing unit for contaminant recovery (Figure 2). The subsequent exhaust gas stream is passed through a secondary vacuum unit and an activated carbon filter before discharge to the atmosphere. The treated solids are discharged (hot) via a discharge flap into a cooling bunker, and subsequent treatment batches are initiated while the prior batch cools.

Figure 3. Batch Vacuum Mixer Products

Treated soil inside evaporator chamber	Recovered mercury	Recovered hydrocar-bons	Recovered water

Source: ECON Industries GmbH

Figure 2. Typical Batch Vacuum Mixer Process (Indirectly Heated)



Source: ECON Industries. See process animation @ www.youtube.com/watch?v=3i_jxWDX2sY

Ex-situ Thermal Treatment - Rotary Kilns

Rotary kilns provide continuous treatment under minimal vacuum (Figure 4). The waste material is continuously fed and conveyed through the rotating kiln by a screw conveyor, where it is heated to the desired treatment temperature (typically 650 to 1,100°C). Additional mixing blades can be installed in the kiln to enhance mixing and increase retention time. The treated material drops out of the rotary kiln and is cooled on a cooling conveyor before discharge.

The off-gas is first directed through a cyclone for particulate removal, and then processed in an after-burner chamber where it is exposed to oxidizing conditions at 850°C for approximately 4 seconds to avoid formation of toxic substances (e.g. dioxins). Following treatment, the water and Hg in the off-gas is condensed, and the off-gas is then scrubbed and filtered before being treated by activated carbon and discharged to the atmosphere.

Direct-fired rotary kiln units are equipped with a refractory lining or a layer of heat-resistant concrete and the waste material is heated directly by a front-mounted burner. Although rarely used, the indirectly-heated rotary kilns typically consist of a steel cylinder without an inner refractory lining. In this case, the kiln is indirectly heated by the hot exhaust gases from a gas burner.

Source: ECON Industries GmbH

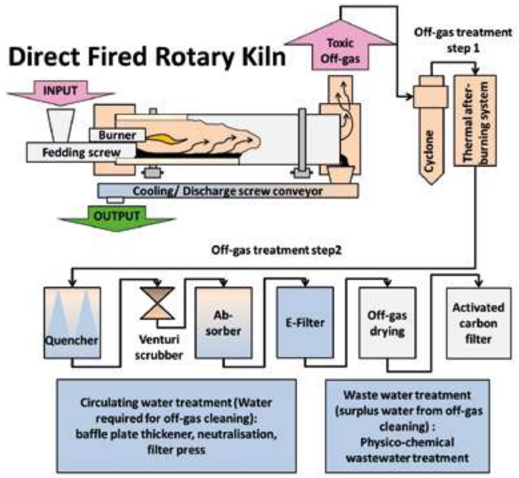


Figure 4.
Direct-fired Rotary Kiln including Off-Gas Treatment

Ex-situ Thermal Technology Comparison
A comparison of the batch vacuum mixer and rotary kiln technologies is provided in Table 5. Due to the lower operating temperatures, the indirectly-heated batch vacuum mixer is typically used when no cinnabar (HgS) or Hg(I/II)chloride is present in the waste material to be treated, including:

- Excavated soils and demolition waste from industrial sites;
- Sediments from lakes and streams; and
- Sludge from gas exploration and production.

There are no limitations with respect to the water content, or concentrations of hydrocarbons or Hg for treatment in a batch vacuum mixer. The process is a closed system, and so can usually be permitted for use in sensitive areas.

In comparison, the rotary kiln technology can be applied to waste containing all Hg species, including HgS and Hg(I/II)chloride, and has been used to treat the following waste streams:

- Catalysts from petro-chemical processes;
- Disposed activated carbon;
- Some types of impacted soil (e.g vinyl chloride production sites); and
- HgS-rich sludges from industrial wastewater treatment processes.

The rotary kiln process is generally more energy-intensive than batch vacuum mixers, and is therefore less economical for materials with elevated water content. Wastes with hydrocarbon content greater than 5 % can cause overheating of the kiln.

Rotary kilns typically produce more air emissions than batch vacuum mixers, require sophisticated off-gas treatment systems and monitoring, and can be difficult to permit for use within sensitive areas. The process can also produce significant quantities of wastewater (c.0.5-1.0 T of wastewater per T of treated waste) due to the need for off-gas scrubbing.

	Batch Vacuum Mixer (Indirect Heating)	Rotary Kiln (Direct Fired)
Typical Application		
Elemental Mercury	✓	✓
Methyl Mercury	✓	✓
Mercury (I/II) Chloride	X	✓
Mercury Sulphide/Cinnabar (HgS)	X	✓
Hydrocarbons	(No Limit)	(Up to 5 % Max)
PAHs, TPH, PCBs, Dioxins, Furans, Organo-lead	✓	✓
Elevated Water Content	No Limit	Up to 25 % (Max)
Elevated Mercury Content	No Limit	No Limit
Waste characteristics	Sludge, soil, filter cakes, including poorly-conveyable and highly-viscous materials	Sludge and soil (up to 25 % moisture)
Mobile installation for on-site treatment	✓	(with appropriate air emissions controls)
Typical plant throughput capacities	10 000-50 000 T/annum	30 000-50 000 T/annum
Treatment Efficiencies and Other Considerations		
Hg levels after treatment	< 1 ppm	< 1 ppm
Typical Max Process Temperatures	Up to 370°C	650°C to 1,150°C
Off-gas Stream	100 – 1 000 Nm3/hr	5 000 – 25 000 Nm3/hr
Distillates	Distillates can be recovered separately (no combustion)	Mercury is recovered
Off-gas treatment	Vapour filter, two-stage condensation unit, and activated carbon filter	Cyclone, post-combustion chamber, gas-scrubber, e-filter, and active carbon filter
Air emissions	Minimal	Typically > batch vacuum mixer. Requires sophisticated off-gas treatment system and monitoring
Additional produced wastewater	None	~ 0.5 -1 T wastewater per T material treated (from off-gas scrubbing)
Approx. Energy consumption per ton soil treated (sandy; 15% moisture)	~ 210 kWh/t	~ 700 kWh/t
Safety	Operation under vacuum (50 mbar absolute), inert atmosphere	Limited vacuum (3 mbar differential), oxidizing atmosphere
Environmental permitting	State of the art technology, permitting often possible in sensitive areas (closed system)	State of the art technology, permitting can be difficult in sensitive areas

Table 5. Comparison of Ex-situ Thermal Treatment Methods

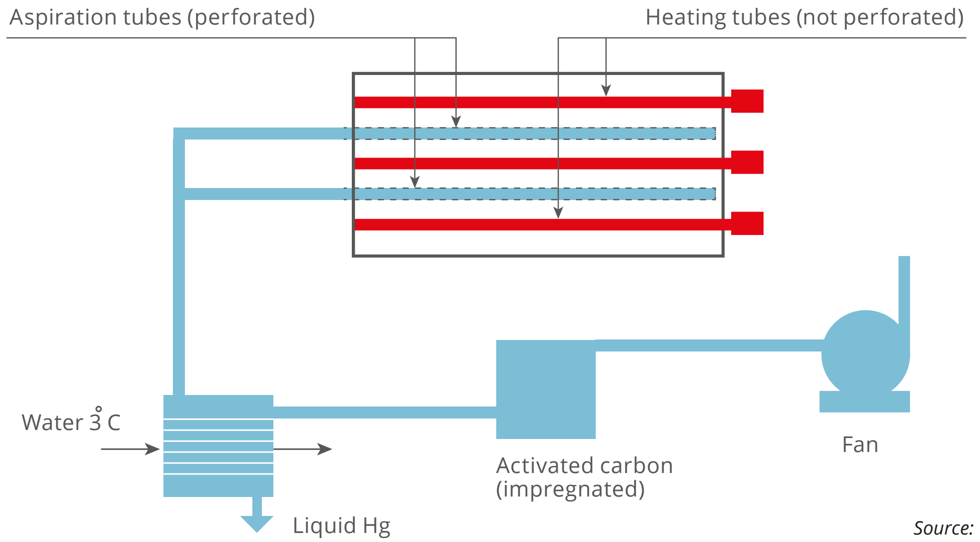
In-situ Thermal Desorption

In recent years, thermal desorption has been developed and is being applied to in-situ remediation of impacted soils and biopiles. As for the ex-situ treatment methods described above, the temperature of the impacted soil is raised using a network of heating tubes to achieve the appropriate temperature, pressure, and residence time for contaminant desorption from the soil matrix. The tubes are typically heated through the circulation of high-temperature combustion gases in a closed loop (Figure 5). The mobile combustion burners are typically run on either propane or natural gas.

Compared to conventional ex-situ thermal desorption technologies (e.g. rotary kilns, batch vacuum mixers), where the soil residence times are typically around 20 minutes, the heating time for the in-situ process takes much longer (e.g. several weeks). However, the treatment "batches" can be substantially higher, allowing potentially similar monthly treatment capacities.

In-situ thermal desorption is an emerging technology for the management of Hg impacted sites. In this application, desorbed Hg (and other volatile co-contaminants) are collected within collection pipes under negative pressure and condensed/recovered. Exhaust gas treatment is often required (e.g. sulphur-enriched activated carbon). However, one concern associated with in-situ thermal treatment is the potential for un-controlled condensation of elemental Hg in areas of relatively lower temperature..

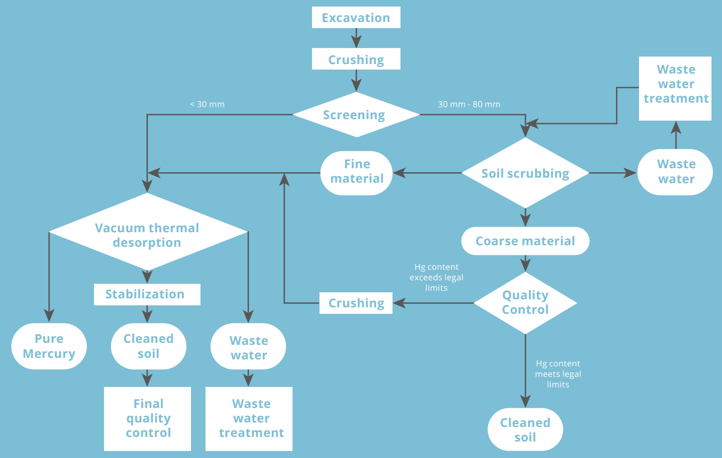
Figure 5. Schematic of In-situ Thermal Remediation Unit



Source: TPS Tech

CASE STUDY 6:
MIRAMAS INDUSTRIAL SITE, SOUTHERN FRANCE

INDUSTRIAL SITE SINCE 1918, INCLUDING THE PRODUCTION OF LIGHT ISOTOPES THROUGH LITHIUM-MERCURY AMALGAM ISOTOPE SEPARATION (1960-2009). ON-GOING EXCAVATION AND TREATMENT OF C. 70,000 T OF HG-IMPACTED SOIL AND BUILDING RUBBLE CONTAINING HYDROCARBONS, WITH HG CONCENTRATIONS RANGING TO > 2,600 MG/KG AND LEACHATE TEST RESULTS OF UP TO 1.3 MG/L MERCURY. THE SITE IS CLOSE TO RESIDENTIAL HOUSING AND POTENTIAL AIR EMISSIONS ARE OF CONCERN TO THE LOCAL COMMUNITY.



Key learnings

- A combination of crushing, soil-washing, vacuum thermal desorption and stabilization was utilised to achieve cost-effective treatment.
- Coarser material (30 mm > 80 mm diameter) treated through soil washing.
- Finer material (< 30 mm) treated in a vacuum thermal desorption unit.
- Gradual heating in the vacuum thermal desorption unit allows recovery of high-purity Hg.
- The closed vacuum system ensures Hg emissions are well below regulatory limits.
- Stabilization of treated materials required for several co-contaminants, including As, Cd, and other metals.
- After stabilization, the treated material is re-used on site.
- Key project and design characteristics:
  - Project duration: 2010 – 2015 (planned).
  - Hg content of treated material: from 0.1 – 1 mg/kg with leach test results < 0.01 mg/l.
  - Treatment batch size: 8.4 m^3.
  - Heating system: 1,800 kW/400°C thermal oil unit heated by natural gas.
  - Operating pressures: 10 to 800 mbar (absolute).

CASE STUDY 7:
WASTE-WATER SETTLING POND, SWITZERLAND

SITE OPERATIONS DATING BACK TO THE LATE 19TH CENTURY INCLUDED THE ELECTROLYSIS OF SODIUM CHLORIDE SOLUTIONS USING HG ELECTRODES, AND THE SYNTHESIS OF AMINO-ANTHRAQUINONE USING AN HG-BASED CATALYST. A SITE ASSESSMENT, CONDUCTED FOLLOWING THE ESTABLISHMENT OF THE SWISS CONTAMINATED SITE ORDINANCE IN 1998, IDENTIFIED AN AREA IN THE VICINITY OF A FORMER WASTE WATER SETTLING POND AS A HIGH PRIORITY FOR FURTHER INVESTIGATION. THE SETTLING POND WAS BUILT IN 1932, AND UNTIL 1972, COLLECTED WASTE WATER FROM THE PRODUCTION FACILITY AND COMMUNITY PRIOR TO DISCHARGE INTO A NEARBY RIVER. SUBSEQUENT INVESTIGATIONS AND RISK ASSESSMENT IDENTIFIED POSSIBLE RISKS TO ENVIRONMENTAL RECEPTORS UTILISING THE HEAVILY-VEGETATED POND (E.G., AMPHIBIANS, DUCKS, SWANS AND OTHER BIRDS.) THE SELECTED REMEDIAL ACTION INCLUDED SLUDGE/SEDIMENT REMOVAL FROM THE POND BOTTOM FOLLOWED BY EXCAVATION OF UNSATURATED SOILS BENEATH THE POND.

Key learnings

- Total Hg concentrations of up to 200 mg/kg were measured in the pond sediments/sludge, with isolated hot spots up to 700 mg/kg Hg. Due to the low concentrations of Hg in site groundwater (< 1 µg/L), laboratory Hg speciation analyses were not conducted.

- Potential risks associated with groundwater down-gradient of the pond were related to organic co-contaminants and not Hg.

- The site characterisation (grid-based sampling) showed significant variability in the horizontal and vertical distribution of Hg within the pond. The highest concentrations were found within pond sediments/sludge and at the base of the dam supporting the pond.

- A risk-based remediation target value of < 20 mg/kg total Hg was initially established for the site, with the acceptance that complete decontamination of the site would not be possible, and that the site would remain in the Canton registry of contaminated sites.

- Down-gradient hydraulic containment was implemented during the removal action as a precautionary measure. However, Hg issues were not identified in groundwater during or after the remediation.

- A vacuum extraction technique applied under wet conditions was selected for the pond sediment/sludge rather than dry excavation under a tent. This technique had the advantage of avoiding dust generation and significant air emissions during sludge removal.

- The extracted sludge was dewatered through an extruder and the pressed soil cake (max concentration of 150 mg/kg Hg) transported to Germany for thermal desorption or incineration, based on the Hg concentrations.

Source: NICOLE member

- Hg concentrations in the generated filtrate (30 m^3/hr) were below applicable criteria for discharge to the municipal sewage treatment plant.

- After removal of the pond sludge and sediment, it became apparent that previous sludge removal activities conducted in the 1970's had likely disturbed the low permeability layer beneath the pond and resulted in Hg migration deeper into soils beneath the pond. This prompted further soil excavation down to the average groundwater level. The additional remediation step resulted in an average total Hg concentration of < 5 mg/kg, which was the revised threshold value after this remediation phase.

Source: NICOLE member

5.5 OTHER SOIL TREATMENT TECHNOLOGIES UNDER DEVELOPMENT

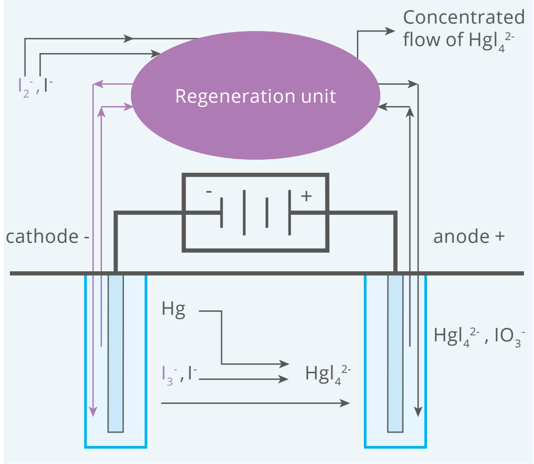
A number of other Hg remediation technologies are emerging for soils, although to date these have had limited commercial application or have not progressed beyond pilot stage. Some have significant technical hurdles to overcome prior to being readily available technologies. These include:

- In-situ electro-remediation;
- Bio-treatment (Fixed-Bed Bioreactors); and
- Phyto-extraction.

In-Situ Electro-Remediation

Electro-remediation involves the application of a low-intensity direct current across electrodes to drive migration of charged molecules to the opposite sign electrode. Electro-remediation is only effective on mobile contaminants. In most Hg-impacted soils, Hg is not mobile enough for the technology to be effective without the use of a mobilising agent. Promising results were shown at bench-scale using an iodine/iodide mobilising solution. A pilot test was built to evaluate the technology for the treatment of the unsaturated zone. At the start, the electro-osmotic flow that developed at the cathode was higher than expected, hence creating a risk of uncontrolled migration of mobilising solution. As a result, all partners in this project (technology provider, industrial operator, regulatory authority) decided to stop the pilot test. The control of this electro-osmotic flow is a major challenge to be solved for this technology.

Figure 6. In-Situ Electro-Remediation Schematic



Principle (patented EP 1 090 695 A1)

Bio-Treatment (Fixed-Bed Bioreactors)

Bio-treatment can be achieved using either an aerobic process which converts soluble ionic Hg (Hg^{2+}) to elemental Hg (Hg^0) for extraction/recovery, or a combined aerobic/anaerobic method which converts soluble ionic Hg to insoluble mineral phases. In both approaches, proprietary microbial cultures are used, and the effluent produced typically requires further treatment.

Phyto-Extraction

Phyto-extraction involves plants either naturally taking up chemicals into their biomass, or the same effect being chemically induced by mobilising agents. No plants have yet been identified which naturally hyper-accumulate Hg, although evidence exists of elemental Hg uptake from ambient air by plant leaves . Chelating agents (such as thiosulfate) have been shown to materially increase Hg mobilisation in soil solution, hence to increase uptake by plants. Phyto-extraction is limited to the root zone of the particular plant being used and off-site disposal of Hg-impacted biomass is a major cost that needs to be factored into the design. The potential for Hg leaching below the plant root zone and the potential of bacterial reduction of ionic Hg to elemental Hg in the root zone need to be considered when contemplating phyto-extraction as a site management solution.

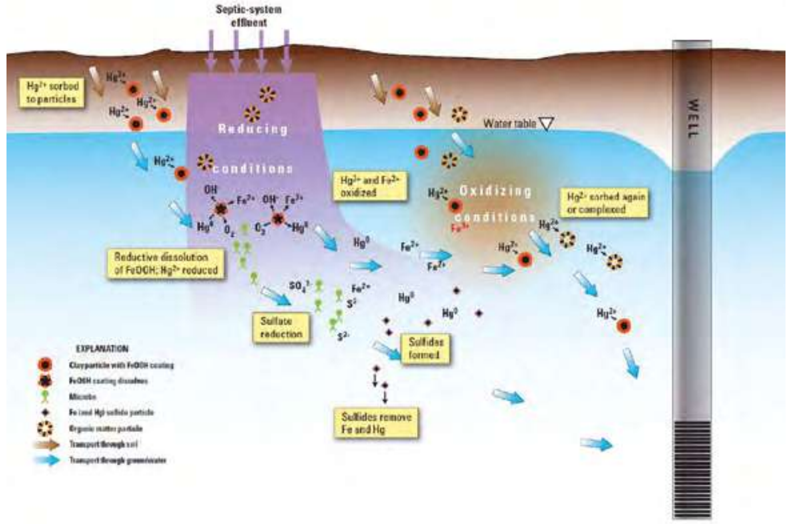
5.6 TECHNIQUES TO ADDRESS GROUNDWATER

Developing a robust CSM, by understanding the ambient and anthropogenic geochemistry, hydrogeological regime and current/future Hg speciation, is strongly advised prior to committing to implementation of groundwater remediation. Where remedial systems have been implemented to manage Hg-impacted groundwater, proven technologies include:

- Hydraulic Containment;
- Pump and Treat;
- Interception and amendment, permeable reactive barriers;
- Interception and capture, in-ground carbon walls (or other absorbents) in funnel and gate systems; and
- Containment using engineered in-ground barriers.

For hydraulic containment, pump and treat (via carbon absorption) and containment using engineered in-ground barriers, the technologies are well proven and much literature is present describing the merits of each approach.

This booklet is focussed on describing options that provide a variety of approaches which have a particular application with regard to Hg, such as the use of technologies designed to amend plume chemistry and capture Hg[70,71,72].

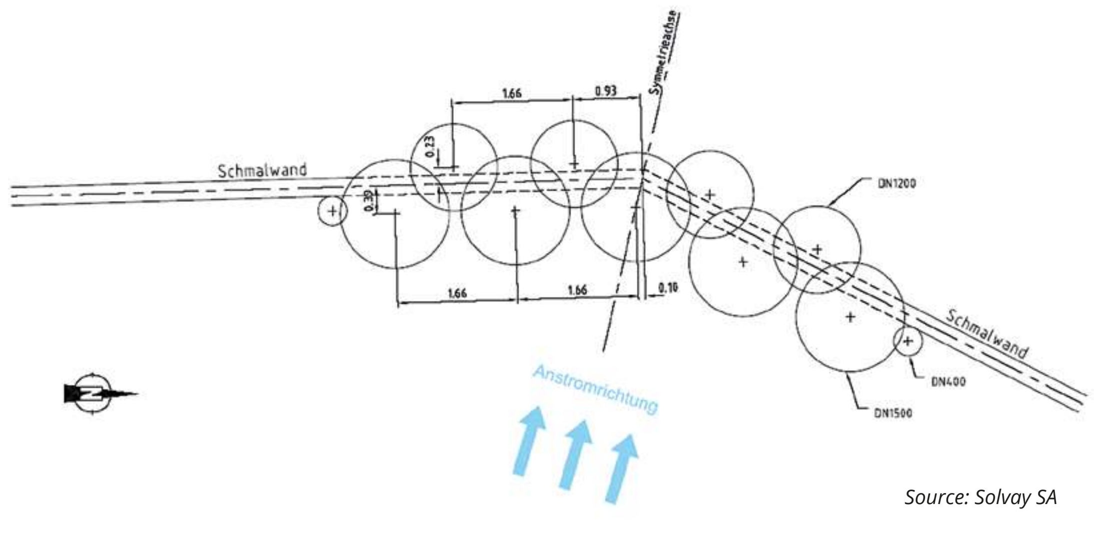


Mobilization of Hg from land to groundwater and biological transformation along flow paths in an unconsolidated sandy, acidic aquifer.

(Source: Occurrence and Mobility of Mercury in Groundwater[73]. http://dx.doi.org/10.5772/55487)

CASE STUDY 8:
FUNNEL AND GATE, AUSTRIA

FOLLOWING CESSATION OF OPERATIONS AND HOT SPOT REMOVAL (50 MG/KG SOIL TARGET), A FUNNEL AND GATE SYSTEM WAS CONSTRUCTED AT A CHLOR-ALKALI PLANT IN AUSTRIA. THE GATE WAS A MIXTURE OF GRAVEL AND ACTIVATED CARBON DESIGNED TO HAVE A LIFE-SPAN OF SEVERAL YEARS. THE RESIDUAL GROUNDWATER PLUME IS FUNNELLED TOWARDS AN ACTIVATED CARBON BOX IN THE GATE, AND HG IS REMOVED AS GROUNDWATER PASSES THROUGH. THE MAXIMUM LOADING WAS ESTIMATED AT 6 G/D HG FROM A RESIDUAL PLUME OF UP TO 50 μG/L. A SENSITIVE RECEPTOR IS LOCATED 350 M DOWN-GRADIENT OF THE SITE AND LONG-TERM MONITORING RESULTS SHOWED A STABILIZATION OF HG LEVELS DOWN-GRADIENT OF THE GATE BELOW THE 1μG/L TARGET.



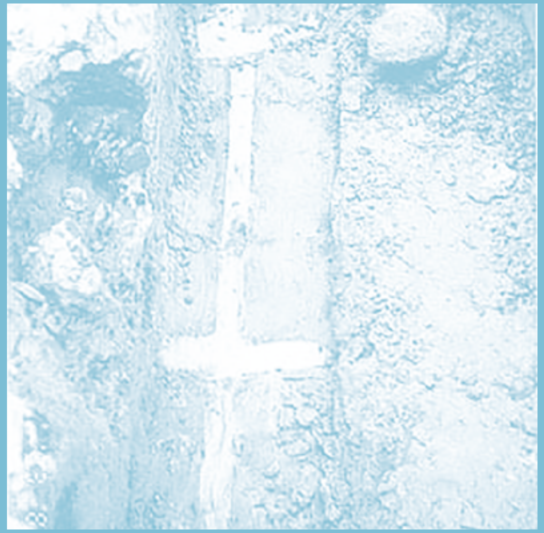
Source: Solvay SA

Key learnings

- The system was built in two steps, with the funnel being built in 2001. This was initially operated by continuously pumping at 12.5m³/h for two years. This period was use to define the best material for the gate.

- The vibrating beam method was used to install the vertical barrier (funnel). A beam was vibrated down to the deepest point and then grout injected into the void created while withdrawing the beam. The final funnel characteristics are:

Total length	245 m
Depth	22-24 m-bgs
Thickness	0.06 m
Barrier starts at	0.6 m-bgs
Barrier ends at	2 m in the fine sands
Permeability	1x10-8 m/s



- A permanent gate was then built in 2004 by excavating 9 overlapping cylinders through the wall down to a depth of 15.5 m-bgs. Each column was then backfilled with a mixture of activated carbon and gravel from the base to up to 5.5 m-bgs (i.e. 0.5 m above mean ground water table).

- Renewal of the gate will be achieved by excavating the spent activated carbon and refilling with new carbon once the capacity has been reached. The final gate characteristics are:

Permeable gate volume	150 m³
Water residence time	205 minutes
Activated carbon	100 m³ (53 T)
Gravel	50 m³ (98 T)

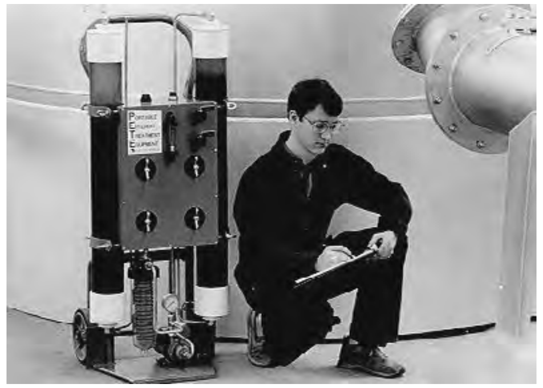
5.7 OTHER GROUNDWATER TREATMENT TECHNOLOGIES UNDER DEVELOPMENT

There is on-going effort to develop effective treatment processes for dissolved Hg in groundwater. Current processes include absorptive systems and reactive systems. Absorbent systems include conventional activated carbon technologies. However, other absorbents are also being developed and offer potential advantages in certain circumstances. Absorbents may be based on natural products (e.g., immobilised algae, biochar) or may be synthetic chemicals (e.g., chelating agents, nanotechnologies). Reactive systems include technologies such as chemical reduction and stripping and the use of copper or brass shavings.

Immobilised Algae

Bio-Recovery Systems Inc. recently conducted a project as part of the US EPA's Superfund Innovative Technology Evaluation (SITE) Program to evaluate the ability of immobilised algae to adsorb Hg from impacted groundwater in laboratory studies and pilot-scale field tests. The algal biomass was incorporated in a permeable polymeric matrix within the treatment unit .

The product, AlgaSORB©, which was packed into adsorption columns made up of permeable polymeric matrix, reportedly exhibited excellent flow characteristics, and functioned as a "biological" ion exchange resin. Like ion-exchange resins, AlgaSORB© can be regenerated. A sequence of eleven laboratory tests demonstrated the ability of this product to adsorb Hg from groundwater that contained high levels of total dissolved solids and hard water characteristics. However, use of a single AlgaSORB© preparation yielded non-repeatable results with samples collected at different times of the year[54].



Portable Effluent Treatment Equipment using AlgaSORB©.
Source: *www.clu-in.org*

The strategy of sequentially extracting the Hg from groundwater through two columns containing different preparations of AlgaSORB© was developed and proved successful in laboratory and pilot-scale field tests. Field test results indicate that AlgaSORB could be economically competitive with ion exchange resins for removal of Hg, with the advantage that hardness and other dissolved solids do not appear to compete with heavy metals for binding capacity[54,55].

Biochar

A study conducted in 2013 at UMBC evaluated a range of biochars made from a number of agricultural residues, phragmites (beneficial use of invasive species in wetlands), and hardwoods. In addition, some of the biochars were activated either physically or chemically to enhance their sorptive properties. Some of the biochars were impregnated with iron oxides to evaluate the enhancement of sorption of Hg and methyl-Hg.

The study showed that biochars were able to sorb organic contaminants, Hg and methyl-Hg, making them attractive alternatives to activated carbon for sites impacted with both organic and inorganic contaminants. Activated carbon products have a limited amount of sorption sites available for inorganic contaminants relative to biochars, and their performance typically drops with increasing Hg concentrations. The biochars, particularly those derived from poultry litter, were able to remove more Hg from solution at higher Hg concentrations compared to other carbons (>99% Hg removal in a study). It is possible that the high phosphate content of these poultry litter biochars is responsible for the enhanced Hg sorption[57].

In one laboratory-scale study of Hg-impacted sediments, 40 different substrates were charred to get the most optimal characteristics for absorbing Hg. Of these, a biochar called "Cowboy Charcoal", made from Red Oak from Kentucky, was narrowed down as the best. Mercury was present in the sediment as insoluble sulfides (metacinnabar) and also in soluble forms. The "Cowboy Charcoal" was able to remove considerable amounts of Hg from the water phase/sediment pore water. Adsorption/absorption sites remained available after treatment (the capacity was not fully utilized), and the biochar retained the adsorbed Hg better than GAC (SediMite)[58]. Based on the results of the laboratory testing, further pilot testing is planned.

More information regarding Biochar can be found at http://www.biochar-international.org.

Use of Chelating Agents

Chelating resins are commercially available and used for the removal of low-levels of Hg and soluble Hg salts from wastewaters such as brine and other industrial effluents, including from chlor-alkali processing facilities. Following treatment, the Hg is strongly bound to the resin's functional groups to form stable complexes. These properties are reportedly largely unaffected by high chloride or sulphate content in the water treated. Effluent solutions containing 2-20 mg/l Hg can be treated using resins such as Purolite® S-920 to reduce the concentration in solution to less than 0.005 ppm[59]. Other chelating agents, such as Evonik Industries TMT 15® are also commonly used to remove heavy metals such as Hg from industrial waste waters, such as gas scrubber waters and other process waters[60].

A pilot study has been undertaken[61] to examine the removal of low-levels of Hg from groundwater near a chlor-alkali plant using a synthetic chelating ligand. One commercially-available compound was found to be capable of reducing Hg concentrations to below detection limits (0.05 µg/l), with the added benefit of producing a stable precipitate.

Nanotechnology

Nanotechnology (Thiol SAMMS), developed by Pacific Northwest National Laboratory, comprises nano-porous ceramic substrate with a high surface area with layers of adsorptive plates with selective affinity for Hg. Testing shows Hg loading as high as 635 mg/l and sequential treatment yielded effluent < 0.1 mg/l[62].

Chemical Reduction and Stripping

Field and laboratory tests have confirmed the use of chemical reduction and air stripping for treatment of water containing Hg^{2+}. The process consists of dosing the water with low levels of stannous chloride (tin^{2+} chloride) to reduce the Hg to elemental Hg (Hg^0). The Hg^0 can then be removed from the water by air stripping. Reagent doses, with Sn to Hg ratios greater than about 5 to 25, showed nearly complete removal (~94%) and yielded final Hg concentrations of < 0.01 µg/L. The purge air can be treated with activated carbon as needed[63].

Use of Copper or Brass Shavings

The use of copper shavings to remove Hg from impacted groundwater by amalgamation has been investigated at an experimental level. Batch sorption experiments showed that 96 - 98 % of Hg^{2+} was removed within 2 hours. Column experiments were also performed with an Hg solution, which showed that no Hg breakthrough (> 0.5ug/l) could be detected after more than 2,300 percolated pore volumes. Copper was released from the shavings due to the amalgamation process and due to copper corrosion by oxidation, resulting in concentrations of mobilised copper of 0.2–0.6 mg/l. The authors suggest that given the efficient removal of Hg^{2+} from aqueous solutions, that copper shavings could be employed in a sequential system of Hg amalgamation followed by removal of mobilised copper using an ion exchanger (e.g. zeolites).

Brass (copper-zinc alloy) is being used in situ at pilot scale at a former wood treatment facility in order to treat an Hg plume by amalgamation[65].

6

BEST PRACTICE RECOMMENDATIONS

NICOLE PUTS FORWARD THE FOLLOWING BEST PRACTICE RECOMMENDATIONS, FIRSTLY FOR CHARACTERISATION AND RISK ASSESSMENT, AND THEN SITE MANAGEMENT.

NICOLE BEST PRACTICE RECOMMENDATIONS CHARACTERISATION AND RISK ASSESSMENT

1. Keep thorough historical records of industrial process and building structures, including infrastructure (foundations, networks). These are key elements of the Conceptual Site Model (CSM) and help to focus characterisation.
2. Sufficient characterisation is needed to build a robust CSM, set adequate reserves, negotiate the right clean-up goals and control project costs.
3. Select investigation/sampling techniques that avoid Hg migration and obtain representative data. Allow for full-time supervision by trained and experienced site engineers.
4. Understand Hg speciation and ambient/anthropogenic geochemistry, to quantify current and future Hg mobility/toxicity and potential risks.
5. Beware of “nugget effects”: use on-site measurements, increase sampling frequency, use statistical methods (e.g. 95 % UCL) for risk quantification.
6. Use direct measurement wherever possible (vs. relying on modelling) to characterise exposure media and migration pathways, so as to best quantify potential risks.
7. Make sure potential co-contamination is understood (e.g. dioxins, CVOCs).
8. Proactive management of Health & Safety risks needed during characterisation.

NICOLE BEST PRACTICE RECOMMENDATIONS REMEDIATION AND OTHER MANAGEMENT MEASURES

1. The management strategy should balance remediation with other management measures (e.g. deed restrictions) to mitigate risks and reduce long-term liability.

2. Negotiate appropriate and achievable clean-up goals. These should be risk-based, respect sustainable remediation principles and deliver Net Environmental Benefit.

3. Do not define clean-up thresholds for Total Hg, as these tend to be overly conservative. Instead, focus on mitigating Hg species driving risk and/or a mass removal approach.

4. Select the right remediation technique for the Conceptual Site Model, if needs be following appropriate feasibility testing (e.g. lab-scale tests, pilot trials).

5. Use qualified and experienced service providers (consultants, contractors).

6. During excavation and other ground disturbance, implement oversight by qualified personnel to optimise soil volumes and minimise the risk of downward Hg migration.

7. Given the high costs of off-site disposal, optimise soil volumes (e.g. careful segregation during excavation, sorting, washing).

8. Stringent health and safety management during remediation, including biological and air monitoring.

TWO KEY RESEARCH AREAS HIGHLIGHTED FOR CONSIDERATION:

1. Experimental work (laboratory, field) on the physic-chemical behaviour of Hg in the environment, so as to validate predictive models; and

2. Long term efficiency of in-situ stabilisation/solidification, including implementation of long-term monitoring programmes.

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