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Mitigation of mercury contamination at retired nuclear facilities

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ABSTRACT: Elemental mercury contamination poses distinctive problems in retired nuclear facilities. A universal demercurization process, UNIDEMP™, has been developed as an innovative low-cost method for removing mercury from a wide variety of hazardous materials in these facilities. In this process, the feed materials are reduced to appropriate size and treated under suitable oxidizing conditions at 823-923K in a counter-current rotating furnace. The mercury is volatilized and condensed, while the other solid materials are recovered as recyclable products. No mercury-containing secondary waste is generated. UNIDEMP™ is applicable to nearly all types of solid and aqueous mercury waste streams, such as metals, concrete, soils, asbestos, plastic, and cable, as well as amalgams and mercury compounds. The equipment is mobile; and it can be easily adapted to meet specific user requirements of residual mercury levels, processing rates, and feed materials, while achieving very low unit processing costs.

1 INTRODUCTION

Nuclear research and processing activities have left a number of facilities with significant quantities of elemental mercury contamination; this contamination poses distinctive problems in retired nuclear facilities. For instance, elemental mercury is known to cause liquid metal embrittlement of steels and other structural alloys, which can lead to loss of structural integrity of these facilities. Even though these retired nuclear facilities are no longer actively operating, the release of mercury presents an unacceptable risk of exposure to the public and the environment; and the risks are magnified and compounded by the presence of radioactive isotopes in the facilities. These risks are driving a major incentive to remove the mercury from these facilities.

In both elemental and speciated forms mercury is highly mobile and can be easily released to the environment through soils, groundwater, and air [1]. In the United States, such waste is designated special hazardous waste and presents a particular challenge for disposal. The presence of radioactive isotopes makes these waste streams mixed waste. The regulations governing the designation and disposal of such mercury-containing mixed waste in the United States and abroad are extremely stringent, and these wastes are very difficult and expensive to dispose. Therefore, removal of the mercury from these mixed waste streams and recycling are economically and ecologically attractive options.

A universal demercurization process, already trade named UNIDEMP™, has been developed as a low-cost innovative process for removing mercury from a wide variety of materials [2]. Patents have been filed for the UNIDEMP™ Process [3,4]. In this process, the mercury-contaminated materials are reduced to appropriate size and treated under suitable oxidizing conditions in a counter-current rotating furnace at 823-923K. The mercury is volatilized and condensed, while the other solid materials are recovered as recyclable products. The flue gas and waste water are treated to produce emissions that meet clean air regulations and water that can be recycled to the process.

2 MERCURY TREATMENT TECHNOLOGIES

Several options exist for treating mercury-contaminated wastes [1, 5-9], including physical processing, chemical treatment, immobilization, thermal treatment, biological treatment, electrolytic treatment, in situ vitrification, and isolation by barriers or liners. Of these processes, immobilization, in situ vitrification, and isolation by barriers or liners fix the mercury in the waste matrix, which must then be disposed in a waste repository. There is no volume reduction; on the contrary, fixing the mercury in the waste matrix increases the volume of waste for disposal. There also is no further possibility of recycling potentially valuable materials from these waste matrices. The other processes, physical processing, biological, electrolytic, chemical, and thermal treatment actually remove mercury from the wastes streams. As discusssed in the following paragraphs, each of these mercury removal processes presents disadvantages.

Of the mercury removal processes, physical processes alone, such as vacuum extraction or gravity separation, can only remove elemental unbound mercury. Residual mercury levels achievable with these methods are generally >1% (in rare instances, such as mixed mercury and glass waste without amalgams, residual mercury levels of 1 ppm can be achieved). The use of chemical additives to enhance mercury recovery from solution, such as in flotation processes, is only applicable to limited waste streams. However, chemical additives increase the potential for mercury transformations and also increase the volume of secondary waste for treatment and disposal.

Chemical treatment processes are based on the reactivity of mercury compounds; the metal itself is chemically "noble". These processes generally employ solution leaching of the mercury-contaminated waste streams. Most commonly used solutions are oxidizing acids, such as nitric and sulfuric acids and hypochlorous acid. These oxidizing solutions convert the mercury to solubilized ionic mercury, which can be treated to recover elemental mercury. Laboratory-scale tests have shown certain chemical treatments can achieve residual mercury levels to 1 ppm in selected simple materials. For most complex waste streams, such as mercury batteries or fluorescent lamps, however, chemical treatment results in residual mercury levels of 10-20 ppm in the product after treatment. There are several other disadvantages with chemical treatment: use of toxic and corrosive solutions; spent solutions cannot be easily regenerated; large volumes of secondary waste are generated; each chemical step must be followed with a neutralization step, making the process progressively more complicated and expensive, especially for complex waste streams; insoluble waste materials, such as plastic and rubber, cannot be easily treated; and overall process costs are very high (typically $10,000 per ton in the case of mercury batteries).

Thermal treatment (retorting or roasting) is considered the United States Environmental Protection Agency (USEPA) BDAT (Best Demonstrated Available Technology) and is required for treatment of waste materials containing greater than 260 ppm of mercury [10]. As currently practiced, retorting or roasting is generally carried out by heating the waste materials in a vacuum or under reduced inert gas atmosphere at temperatures as high as 1473K. The principal disadvantage of these thermal processes is the inability to treat bound mercury waste streams, such as metal amalgams or mercury compounds. The condensed mercury obtained is contaminated and/or mixed with volatile components, such as zinc, cadmium, lead and oils. Additionally, under the above conditions, plastics and other organic materials will form a viscous mass rather than being incinerated, thereby effectively preventing the mercury from being removed from these materials. Also, such high temperatures require refractory-lined furnaces, resulting in very high capital and operating costs. In general, the current thermal treatment processes require long treatment times (8 to 24 hours) and cannot achieve residual mercury levels below 3-5 ppm. The total costs range from $6,000 to $10,000 per ton of material for complex waste streams, such as mercury batteries. These processes are also ineffective in treating waste streams such as metals and amalgams, plastics, rubber, asbestos, and activated charcoal.

The principal disadvantage of biological treatment methods is that they do not remove mercury from the waste stream (primarily soils), but rather convert it to other forms. Thus, the soils will require further treatment to remove and recover the mercury. These methods do have some application in converting soluble ionic mercury to elemental mercury or methyl mercury, which can, in turn, be biologically converted to elemental mercury. In general, these processes are slow and must be carried out in several steps, or they must be combined with other processes to effectively remove mercury from very limited waste streams. Thus, any cost advantage is nullified.

Electrolytic processes are also limited in their application to liquids and solutions containing dissolved mercury. The applied electric current converts heavy-metal ions to stable metal oxides, which can be precipitated from solution. As proposed, the process usually involves physical separation or chemical leaching in the first step, followed by electrolytic treatment to remove dissolved mercury compounds from the waste stream. This process is capable of converting more than 90% of heavy metals to their oxides. Clearly, the disadvantages are limited applicability only to liquid waste streams, multiple processing steps, secondary waste generation, insufficient mercury recovery, and high residual mercury levels.

These disadvantages of the current thermal treatment processes have been overcome in the UNIDEMP™ oxidative thermal treatment process.

3 GENERAL PROCESS DESCRIPTION

The proposed mercury removal technology, UNIDEMP™, is an oxidative thermal treatment process. As shown in Figure 1, the feed materials in UNIDEMP™ are reduced to a suitable size (20x20x20 mm or less) and fed into a counter currently operated furnace. Size reduction increases the surface area available for oxidation, which provides shorter diffusion paths for mercury. In the furnace, the material is heated in an oxidizing atmosphere to ~ 1073K in the center of the furnace and ~ 873K at the wall as it flows toward the flame zone, thus liberating organics, water, and mercury. At these temperatures, all known organic and inorganic mercury compounds decompose to elemental mercury. As material travels through the furnace, it is constantly rotating and oxidizing at the surface of the individual particles of the materials. Because the temperature of the waste materials does not exceed 923K in the solids as a rule, there is no liquid slag formation. At the walls of the furnace, the temperature ranges from ~ 623K at the outside wall to ~ 823K at the inside wall, thereby requiring no refractory lining which, in turn, results in reduced maintenance and capital costs.

The flue gas leaving the furnace is directed to a cyclone where solid particles are separated before the gas enters a post combustion chamber (PCC) to complete the combustion of partially incinerated organics. The flue gas next enters the scrubbing system. The gas is quenched and further cooled (cooling water) to condense the mercury. From the wet scrubber, the exiting flue gas is filtered to remove any dust particles and any remaining mercury in the flue gas is captured in an activated charcoal bed. The spent charcoal, containing mercury, is added to the input feed stream and incinerated in the furnace.

The condensed wastewater from wet scrubbing contains non-dissolved mercury, which is removed by gravity settling. The wastewater is then treated in an attached wastewater treatment unit, in which residual dissolved mercury and other heavy metals are separated by classical TMT-15 treatment. A filter unit makes it possible to achieve concentrations of the heavy metals below regulatory limits. The sludge, containing mercury from this treatment step, is returned to the furnace and incinerated.

3.1 Products and Discharges

The proposed process does not produce any mercury-containing secondary waste. By employing appropriate combustion temperatures and residence times, it is possible to achieve mercury levels in a wide range from 0.1 to 2 ppm in the solid products leaving the furnace.

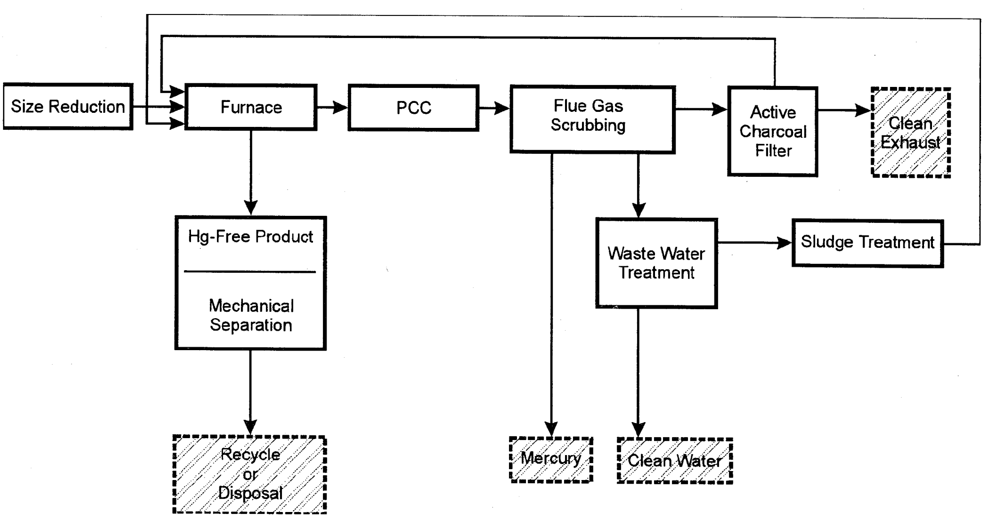

Figure 1. UNIDEMP™ is characterized by a simple process flowsheet.

Depending on the waste streams, the products from the process are

- Liquid mercury, which can be recycled following refining, if necessary
- Dry mercury-free solid product, which can be recycled to the secondary metals market or disposed as non-mercury waste.

The two discharges from the process are

- Clean exhaust gas from the PCC
- Cleaned water from the wastewater treatment unit, which is recycled to the process, or it can be discharged.

The clean exhaust gas and the discharged water from the process meet state-approved air and water discharge quality regulatory requirements.

4 EXPERIENCE FROM BATTERY DEMERCURIZATION

UNIDEMP™ is based on 10 years of successful experience with the demercurization of mercury-containing batteries [11-15]. The equivalent process for batteries, DEBATOX, has been successfully field tested in Europe (1994 and 1995 trials in Germany, Holland, and Austria) in a 350 metric ton (MT) plant using a variety of batteries (up to 30,000 ppm Hg) [16, 17]. The field trials yielded very low residual mercury levels. For example, residual mercury levels of 0.5 ppm were obtained in the product within 60-90 minutes at 823-923K, largely independent of the mercury content of the input materials. The process has also been reviewed in detail by the European Portable Battery Association (EPBA), which has led to close cooperation with the EPBA. One or two commercial plants (5,000-7,500 MT annual throughput) are scheduled to begin commercial operations in Europe in 1997.

Mercury-containing batteries are the most complex mix of waste materials for demercurization, including moisture; oils; plastics; paper; organics; non-volatile high melting metals; low melting volatile metals such as Zn, Cd, and Pb; metal oxides; PCBs; metal amalgams; and volatile materials, such as NH_4Cl and $ZnCl_2$. The demercurization of this complex mix has been successfully demonstrated on an industrial scale, including safe handling and operation simultaneously of all process operations. This demonstrates the functionality and feasibility of the battery demercurization process. Demercurization of all other mercury-containing waste streams is essentially simplified versions of the most complex mercury-containing battery mix.

5 ADVANTAGES OF UNIDEMP™

UNIDEMP™ is characterized by several unique features, including very low unit costs; effective treatment of amalgams; residual mercury levels in the solid product (< 1 ppm); and applicability to a wide range of materials such as soils, sludge, metals, concrete, activated charcoal filters, plastic and cable, and asbestos. No other existing chemical or physical process can treat the combination of complex materials to achieve the residual mercury levels in the solid product for the unit costs of UNIDEMP™. Other advantages of UNIDEMP™, compared with alternative chemical and physical processes, are detailed below.

- Mercury-free products are obtained. Residual mercury levels of < 1 ppm can be achieved within 60-90 minutes at 823-923K, largely independent of the initial Hg content of the feed materials.
- The process is applicable to a wide variety of materials such as metals and amalgams, concrete, soils, asbestos, plastic, and cable.
- The process converts mercury-contaminated hazardous waste to Hg-free recyclable products. **No mercury-containing secondary waste is generated.**
- The process is operated as a closed system.
- Available state-of-the-art industrial equipment used to reduce costs.
- The method incorporates experience from industrial pyrometallurgical processes.
- Total energy consumption and costs are very low.
- Ninety percent of the energy consumption is primary energy.
- The method involves simple operation and process control.
- It provides for complete flue gas and wastewater treatment.
- There is no manual handling and easy working conditions are employed.
- It is an economical process.
- There are minimum personnel exposure and very low worker risks

The equipment is mobile and it can be easily adapted to meet specific user requirements of residual mercury levels, processing rates, and waste streams, while achieving very low unit processing costs. In fact, results from laboratory scale tests can be extrapolated to full scale process operation. The process is also amenable to meeting future, more stringent, requirements for residual mercury levels in the solid products.

The unit costs for demercurization of non-radioactive materials by UNIDEMP™ are estimated to be in the range of $300-$600 per tonne (MT), based on capital and operating costs and plant amortization for a commercial-scale plant (~5,000 MT/year throughput). These costs are nearly 80-90 percent lower than the unit costs of processing by other chemical, physical and thermal mercury treatment processes for similar waste materials and given requirements.

6 APPLICABLE WASTE MATERIALS

All types of mercury-containing waste streams can be treated with UNIDEMP™, including soils, sludges, complex organic compounds, mercuric oxide, mercury salts, metals, plastics, asbestos, and concrete. It can also treat amalgams, which are commonly formed with mercury in contact with metals. The process is also amenable to meeting future, more stringent, requirements for residual mercury levels in the solid products. Aqueous waste streams can be treated by UNIDEMP™ by judicious mixing with solid materials. The process can also effectively treat PCBs and halogenated organics, which are completely incinerated in the post-combustion chamber.

7 SUMMARY

A universal demercurization process, UNIDEMP™, has been developed as an innovative low-cost method for removing mercury contamination found in a wide variety of materials in retired nuclear facilities. In this process, the feed materials are reduced to appropriate size and treated under suitable oxidizing conditions at 823-923K in a counter-current rotating furnace. The mercury is volatilized and condensed, while the other solid materials are recovered as recyclable products. No mercury-containing secondary waste is generated. Pilot-scale tests on mercury batteries consistently yielded residual mercury levels of 0.5 ppm in the product within 60-90 minutes at 823-923K, largely independent of the Hg content of the feed. UNIDEMP™ is applicable to nearly all types of solid and aqueous Hg waste streams, such as metals, concrete, soils, asbestos, plastic, and cable, as well as amalgams and Hg compounds. The equipment is mobile, and it can be easily adapted to meet specific user requirements of residual mercury levels, processing rates, and waste streams, while achieving very low unit processing costs.

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