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Behaviour of Mercury from Hazardous Solid Waste Generated by Chlor-Alkali Cuban Industry. Remediation Proposal at Pilot Scale

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One of the major concerns from the chlor-alkali industry is the mercury solid waste generated by the process. A pilot-scale thermal treatment technology to treat high mercury containing waste generated by the chlor-alkali Cuban process was designed. Mass and energy balances at steady-state, the upscaling methods as well as the mercury reaction scheme were used for the design of the plant. Two operating alternatives have been analyzed. In the first alternative, the plant operates to achieve the maximum mercury removal. In the second alternative, the waste is treated to a point where it meets the TCLP leaching limit. The proposed pilot plant with 960 t of waste/y of processing capacity is able to recover 639 kg of metallic Hg/y and 479 t/y of treated waste (arid) that can be sold. "Arid" is a Cuban term referring to aggregate materials that are used as a component of construction material. The second alternative is most advantageous from the techno-economic point of view if an integrated economic analysis with the chlor-alkali Cuban plant is done. An annual gross profit of US$ 166,450, a return on investment of 10.6 %/y and net present value of US$ 12,157 could be realized.

1. Introduction

Contamination of soils by heavy metals is a common problem throughout the world due to intensive use of the land, industrial activities and improper hazardous waste disposal (Antonucci et al., 2013). Significant and negative impacts to the human health and environment can be correlated with the use of mercury due to its unique high toxicity, volatility, and persistence in the environment and easiness of bio-accumulation (Zhang et al., 2009). A recent study (Lamborg et al., 2014) reported that anthropogenic perturbations to the global mercury cycle have led to an approximately 150 % increase in the amount of mercury in thermocline waters and have tripled the mercury content of surface waters compared to pre-anthropogenic conditions. The main sectors of anthropogenic sources identified are artisanal and small scale gold mining, coal combustion, production of non-ferrous metals, cement production, and disposal of waste containing mercury (AMAP/UNEP, 2013).

Chlor-alkali industry represents one of the major concerns of mercury emissions due to the large amount of waste containing mercury generated by the process. The management and ultimate disposal of mercury contaminated hazardous waste is controlled by US EPA regulations known as the Land Disposal Restrictions (LDRs) (40 CFR, Part 268). Under the current LDR program, US EPA (2008) recommended thermal recovery (e.g., roasting/retorting treatment) as the best demonstrated available technology (BDAT) for treatment of waste containing more than 260 mg/kg of mercury. For treatment of waste with less than 260 mg/kg of mercury, other extraction technologies (e.g., acid leaching) or immobilization technologies (e.g., stabilization/solidification) may be considered.

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Although, mercury cell chlor-alkali plants are not anymore considered a good industrial practice (Directive 2008/1/EC, 2008), this technology is still used in many countries in the world, including Cuba. The only way to reduce the mercury hazards is to deal with it by adopting proper safety and remove it from process streams efficiently (Tauqeer et al., 2015). The chlor-alkali Cuban plant “Elpidio Sosa-ELQUIM” currently hosts more than 7,000 t of mercury contaminated waste buried in concrete niches. Mercury waste generated by the electrochemical Cuban plant process can be categorized as 'high mercury waste' (total Hg content exceeding 260 mg/kg), according to the US Land Disposal Restrictions (Busto et al., 2011).
Thermal treatment of waste represents an integral part of well-developed waste management systems worldwide (Kropac et al., 2013). Several studies have demonstrated the efficiency of thermal treatment at pilot and full scale to treat solid waste highly contaminated with Hg focused primarily on the increase the mercury removal efficiency of the treatment (Huang et al., 2011). Operational parameters (time and temperature) have been extensively investigated for designing thermal technologies to treat mercury contaminated waste. However, no studies have considered the reaction mechanisms and kinetics of mercury during thermal treatment as important parameters for a proper technological design of this process.
The potential of the thermal treatment to remove Hg from the contaminated solid waste generated by the chlor-alkali Cuban industry have been evaluated and its effectiveness proven (Busto et al., 2011). Moreover, the kinetic reaction mechanism which represents the behavior of mercury and mercury compounds, within the waste matrix during the thermal treatment was developed by Busto et al. (2013). To design a more feasible technology, the reaction mechanism and kinetic of mercury during the thermal treatment should be considered. In the present work, the mass and energy balances at steady-state, the upscaling methods, as well as the mercury reaction scheme were used for the design of a remediation thermal plant. The remediation proposal was also evaluated from techno-economic point of view. The main objective of this study is to propose a technological design of the thermal treatment (retorting) to treat mercury contaminated waste generated by the chlor-alkali Cuban plant.

2. Material and methods

2.1 Bench-scale thermal treatment process

Mercurial sludge was sampled following the same procedure detailed by Busto et al. (2011). In this study we treated mercury containing waste from the chlor-alkali Cuban plant by a thermal treatment process to recover the mercury. Figure 1 shows the flow diagram of the bench-scale thermal treatment process, which includes three main stages: drying, crushing and mercury removal of the mercurial waste sample.
Five grams of mercurial waste were heated at 45 °C during 24 h in a ceramic muffle furnace (L9/11/SKM/P330 Model, Nabertherm, Germany) to determine the moisture content of the sample by weight difference analysis. The initial particle size of the mercurial waste sample was analysed using the Pipette method (Konert and Vandenberghe, 1997). Total Hg content was determined using 1 g of waste sample following the analytical method explained in Busto et al. (2013). The drying stage was carried out using a heating/drying oven with air forced convection (FD-115 Model, Binder, Germany). For the crushed stage the waste was hand crushed in a mortar and passed through a 2 mm sieve. The mercury removal stage was performed using a ceramic muffle furnace (L9/11/SKM/P330 Model, Nabertherm, Germany) which has a temperature control accuracy of ±1 °C and 0.24 x 0.24 x 0.17 m of dimensions.

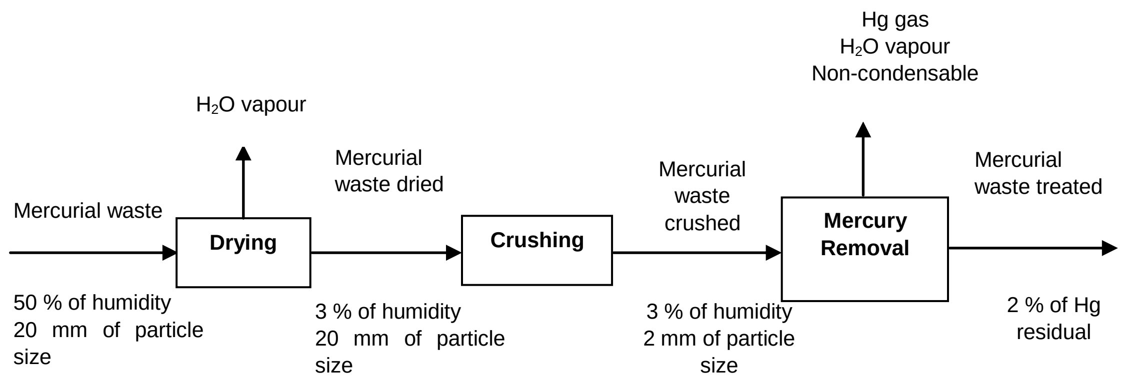

Figure 1: Flow diagram of the bench-scale thermal treatment process

For the drying stage the main operating conditions were the time and temperature. A drying test was carried out using the procedure reported by Green and Perry (2007) to obtain the regimen curve of drying as well as the drying time of the waste sample. One hundred grams of mercurial waste exactly weighted were dried at 80 °C and an air recirculation flow set at $1.17 \cdot 10^{-3}$ m^3/s to determine moisture content of samples (by weight difference) each 30 min. During drying the moisture content was reduced from 50 % to 3 %. Since a 3 % of moisture content was observed at 4 h of drying, this drying time was selected to perform the drying stage at pilot-scale. For the crushing stage the material was crushed to pass through a 2 mm sieve. For the mercury removal stage at laboratory scale, the operating conditions of the ceramic muffle furnace were 450 °C of retorting temperature and two retorting times (1 h and 3 h). It must be highlighted that the first 30 min of the thermal treatment were required to reach 450 °C.

2.2 Scale-up of thermal treatment at pilot-scale

The scale-up of the thermal treatment from bench to pilot-scale was effectively performed specifically for the mercury removal stage (which takes place in the ceramic muffle furnace) as the reactions of mercury in the mercurial waste occurs in this stage. To design the furnace at pilot-scale by scale-up, principles of geometric, chemical and thermal similarity were followed (Nauman, 2002). Geometric similarity between the laboratory muffle furnace (prototype) and the pilot plant furnace (model) was obtained keeping constant the prototype area (0.06 m^2). Chemical similarity was acquired using the same waste sample in both scales (bench and pilot) in order to keep constant the chemical composition during the treatment. Thermal similarity was achieved maintaining the prototype power consumption constant in order to obtain an equal temperature profile inside the furnace. To scaling-up the furnace at pilot-scale, the parameters (area and power consumption) were affected by a scaling-up factor. The thickness of the waste layer that has been proposed to operate at pilot scale was determined by upscaling. The scaling-up factor employed to design the pilot plant furnace was calculated considering that the ratio of power consumption to waste mass was the same for the laboratory furnace (prototype) and the pilot plant furnace (model).

2.3 Pilot-scale thermal treatment process

Figure 2 shows the schematic diagram of the proposed pilot-scale thermal treatment process, which can be divided into a mercury waste pre-treatment system, a thermal treatment system, a mercury recovery system and a co-products recovery system. The mercury waste pre-treatment system includes the waste extraction from the niche (excavator), an equipment to contain and to feed the mercurial waste into the trays (feed hopper), an equipment to transport the mercurial waste to the drying machine (conveyor), an equipment to reduce the waste moisture content (drying) and a machine for crushing the mercurial waste (mill).

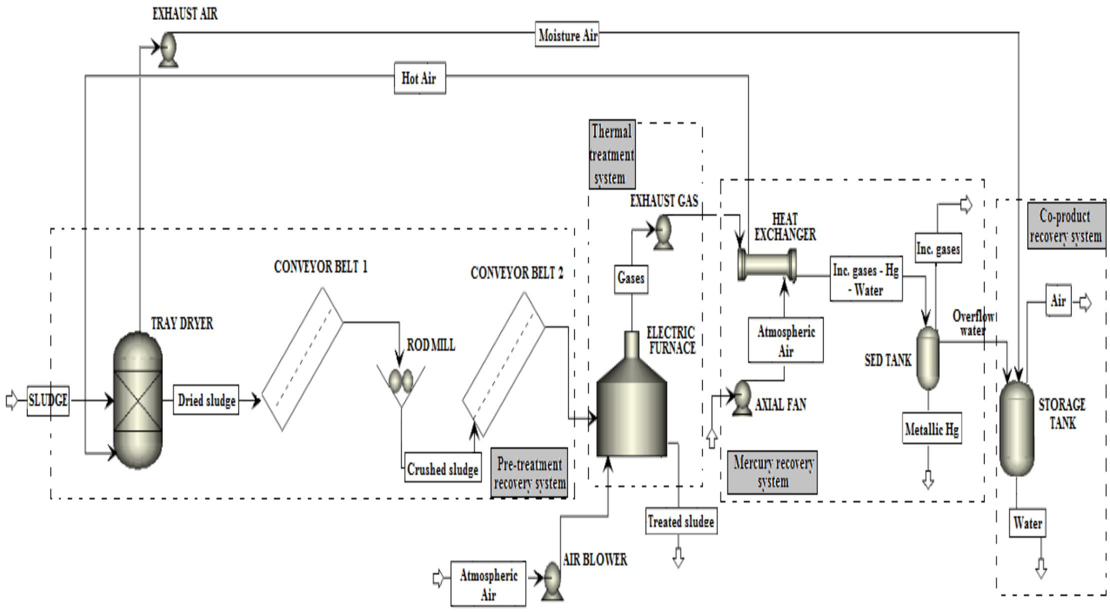

Figure 2: Schematic diagram of the proposed pilot-scale thermal treatment plant

The thermal treatment system includes the oven (furnace) while the mercury recovery system includes an energy recovery machine for the outgoing gases (heat exchanger) in which the mercury condensation occurs and a sedimentation equipment to recover the metallic mercury (sedimentation tank). The final stage of the process incorporates a co-products recovery system with a water recovery system (storage tank) and a treated waste recovery system (retention hopper).

Mass and energy balances were carried out for each step of the thermal treatment process. Balance equations (steady-state) at bench scale were developed taking into account the mercury reaction scheme reported in Busto et al. (2013). A scaled-up factor (Sf) of 5,150 was used to design the electric resistance furnace at pilot-scale, considering the waste mass input to the pilot plant furnace (386 kg) and the waste mass input to the laboratory furnace (75 g). This scaled-up factor was included in the solution of the mass and energy balances at pilot scale.

2.4 Techno-economic analysis

Techno-economic analysis of the thermal treatment technology at pilot scale was carried out considering two possibilities of treatment: working to achieve a maximum mercury removal (alternative 1, T = 450 °C and time = 3 h) or to reach the TCLP permissible limit (alternative 2, T = 450 °C and time = 1 h). The economic assessment was done for both technical alternatives using the factorial method of cost estimation reported by Towler and Sinnot (2008) to calculate static economic indicators such as Total Capital Investment (TCI) and Total Production Cost (TPC). Moreover, the dynamic economic indicators including Net Present Value (NPV), Internal Rate of Return (IRR) and Payback Period (PP) were determined considering the proposed technology as a residual (mercurial waste) treatment plant of the electrochemical factory “ELQUIM”.

3. Results

3.1 Operating conditions of the proposed thermal treatment plant

The proposed pilot plant was designed to treat 3 t of waste/d, and thus could process all buried mercurial waste in less than 8 y. The proposed thermal treatment plant will works 4 batch/d, treating 750 kg of mercurial waste/batch, will operates 320 d/y keeping 45 d/y for the plant’s maintenance and other eventualities and will needs 3 workers/batch.

3.2 Mass and energy balance of the overall process

Mass and energy balances in steady-state were considered in order to quantify the unknown operating variables as well as the inlet and outlet streams of the process. From this analysis, 0.49 kg of mercury (alternative 1) and 0.48 kg (alternative 2) was recovered per process batch. Although the differences of mercury recovered values were not significant, considerable differences in mercury concentrations from TCLP leaching test of 0.14 mg/L (alternative 2) and 0.02 mg/L (alternative 1), were observed (Busto et al., 2013). Moreover, it can be noticed that significant energy consumption is required mainly by the thermal treatment system (804 kW/batch). Since the thermal technology by its own requests high energy consumption, the technology was designed to recover the energy that comes from the hot exhaust gases emitted on the electric resistance furnace (665 kW/batch) using it to increase the inlet temperature of the flow air required in the drying stage. On the other hand, the water flow that comes out from exhaust air emitted in the drying equipment (0.033 kg/s) was designed to be recovered in the storage tank, allowing its reuse for auxiliary process (cleaning water) of the plant. The integration of these mass and energy flows turns out the process into a more sustainable technology.

3.3 Full description of the thermal treatment process at pilot-scale

The proposed remediation process starts with the excavation of 1 m^3 of the waste material from the niche which is deposited in a feed hopper of that capacity. One operator is in charge of distributing 750 kg of waste in 11 trays that are introduced later in the drying equipment by means of the conveyor belt. For the drying stage which takes 4 h/batch, a constant flow of hot air (0.574 kg/s) at 118 °C and 1.1 atm is supplied to reduce the water amount in the waste sample from 50 % to 3 %. Following, the total mass of dry waste (386 kg) is introduced into the rod mill to reduce particle size from 20 mm to 2 mm and homogenize the material. After that stage, the dried and homogenized mercurial waste must be input to the electric resistance furnace. In this equipment, the occurrence of a mercury reaction mechanism at 450 °C and 1 atm allowing to obtain around a 98 % of mercury removal efficiency was proposed (Busto et al., 2013). It is worth to explain that from thermal analyses at laboratory scale (Busto et al., 2013), two operating conditions in the furnace (working 1 h to obtain mercury removal until the TCLP limit and working 3 h to obtain the maximum mercury removal) were suitable to be assessed at pilot plant scale.

An outlet gas flux of 0.051 kg/s that includes incondensable gases (O_2, N_2, SO_2 and Cl_2), H_2O vapour and Hg is supplied to the double pipe heat exchanger. A heat exchange area of 16 m^2 is required to balance the process. First, this allows recovering energy from the hot gases (450 °C) that leave the thermal

treatment system (furnace), which can be used to heat the atmospheric air used in the drying stage. Second, it works as a condensation unit for water and mercury gases obtained from the thermal treatment system. Subsequently, the outlet gases from the heat exchanger at 40 °C were supplied to the sedimentation tank containing 0.05 m^3 of water by using a downpipe. In this equipment, the incondensable gases escape to the atmosphere while the condensed Hg and H_2O are collected. Excess H_2O overflows to a storage tank. It is worth to remark that SO_2 ($6.8 \cdot 10^{-3}$ ppm) and Cl_2 ($8.4 \cdot 10^{-3}$ ppm) generated by the thermal treatment process are emitted to the atmosphere. These compounds do not represent any risk for the environment because the emitted flows are below the recommended exposure limit (REL) of 2 ppm for SO_2 gas and 0.5 ppm for Cl_2 gas (NIOSH, 1992).
Finally, a water storage tank of 2 m^3 of capacity was used to recover the flux of water that comes from the outlet humid air of the drying equipment (0.033 kg/s) and the overflow water (0.0011 kg/s) from the sedimentation tank. The clean treated waste (374 kg/batch) is stored in a retention hopper for its next packaging. According to the chemical composition of the waste obtained after the thermal treatment and the Cuban standard for the construction material (NC: 251/2005, 2005), this material could be potentially employed as "arid". "Arid" is a Cuban term referring to aggregate materials that are used as a component of construction material.

3.4 Integrated economic assessment

An integrated economic analysis of the proposed technology with the chlor-alkali Cuban plant "ELQUIM" was carried out for both alternatives of the thermal treatment technology. For this integration, the values of Capital spending (US$) and Annual sales (US$) reported in 2014 by the ELQUIM plant were used. A higher annual gross profit was observed for the Integrated alternative 2 (US$ 166,450) in comparison with the Integrated alternative 1 (US$ 109,824) (Table 1).
This phenomenon can be attributed to the fact that the annual sales for both integrated alternatives have no perceptible effect in the annual gross profit. However, a significant increment of the annual total production cost for the integrated alternative 1 has a negative impact in its annual gross profit. At the same time, for the integrated alternative 2 a payback period of 4.2 y and a return on investment of 10.2 %/y was achieved while for the integrated alternative 1 a higher payback period was required (5 y).
From this integrated economic assessment it is clearly demonstrated that the integrated alternative 2 represents the most suitable alternative to treat the mercurial waste generated by the chlor-alkali Cuban factory. Considering the annual sales of the proposed technology plus the annual sales of the electrochemical plant, in 4.2 y the total capital investment can be paid and the potential risk that represents the thousands of tons of mercurial waste that are currently buried in niches can be solved. Alternative 2 leads to a residual Hg level in the treated waste of 29 mg/kg. However, this does not prohibit its reuse as a component of the construction materials, based on the Cuban standard NC: 251/2005 of aggregates for hydraulic concrete productions as no regulations about the content of mercury are established. Nevertheless, further experimental studies to investigate the possibility of considering the treated waste as a "pozzolanic material" need to be done.

Table 1: Economic assessment of both integrated alternatives using static and dynamic economic indicators

Economic Indicators	Integrated Alternative 1	Integrated Alternative 2
Annual sales (US$)	10,795,808	10,795,753
Annual Total Production Cost-TPC (US$/y)[a]	10,517,284	10,460,603
Annual depreciation (US$/y)[b]	168,700	168,700
Annual Gross Profit - AGP (US$)	109,824	166,450
Return on investment - ROI (%/y)	7	10.6
Payback period - PP (y)	5	4.2
Net Present Value - NPV (US$)	-216,534	12,156
Internal Rate of Return - IRR (%)	10	15

[a] The market price of Hg used was 1,850 US$/flask of metallic Hg (George, 2015) and the price of the treated waste marketed as arid was 20 US$/$m^3$ (ECOI 25, 2012).
[b] Considering an annual depreciation factor of 0.125 (8 y of project's health life).

4. Conclusions

A remediation process based on thermal treatment technology to treat high mercury containing waste from chlor-alkali plants was proposed. A pilot plant with a treatment capacity of 960 t of waste/y, able to recovery 639 kg of metallic mercury/y and 479 t/y of treated waste ("arid" that can be sold) was designed.

The cost-benefit assessment of the studied technological alternatives clearly indicates that alternative 2 is preferred due to a high mercury removal efficiency (97.8 %) at a lower total production cost (56,681 US$/y less than alternative 1). These findings could be important for decision makers in the chlor-alkali industry sector as a strategy for risk reduction of mercury emissions for developing countries.

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