Faculty of Bioscience Engineering

Faculteit Bio-ingenieurswetenschappen

THERMAL TREATMENT FOR DECONTAMINATION OF MERCURY CONTAINING WASTES FROM CHLOR-ALKALI INDUSTRY

THERMISCHE BEHANDELING VOOR DE DECONTAMINATIE VAN KWIK AFVAL UIT DE CHLOOR-ALKALI INDUSTRIE

Yailen Busto Yera

Thesis submitted in fulfillment of the requirements for the degree of Doctor (PhD) in Applied Biological Sciences

Proefschrift voorgedragen tot het bekomen van de graad van Doctor in de Toegepaste Biologische Wetenschappen

Promoters:

- Prof. Dr. ir. Filip Tack
  Department of Applied Analytical and Physical Chemistry
  Faculty of Bioscience Engineering
  Ghent University
  Belgium
- Prof. Dr. ir. Xiomara Cabrera Bermúdez
  Chemical Engineering Department
  Faculty of Chemical and Pharmacy
  Central University of Las Villas
  Cuba
- Prof. Dr. ir. Luis M. Peralta Suarez
  Chemical Engineering Department
  Faculty of Chemical and Pharmacy
  Central University of Las Villas
  Cuba

Dean:

Prof. Dr. ir. Guido Van Huylenbroeck

Rector:

Prof. Dr. ir. Paul Van Cauwenberge

WORD OF THANKS

This thesis reflects between its lines, some years of hard work, but more than that, it represents an invaluable experience not only as a professional but as a person, and I would like to thank to all that were involved in it.

I am extremely grateful to my dear parents Miriam and Roberto and my incredible sister Yairen, who form with the rest of my loving family, the origin of my happiness. I would like to thanks also, to my dear grandmother Elena, for always watching over me and guiding my steps like a star from the heaven. Their love and support without any complaint or regret have enabled me to complete this Ph.D. study.

I would like to give my sincere thanks to my supervisor, Prof. Dr. ir. Filip Tack for all the advice, support and supervising that he offered me every time when I called his door. Without his help I could not have finished my doctorate successfully.

I would like to thank to my supervisors Prof. Dr. ir. Xiomara Cabrera and Prof. Dr. ir. Luis M. Peralta who have helped and supported me throughout the work of this thesis and especially to that extraordinary person who held out me his hand only for the pleasure of help.

Also I would say thanks to the fellows of the Laboratory for Analytical Chemistry and Applied Ecochemistry of Ghent University for their support in the experimental work and much more than that, in my life in Gent. I would also like to thank the personal of the Chlor-alkali Cuban plant for their help and support.

I appreciate as well the advice of the committee members, Prof. Dr. ir. Valérie Cappuyns, Prof. Dr. ir. Gijs Du Laing and Prof. Dr. ir. Frederik Ronsse, for their critical comments, which enabled me to notice the weaknesses of my dissertation and make the necessary improvements according to their comments.

I would like to thank to my truly friends (too many to list here but they know who they are!) for being always there when I needed.

Finally I would like to say thanks only for being live in this world sometimes ruthless but where I have had the privilege to meet during these intense years of Ph.D. research hearted people willing to give “Goodwill Love”.

Thank you very much!

Dank u wel!

Muchas Gracias!

Yailen Busto Yera, December 2012.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

L/S	Liquid to solid ratio (unitless)
CMR	Cumulative mercury leaching (mg Hg/kg dry sludge)
F1	Water soluble fraction (unitless)
F2	Exchangeable fraction (unitless)
F3	Organic fraction (unitless)
F4	Residual fraction (unitless)
i	Components involved in each reaction (unitless)
j	Chemical reactions (unitless)
α_i, β_i, γ_i	Coefficients which correlate heat capacity and temperature for each component (kcal)
Cp	Heat capacity of components in the thermodynamic analysis (kcal/mol K)
T	Temperature (K)
Tr	Reference temperature (K)
Ke_j	Equilibrium constant (unitless)
ΔG^0	Gibbs free energy at reference temperature (kcal/mol)
ΔH^0	Heat of Formation at reference temperature (kcal/mol)
ΔG_j	Gibbs free energy variable with temperature (kcal/mol)
ΔH_j	Heat of Formation variable with temperature (kcal/mol)
IK_j	Integration constant to calculate ΔGi (unitless)
IH_j	Integration constant to calculate ΔHi (unitless)
E	Activation energy (kJ/mol)
A	Pre-exponential factor (min^{-1})
R	Universal gas constant (kJ/mol K)

LIST OF SYMBOLS

α	Total mercury conversion in the solid matrix (unitless)
t	Retorting time (min)
$d\alpha/dt$	Variation of mercury conversion with the time (min^{-1})
n_0	Initial moles (mol)
n	Final moles (mol)
$f(\alpha)$	Mathematical function of α referred at the total solid mercury converted (unitless)
mT	Inlet sludge mass (g)
n_{ij}	Moles of each component in each reaction (mol)
Vlf	Volume of laboratory furnace (m^3)
R_j	Rate expression of each reaction
Pm_i	Molecular weight (g/mol)
F_i	Outlet molar flux of the process (mol/min)
R_{jfs}	Kinetic reaction rate of thermal decomposition of Hg compounds in the solid phase
k_j	Kinetic constant ($min^{-1}\ g^{-1}$)
n_r	Reaction order (unitless)
α_f	Final conversion (%)
pHgS	Partial pressure of HgS (atm)
pO_2	Partial pressure of O_2 (atm)
$pHgSO_4$	Partial pressure of $HgSO_4$ (atm)
F_{obj}	Objective function to optimize the adjustment of the model kinetic parameters
α_{fmod}	Final conversion by the model (%)
α_{fexp}	Final conversion by the experimental data (%)
mT_0	Sludge mass inlet to the laboratory furnace (g)

hT_0	Sludge humidity (g)
xMs_0	Mass fraction of HgS (g HgS/g total Hg)
$xMcm_0$	Mass fraction of $HgCl_2$ (g $HgCl_2$/g total Hg)
xMm_0	Mass fraction of metallic Hg (g Hg^0/g total Hg)
$xMsu_0$	Mass fraction of $HgSO_4$ (g $HgSO_4$/g total Hg)
xMT_0	Total initial Hg content in the sludge/g of sludge (g total Hg/g sludge)
xMO_0	Organic matter content/g of sludge (g OM/g sludge)
xCa_0	Carbonate content/g of sludge (g $CaCO_3$/g sludge)
mMm	Desorbed mass of Hg (g)
mCM	Desorbed mass of $HgCl_2$ (g)
mST	Desorbed mass of HgS (g)
mSuT	Desorbed mass of $HgSO_4$ (g)
l, w, h	Length, width and height of the laboratory furnace (m)
nut	Number of electric resistance strip
lt, lct	Length of the strip and hot strip (m)
kwe	Power of the simulated furnace (kW/cm of steel)
hair	Air humidity (%)
mSd^{in}	Sludge inlet mass in the drying (kg)
mSd^{out}	Sludge outlet mass in the drying (kg)
mWd^{evap}	Water evaporated mass in the drying (kg)
$fmWd^{out}$	Water outlet mass flow in the drying (kg/s)
$fmWd^{in(air)}$	Water intlet mass flow (by the air) in the drying (kg/s)
$fmWd^{evap}$	Water evaporated mass flow in the drying (kg/s)

LIST OF SYMBOLS

$mWd^{in(sludge)}$	Water inlet mass (by the sludge) in the drying (kg)
$mWd^{out(sludge)}$	Water outlet mass (by the sludge) in the drying (kg)
$fmAd^{out}$	Air outlet mass flow in the drying (kg/s)
$fmAd^{in}$	Air intlet mass flow in the drying (kg/s)
CpSd	Sludge heat capacity in the drying (kJ/kg °C)
T_{2d}	Outlet temperature in the drying (°C)
T_{1d}	Inlet temperature in the drying (°C)
η_d	Efficiency of the drying equipment (%)
$Q_{cd(air)}$	Heat liberated by the air (kJ/s)
$Q_{gd(sludge)}$	Heat delivered by the sludge (kJ/s)
λ_{H2O}	Latent heat of water (kJ/Kg)
$mMlf^{out}$	Mercury outlet mass in the laboratory furnace (g)
$mMfl^{in}$	Mercury inlet mass in the laboratory furnace (g)
$mMlf^{gen}$	Mercury generated mass in the laboratory furnace (g)
nMlf	Mercury inlet moles in the laboratory furnace (mol)
nMClf	Mercury chloride inlet moles in the laboratory furnace (mol)
nMSlf	Mercury sulphide inlet moles in the laboratory furnace (mol)
nMSulf	Mercury sulphate inlet moles in the laboratory furnace (mol)
n_{estM}/n_{estMC}	Stoichiometric molar ratio of Hg generated and $HgCl_2$ consumed (unitless)
n_{estM}/n_{estMS}	Stoichiometric molar ratio of Hg generated and HgS consumed (unitless)
n_{estM}/n_{estMSu}	Stoichiometric molar ratio of Hg generated and $HgSO_4$ consumed (unitless)
MM_{Hg}	Molecular weight of mercury (g/mol)
$nOlf^{in}$	Oxygen inlet moles in the laboratory furnace (mol)

$nOlf^{out}$	Oxygen outlet moles in the laboratory furnace (mol)
$nOlf^{cons}$	Oxygen consumed moles in the laboratory furnace (mol)
$mOlf^{out}$	Oxygen outlet mass in the laboratory furnace (g)
MM_{O2}	Molecular weight of oxygen (g/mol)
MM_{air}	Molecular weight of air (g/mol)
ρ_{air}	Density of humid air (kg/m^3)
$mNlf^{out}$	Nitrogen outlet mass in the laboratory furnace (g)
$mNlf^{in}$	Nitrogen inlet mass in the laboratory furnace (g)
MM_{N2}	Molecular weight of nitrogen (g/mol)
$mSDlf^{out}$	Sulphur dioxide outlet mass in the laboratory furnace (g)
$mSDlf^{gen}$	Sulphur dioxide generated mass in the laboratory furnace (g)
n_{estSD}/n_{estMS}	Stoichiometric molar ratio of SO_2 generated and HgS consumed (unitless)
n_{estSD}/n_{estMSu}	Stoichiometric molar ratio of SO_2 generated and $HgSO_4$ consumed (unitless)
MM_{SO2}	Molecular weight of sulphur dioxide (g/mol)
$mClf^{out}$	Chlorine outlet mass in the laboratory furnace (g)
$mClf^{gen}$	Chlorine generated mass in the laboratory furnace (g)
n_{estC}/n_{estMC}	Stoichiometric molar ratio of Cl_2 generated and $HgCl_2$ consumed (unitless)
MM_{Cl2}	Molecular weight of chlorine (g/mol)
$mWlf^{out}$	Water outlet mass in the laboratory furnace (g)
$mWlf^{in(air)}$	Water inlet mass by the air in the laboratory furnace (g)
$mWlf^{in(sludge)}$	Water inlet mass by the sludge in the laboratory furnace (g)
$mSlf^{out}$	Sludge outlet mass in the laboratory furnace (g)
$Q_{R(LF)}$	Heat liberated by the reactions in the laboratory furnace (kJ/s)

LIST OF SYMBOLS

$Q_{sludge(LF)}$	Heat liberated by the sludge in the laboratory furnace (kJ/s)
$Q_{gases(LF)}$	Heat liberated by the gases in the laboratory furnace (kJ/s)
$\Delta H_{R(M)}$	Heat of reaction of Hg (kcal/mol)
$\Delta H_{R(MS)}$	Heat of reaction of HgS (kcal/mol)
$\Delta H_{R(MSu)}$	Heat of reaction of $HgSO_4$ (kcal/mol)
$\Delta H_{R(MC)}$	Heat of reaction of $HgCl_2$ (kcal/mol)
ΔT	Difference of working temperature in the laboratory furnace (°C)
t_{lf}	Total operating time in the laboratory furnace (min)
Cp_k	Heat capacity of k compounds in the laboratory furnace (kJ/g K)
m_k	Mass of k compounds in the laboratory furnace (g)
k	Gaseous compounds of the laboratory furnace (Hg, Cl_2, SO_2, O_2, N_2 and H_2O)
V_{LF}	Volume of the laboratory furnace (m^3)
$mSerf^{out}$	Sludge outlet mass in the electric resistance furnace (kg)
$mSerf^{in}$	Sludge inlet mass in the electric resistance furnace (kg)
$mMerf^{evap}$	Mercury evaporated mass in the electric resistance furnace (kg)
$mWerf^{evap}$	Water evaporated mass in the electric resistance furnace (kg)
$mIGerf^{out}$	Incondensable gases outlet mass in the electric resistance furnace (kg)
S_f	Scaled-up factor (unitless)
$mOerf^{out}$	Oxygen outlet mass in the electric resistance furnace (kg)
$mNerf^{out}$	Nitrogen outlet mass in the electric resistance furnace (kg)
$mCerf^{out}$	Chlorine outlet mass in the electric resistance furnace (kg)
$mSDerf^{out}$	Sulphur dioxide outlet mass in the electric resistance furnace (kg)

η_{ERF}	Efficiency of the electric resistance furnace (%)
$Q_{R(ERF)}$	Heat liberated (by the reactions) in the electric resistance furnace (kJ/s)
$Q_{sludge(ERF)}$	Heat liberated (by the sludge) in the electric resistance furnace (kJ/s)
$Q_{gases(ERF)}$	Heat liberated (by the gases) in the electric resistance furnace (kJ/s)
$Q_{g(ERF)}$	Heat delivered in the electric resistance furnace (kJ/s)
V_{ERF}	Volume of the electric resistance furnace (m^3)
fmWhe	Water mass flow in the heat exchanger (kg/s)
fmIGhe	Incondensable gases mass flow in the heat exchanger (kg/s)
fmMhe	Mercury mass flow in the heat exchanger (kg/s)
fmAhe	Air mass flow in the heat exchanger (kg/s)
η_{HE}	Efficiency of the heat exchanger (%)
$Q_{c(HE)}$	Heat liberated by the gases in the heat exchanger (kJ/s)
$Q_{g(HE)}$	Heat delivered by the air in the heat exchanger (kJ/s)
CpIGhe	Heat capacity of incondensable gases in the heat exchanger (kJ/kg °C)
$Cp^{v}Mhe$	Heat capacity of mercury (vapor phase) in the heat exchanger (kJ/kg °C)
$Cp^{v}Whe$	Heat capacity of water (vapor phase) in the heat exchanger (kJ/kg °C)
$\lambda_{mercury}$	Latent heat of mercury (kJ/kg)
$Cp^{L}Mhe$	Heat capacity of mercury (liquid phase) in the heat exchanger (kJ/kg °C)
$Cp^{L}Whe$	Heat capacity of water (liquid phase) in the heat exchanger (kJ/kg °C)
$Cp_{m}Ahe$	Heat capacity of humid air in the heat exchanger (kJ/kg °C)
T_{1he}	Air inlet temperature in the heat exchanger (°C)
T_{2he}	Air outlet temperature in the heat exchanger (°C)
$T_{g(in)}$	Gases inlet temperature in the heat exchanger (°C)

LIST OF SYMBOLS

$T_{g(out)}$	Gases outlet temperature in the heat exchanger (°C)
$T_{b(Hg)}$	Boiling temperature of mercury (°C)
$T_{b(H2O)}$	Boiling temperature of water (°C)
$mWstort^{accum}$	Water accumulated mass in the storage tank (kg)
$mWstort^{in}$	Water inlet mass in the storage tank (kg)
$mWst^{overflow}$	Water overflow mass in the sedimentation tank (kg)
SW_0	Sludge initial weight (g)
CW	Crucible weight (g)
X_f	Final humidity of the sludge after drying test (kg of water/kg of dry sludge)
ΔX	Variation of the final humidity of the sludge (kg of water/kg of dry sludge)
N	Drying regimen (unitless)

ABBREVIATIONS INDEX

AGP	Annual Gross Profit
AMAP	Arctic Monitoring and Assessment Programme
AMPL	Average Maximum Permissible Limit
BDAT	Best Demonstrated Available Technology
CAP	Chlor-Alkali plant
CFR	Code of Federal Regulations
CVAAS	Could Vapour Atomic Absorption Spectrometry
DIN	Deutches Institut Für Normung
DOE	Department of Energy
EEA	European Environment Agency
EEC	European Economic Community
EIA	Environmental Impact Assessment
ELQUIM	Electrochemistry Cuban plant
EU	European Union
FAO	United Nations Food and Agriculture Organization
FCI	Fixed Capital Investment
FRTR	Federal Remediation Technologies Roundtable
GMOS	Global Mercury Observation System
GWRTAC	Groundwater Remediation Technologies Analysis Center
ICP-OES	Inductivity Coupled Plasma Optical Emission Spectrometry
IPPC	Integrated Pollution Prevention and Control
IRR	Internal Rate of Return

ISO	International Standards Organization
ITRC	Interstate Technology and Regulatory Council
LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
LDRs	Land Disposal Restrictions
MCCAPs	Mercury Cell Chlor-Alkali Plants
NATO/CCMS	NATO Committee on the Challenges of Modern Society
NC	Norma Cubana (Cuban standard)
NIOSH	National Institute for Occupational Safety and Health
NPV	Net Present value
OM	Organic matter
OSPAR	Oslo and Paris Convention
PP	Payback period
PRC	Professional Regulation Commission
RAAG	Remediation Alternative Assessment Group
REL	Recommended Exposure Limit
REMERC	Retorting or Roasting with recovery of mercury for reuse
ROI	Return on investment
S/S	Stabilization/Solidification
SEP	Sequential Extraction Procedure
TCI	Total Capital Investment
TCLP	Toxicity Characteristic Leaching Procedure
TDAAS	Thermo Desorption Atomic Absorption Spectroscopy

TPC	Total Production Cost
TTLC	Total Threshold Limit Concentration
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
UTS	Universal Treatment Standard
WC	Working Capital
WHO	World Health Organization

ACKNOWLEDGEMENTS

This research has been financially supported by the Belgian Programme for Institutional University Co-operation (VLIR-UCLV). Project 7: Environmental Education and Development of Clean Technologies. The research was conducted at three research groups:

Research Group of the Laboratory of Analytical Chemistry and Applied Ecochemistry (ECOCHEM), Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000 Ghent, Belgium, URL: http://www.ecochem.ugent.be/.

Department of Chemical Engineering, Chemical and Pharmacy Faculty, Central University "Marta Abreu" de Las Villas, Road to Camajuaní Km 5.5. Santa Clara, 54830 Villa Clara, Cuba, URL: http://www.uclv.edu.cu/.

Study Center of Applied Chemistry, Chemical and Pharmacy Faculty, Central University "Marta Abreu" de Las Villas, Road to Camajuaní Km 5.5. Santa Clara, 54830 Villa Clara, Cuba, URL: http://www.uclv.edu.cu/.

SUMMARY

Through the conventional chlor-alkali production process using mercury cells, large amounts of highly mercury (Hg) contaminated waste sludges are produced. This process is not considered good industrial practice anymore and is gradually being phased out. There is an urgent need for a proper management and disposal of mercury wastes generated by chlor-alkali plants worldwide. In Cuba, the Electrochemistry plant "Elpidio Sosa" (ELQUIM), located in the central region of the country, constitutes the main source of mercury pollution. This factory has been producing mercury solid wastes for more than forty years and has caused a widespread contamination with mercury in the surrounding environment. In the present study, a thermal treatment technology for decontamination of mercury containing wastes from chlor-alkali Cuba industry was developed.

In a first part of this work, mercury contaminated wastes from a chlor-alkali plant in Cuba were characterised for mercury contents, fractionation and leaching behaviour. Total mercury content and concentrations in leachates from TCLP test were generally subjected to a large variability (Chapters 3, 5 and 7) demonstrating significant differences in the chlor-alkali production process quality as well as in the sludge stabilisation process done by the factory.

Total mercury content of sludge samples was far above the environmental standard (260 mg/kg) stipulated by LDR 40 CFR, Part 268 US EPA. Consequently, the sludge was classified as "hazardous and high mercury waste". Mercury leachability according to the US EPA TCLP leaching test was higher than the threshold value of 0.2 mg Hg/l, leading to a classification as toxic waste" according to US EPA regulations. The dynamic leaching study (German DIN 38414-S4 test) demonstrated that concentrations of mercury in the leachates were higher than 0.02 mg/l, the maximum limit for a waste to be landfilled according to the 1991 EEC Landfill Directive Draft. This was related to the presence of rather soluble species such as $HgCl_2$. The mercury fractionation study revealed that up to 52% of the total Hg was present in the mobile fractions, that represent water-soluble and exchangeable mercury compounds. This suggests a high risk of Hg mobilisation. Moreover, the water-soluble fraction already accounted for 14% of total Hg, indicating the highly significant hazards that may arise if this material is not stored in tightly sealed conditions. It was clearly demonstrated that the current approach used by the chlor-alkali Cuban plant to stabilize the sludge has not been effective.

A second part of this work deals with the potential of thermal treatment for decontamination of mercury containing wastes from chlor-alkali industry. This treatment was selected because it represents the best demonstrated available technology for the treatment of wastes containing more than 260 mg/kg of mercury (high mercury wastes). The effects of temperature and treatment time on both residual mercury levels and mercury leachability were investigated. In small-scale experiments, it was shown that

this treatment reduces the total mercury content as well as the leachability of the residual mercury. The high mercury removal efficiency (close to 100%) and leachability values below the threshold value of 0.2 mg Hg/l after treatment at a temperature of 400 °C or higher, demonstrated that thermal treatment technology may be used to effectively remove the mercury.

In the third part of this work, a reaction mechanism was proposed to describe mercury removal from solid wastes generated by the chlor-alkali process during thermal treatment. The proposed model was compared to nine previously models reported in the literature, to elucidate the controlling reaction mechanisms. The kinetic model that best describes the thermal decomposition of the mercury solid waste can be represented by the general expression of $R_j = k_j \cdot (\alpha_f - \alpha)^{nr}$. The kinetic parameters (k_j, α_f and n_r) of the chemical reactions involved have been determined. No single mechanism is ruling the process. At high retention times, the diffusion mechanism could be considered the controlling step of the thermal decomposition process while at low times (< 15 min), the third order reaction mechanism also could be controlling the process. Nevertheless, as a first depth-in to the knowledge of the thermal decomposition of this type of systems, polydisperse and multicomponent (mercurial sludge), the diffusion mechanism (D_1) can be considered the overall controlling stage as an increase of temperature smooth the progress of the chemical reactions involved.

In the last part of this work, a pilot-scale thermal treatment technology to treat high mercury containing wastes generated by the chlor-alkali Cuban plant was designed. The proposed pilot plant with 960 ton of sludge/y of processing capacity would be able to recover 639 kg of metallic Hg/y and 479 ton/y of treated sludge ("arid") that can be valorized as construction material. Two operating conditions (alternatives) were evaluated considering as the first alternative working conditions suited to achieve a maximum mercury removal, and as the second alternative, working conditions that allow treating the waste up to a point that it meets TCLP leaching criteria. An integral economic analysis for both alternatives of the proposed technology was performed in the context of the currently operating chlor-alkali plant in Cuba. The second alternative constitutes the most attractive option. An annual gross profit of US$ 166 450, a return on investment of 10.6 %/y, a net present value of US$ 12 157 and an internal rate of return of 15% could be realised under that scenario. Finally, an environmental impact assessment for both operational alternatives and the current treatment applied by the chlor-alkali Cuban plant using Life Cycle Analysis was developed. Also from an environmental point of view alternative 2 emerged as the preferable option. Compared to the existing treatment that is applied in Cuba, the newly proposed technology could reduce the damage on human health by 95%. At the same time, it could reduce the damage on the ecosystem quality by 83% and damage on the resources by 78%. For Cuban conditions, the implementation of the proposed thermal treatment technology (alternative 2) although stand for a project of significant costs, represents considerable benefits for the environment and human health.

SAMENVATTING

Via het conventionele chlooralkali productieproces met kwikcellen worden grote hoeveelheden slibafval gegenereerd, die sterk vervuild zijn met kwik (Hg). Dit procestype wordt niet langer beschouwd als een valabele industriële optie en wordt bijgevolg stapsgewijs afgebouwd. Wereldwijd is er dringend nood aan correct beheer en verwerking van kwikhoudend afval geproduceerd door de chlooralkali industrie. De voornaamste bron van kwikvervuiling in Cuba is het elektrochemisch bedrijf "Elpidio Sosa" (ELQUIM), gelegen in de centrale regio van het land. Deze fabriek genereert al meer dan veertig jaar lang vast kwikhoudend afval, wat geleid heeft tot een uitgebreide kwikvervuiling in de omgeving. In deze studie werd een thermische behandelingsmethode voor kwikhoudend afval afkomstig van de chlooralkali industrie in Cuba ontwikkeld.

In een eerste deel van deze thesis werd kwikhoudend afval afkomstig van een Cubaanse chlooralkali installatie grondige gekarakteriseerd op kwikgehalte, fractionering en uitlooggedrag. Totaal gehalte kwik in het slibafval alsook de kwikconcentratie in de percolaten van TCLP tests vertoonden over het algemeen een grote variabiliteit (hoofdstukken 3, 5 en 7), duidend op significante verschillen in de kwaliteit van het chlooralkali productieproces en het slib stabilisatieproces uitgevoerd door het bedrijf.

Het gemeten totale gehalte aan kwik in de slibstalen lag ver boven de milieunorm (260 mg/kg) bepaald door "LDR 40 CFR, PART 268 US EPA", waardoor het slib geclassificeerd kan worden onder de noemer "schadelijk en hoog geconcentreerd kwikafval". De uitloogbaarheid van kwik, bepaald via US EPA TCLP uitloogtesten, lag hoger dan de drempelwaarde van 0.2 mg Hg/l, waardoor het slib volgens de richtlijnen van de US EPA geclassificeerd kan worden als "toxisch afval". Met een dynamische uitloogproef (Duitse DIN 38414-S4 test) werd aangetoond dat het kwikgehalte in de percolaten hoger lag dan 0.02 mg Hg/l, de in de "1991 EEC Landfill Directive Draft" richtlijn vastgelegde maximale waarde om afval te mogen storten. Dit was gerelateerd aan de aanwezigheid van eerder oplosbare kwik species zoals $HgCl_2$. Met een fractioneringstest werd aangetoond dat tot 52% van het totale kwikgehalte terug te vinden was in de mobile fracties, die water oplosbare en uitwisselbare kwikverbindingen uitmaakt. Dit suggereert een verhoogd risico op Hg mobilisatie. Bovendien werd er aangetoond dat reeds 14% van het totale kwikgehalte terug te vinden was in de water oplosbare fractie, indicatief voor de bijzonder significante gevaren die kunnen ontstaan wanneer dit materiaal niet opgeslagen wordt in goed afgesloten condities. Er werd duidelijk aangetoond dat de huidige benadering van het Cubaanse chlooralkali bedrijf om het slib te stabiliseren, niet bijster effectief is.

Het tweede deel van dit werk behandelt het potentieel van thermische behandeling om met kwik vervuild afval afkomstig uit de chlooralkali industrie te saneren. Deze behandeling werd geselecteerd daar het momenteel de best beschikbare technologie is om afval met een kwikgehalte van meer dan 260 mg/kg

(hoog geconcentreerd kwikafval) mee te behandelen. Het effect van temperatuur en behandelingstijd op zowel het residueel als uitloogbaar kwikgehalte werd onderzocht. Met behulp van kleinschalige experimenten werd aangetoond dat zowel het totale gehalte aan kwik alsook de uitloogbaarheid van residueel kwik verminderd konden worden. De hoge verwijderingsefficiëntie van kwik (~100%) en uitlooggehalten lager dan 0.2 mg Hg/l na behandeling bij 400°C of hoger, toonde aan dat thermische behandeling doeltreffend gebruikt kan worden om kwik te verwijderen.

In een derde deel van dit werk werd een reactiemechanisme voorgesteld om kwik verwijdering vanuit vast afval, gegenereerd door de chlooralkali industrie tijdens thermische behandeling, te beschrijven. Het voorgestelde reactiemechanisme werd vergeleken met negen eerder in de vakliteratuur gerapporteerde reactiemechanismes, om dusdanig de controlerende reactiemechanismen op te helderen. Het kinetisch model dat de thermische decompositie van het vast kwikhoudend afval het best beschrijft kan worden voorgesteld door volgende algemene uitdrukking: $R_j = k_j \cdot (\alpha_f - \alpha)^{nf}$. De kinetische parameters (k_j, α_f en n_f) van de betrokken chemische reacties werden bepaald. Geen eenzijdig mechanisme beheerst het proces. Bij hoge retentietijden kan het diffusie mechanisme beschouwd worden als de controlerend stap in het thermische decompositie proces, terwijl bij korte tijden (<15 min) mogelijk ook een derde orde reactiemechanisme het proces wou kunnen controleren. Desondanks kan, als eerste diepgaande kennis inzake de thermische decompositie van dit type systemen (polydispers en multi component kwikhoudend slib), het diffusie mechanisme beschouwd worden als het algehele stadium wanneer het verhogen van temperatuur de progressie van de betrokken chemische reacties afvlakt.

Tenslotte werd in het laatste deel van deze thesis een thermische behandelingstechnologie op pilootschaal ontwikkeld ter behandeling van hoog kwikhoudend afval, gegenereerd door de Cubaanse chlooralkali fabriek. Het voorgestelde pilootbedrijf met een verwerkingscapaciteit van 960 ton slib per jaar zou in staat zijn om 639 kg metallisch Hg per jaar alsook 479 ton behandeld slib dat gevaloriseerd kan worden als bouwmateriaal, te recupereren. Twee werkingscondities werden geëvalueerd waarvan het eerste alternatief, werkingscondities het best geschikt voor maximale kwikverwijdering, en het tweede, werkingscondities die toelaten het afval te behandelen zodanig de TCLP uitloogcriteria bereikt worden. In de context van de huidig werkzame chlooralkali installatie in Cuba werd er een integrale economische analyse uitgevoerd voor beide alternatieven van de voorgestelde technologie. Het tweede alternatief werd als de meest attractieve optie aangewezen. Onder dat scenario werd een jaarlijkse brutowinst (annual gross profit) van US$ 166 450, een investeringsrendement (return on investment) van 10.6% per jaar, een netto contante waarde (net present value) van US$ 12 157 en een intern rendement (internal rate of return) van 15% bewerkstelligd. Tenslotte werd er een milieueffectrapportage via “Life Cycle Analysis” ontwikkeld voor zowel de beide technologische alternatieven als voor het huidig procedé toegepast door het Cubaanse chlooralkali bedrijf. Vanuit milieukundig standpunt is alternatief twee eveneens als

geprefereerde optie uit de bus gekomen. In vergelijking met het bestaande behandelingsproces in Cuba zou dit alternatief namelijk leiden tot een significante vermindering in milieuschade en -impact. Zo zou bijvoorbeeld de schade voor de menselijke gezondheid met 95%, op de kwaliteit van het ecosysteem met 83% en op de middelen met 78% verminderd kunnen worden. Ondanks het feit dat het voorgestelde thermische behandelingsprocedé (alternatief twee) naar Cubaanse normen een substantiële kost inhoudt, zou de implementatie hiervan zowel voor het milieu als voor de mens significante voordelen inhouden.

GENERAL INTRODUCTION AND CONCEPTUAL FRAMEWORK

1.1. A global view of mercury pollution

Mercury has been recognized as a global pollutant and toxic hazard since ancient times (Hylander and Goodsite, 2006) and is considered a priority matter in the European Union (European Parliament, 2006). Certain forms of mercury can be transported globally following releases to the environment from both natural and anthropogenic sources. Environmental mercury levels have increased considerably in recent years. Even regions with no significant emissions, such as the Arctic, are affected by the transcontinental transport of mercury (Streets et al., 2005). Modeling studies have confirmed the ability of elemental mercury and mercury compounds to be transported over long distances (Seigneur et al., 2001; Travnikov and Ryaboshapko, 2002; Dastoor and Larocque, 2004).

1.1.1. Natural and anthropogenic sources of mercury

The Global Mercury Assessment by the United Nations Environment Programme (UNEP, 2002) has found that nearly every part of the Earth's ecosystem, including air, soils, sediments, vegetation, and water, contains some mercury due to natural degassing or volatilization of mercury from the earth's crust. Furthermore, it distinguished four types of emissions: primary natural sources, primary anthropogenic sources, secondary anthropogenic sources, re-mobilization and re-emission.

Primary natural sources of mercury include volcanic eruptions, crustal degassing, and emissions from forest, lakes and oceans (Dommergue et al., 2002). Natural sources of mercury are responsible for about 40% of the total mercury released annually (550 ton) to the European atmosphere (Pacyna et al., 2001; Pirrone, 2001).

Two groups of anthropogenic sources of mercury can be distinguished: primary anthropogenic sources and secondary anthropogenic sources. Primary anthropogenic sources are those where mercury of geological origin is mobilized and released to the environment. The two main sources within this category are mining and extraction and burning of fossil fuels which contain mercury as a trace contaminant. Secondary anthropogenic sources are those where emissions occurs from the intentional use of mercury, including mercury use in industrial processes, products, dental applications, or in artisanal and small-scale gold mining (ASGM) operations. Emissions to the environment from both primary and secondary sources can occur via direct discharge of exhaust gases and effluents, and through the generation of mercury-containing wastes (Pacyna et al., 2010).

A fourth type of emission was distinguished by UNEP (2002). Mercury can also be re-mobilized and re-emitted to the air. Re-mobilization occurs when mercury that had been taken out from atmospheric circulation is released again. For instance, mercury accumulated in soils or sediments may be re-mobilized by rain or floods to enter the aquatic system. Mercury taken up by vegetation can be re-emitted to the atmosphere during forest fires or biomass burning (UNEP, 2008).

According to Reis et al. (2009) the anthropogenic emissions are leading to a general increase in mercury on local, regional and global scales.

Of the primary anthropogenic sources of mercury, the principle sources are those where mercury is emitted as an unintentional side contaminant by-product. With the exception of mercury mining itself, the mercury emissions arise from mercury that is present as an impurity in the fuel or raw material used. The main emissions are from sectors that involve combustion of coal or oil, production of pig iron and steel, of non-ferrous metals, and cement (Streets et al., 2005; Pacyna et al., 2006).

Secondary anthropogenic sources of mercury are these related to emissions from intentional mercury use. The three largest sources are artisanal and small-scale gold mining (ASGM) (Telmer and Veiga, 2008), production of vinyl chloride monomer (VCM), with the use of mercuric chloride as a catalyst, and the chlor-alkali industry (Swain et al., 2007). Other mercury uses like batteries, dental amalgam, mercury-containing measuring and control devices (thermometers, barometers and manometers) and mercury-containing lamps, among others (Figure 1.1), are still considerable (AMAP/UNEP, 2008).

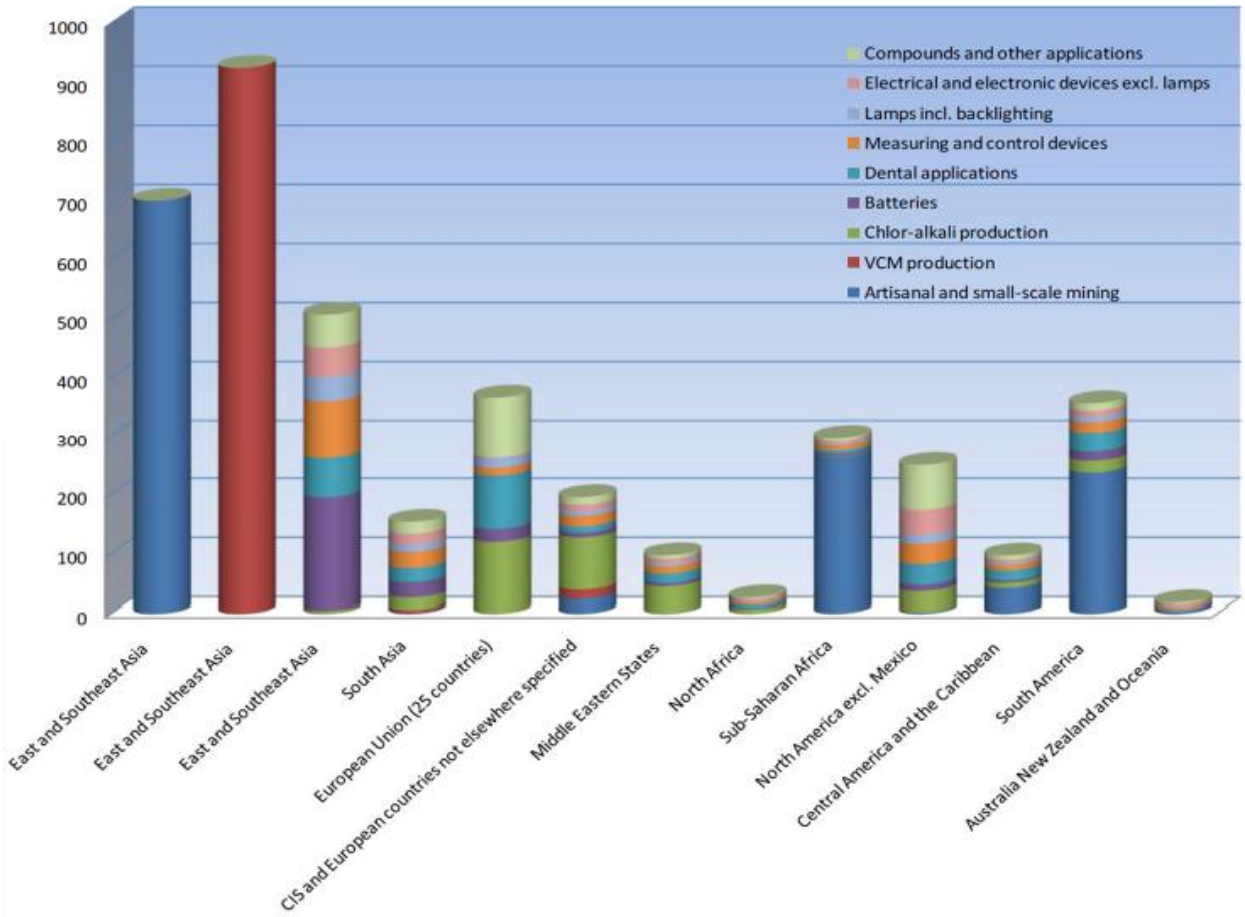


Figure 1.1. Global mercury consumption by application and by region expressed in tonnes (Maxson, 2010 cited in Pirrone, 2012)

As a result of anthropogenic emissions, the global atmospheric Hg deposition rate is approximately three times higher than in pre-industrial times and has increased by a factor of 2-10 in and around the most industrialized regions (Meili, 1995; Bergan et al., 1999; Martinez-Cortizas et al., 1999; Lamborg et al., 2002).

The chlor-alkali industry represents the third major mercury user worldwide (AMAP/UNEP, 2008). In this process, very large quantities of liquid mercury are used as a cathode in electrolytic cells to produce chlorine, sodium hydroxide and hydrogen by electrolysis of brine solution (Southworth et al., 2004).

In the United States, mercury cell chlor-alkali plants (MCCAPs) were estimated to be the largest non-combustion anthropogenic sources of atmospheric mercury pollution, emitting 6.5 ton/y from the 14 operating plants in 1994-1995 (USEPA, 1997d). In 2000 chlor-alkali industry was responsible for about 17% (40.4 ton/y) of the anthropogenic total mercury emissions in Europe (Pacyna et al., 2006). In Western Europe, the total mercury emissions to the air, water and waste products from the chlor-alkali plants were 9.5 ton in 1998. At the level of the individual plant, mercury emissions between 0.2 and 3 g Hg/ton of produced chlorine have been reported (IPPC, 2001). The amount of Hg in wastes from chlor-alkali productions only in the European Union has been estimated at about 990 ton (Mukherjee, 2004).

Significant and negative impacts to the human health and environment can be correlated with the mercury due to its unique high toxicity, volatility, and persistence in the environment and easiness of bio-accumulation (Zhang et al., 2009). However, its impacts are directly linked with the mercury form which acts as a contaminant. After more than 50 years of the Minamata disaster in Japan, the negative effects on the environment and human health due to methylmercury (MeHg) poisoning are still observed. Only in 1995, MeHg poisoning which is also known as Minamata disease, caused the death of 1043 people in Japan (Harada, 1995).

1.2. Mercury in the environment

Mercury is present in the environment in a number of forms including elemental mercury (Hg^0), inorganic mercurous (Hg^+) and mercuric (Hg^{2+}) salts and as organic compounds (e.g. methyl-, ethyl and phenyl-mercury). Each form has different physicochemical properties and toxicity profiles (Clarkson, 1997; Goldman and Shannon, 2001). Once released into the environment (Figure 1.2), the various forms of mercury are subject to complex inter-conversions, principally through oxidation–reduction and methylation–demethylation reactions involving bacteria, and to transport on a global scale, processes that together are termed as the ‘mercury cycle’ (Clarkson, 1997).

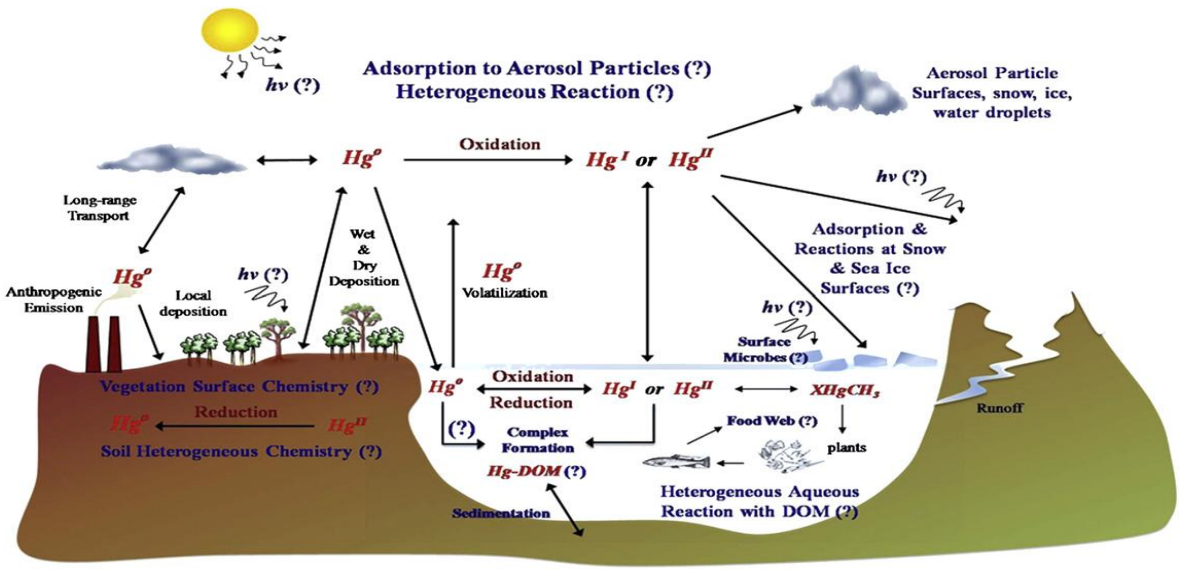


Figure 1.2. Schematic of the mercury transport cycle (Subir et al., 2011)

The organic forms are the principal human source of mercury pollution since all forms of organo-mercury are strongly accumulated in living organisms (Sharma, 1993). Methylmercury (MeHg) is the most stable of the organo-mercury compounds and hence is the primary concern regarding human exposure to this type of mercury (European Commission, 2006). Any mercury form however has to some extent negative impacts on the environment and human health. A considerable body of evidence from experimental animal studies of the toxic effects that may arise from short-term (acute) and prolonged (chronic) exposures to the various types of mercury compounds (Bull, 2007) is now available.

1.3. Mercury impacts to the environment and human health

The environmental impact of Hg emissions from MCCAPs has been demonstrated in several studies (Lodenius and Tulisalo, 1984; Baldi and Bargagli, 1984; Maserti and Ferrara, 1991; Gonzalez, 1991). Workplace environments presenting the largest potential sources of occupational exposure to mercury include chlor-alkali production facilities and cinnabar mining (Dikshith and Diwan, 2003). On the other hand, dietary intake is the most important source of nonoccupational exposure to mercury, with fish and other seafood products being the dominant source of mercury in the diet (WHO 1990, 1991).

For the human health several diseases have been correlated with mercury pollution depending on the mercury form and the time and quantity that the human have been exposed. Mercury is a highly toxic metal that affects the nervous and cardiovascular systems. Nausea, vomiting, diarrhea and severe kidney damage may occur due to exposure to high doses of mercury over a short period of time. Hallucinations, memory loss, nerve damage and the inability to concentrate can occur. Symptoms also include tremors, loss of dermal sensitivity, slurred speech and, in rare cases, even paralysis and death (Nierenberg et al.,

1998). Chronic degenerative diseases of the nervous system such as Alzheimer's disease are likely caused or exacerbated by mercury released from amalgam (Clarkson, 2002).

On the other hand, the negative impacts of mercury pollution on the environment are mainly due to its potential of biomagnification, bioconcentration and bioaccumulation throughout the food chain (Yi et al., 2011). Over the last decades, increased awareness of the environmental and human health impacts of mercury has led to stronger regulations against mercury emissions, leading to decreased emissions (Schroeder and Munthe, 1998).

1.4. Regulatory considerations on mercury contaminated wastes

One of the major concerns from the chlor-alkali mercury emissions are the mercury solid waste generated by the industrial process. In the future there will be fewer and fewer mercury cells operating, as the older plants are shut down or converted into technology membrane cells. During the remaining life of mercury cell plants, however, measures should be taken to minimize current and future mercury emissions from handling, storage, treatment and disposal of mercury-contaminated wastes (Directive 2008/1/EC, 2008).

In the United States, the management and ultimate disposal of mercury hazardous wastes is controlled by USEPA (2008a) regulations known as the Land Disposal Restrictions (LDRs) (40 CFR, Part 268). Under the current LDR program, the USEPA has established thermal recovery (e.g., roasting/retorting) as the best demonstrated available technology (BDAT) for treatment of wastes containing more than 260 mg/kg of mercury. For treatment of wastes 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 (USEPA, 1997c).

The toxicity characteristic leaching procedure (TCLP) in the EPA publication SW-846 plays an important role in determining whether or not the material can be accepted by a landfill. According to the LDR rules (40 CFR, Part 261), mercury hazardous waste is defined as any waste that has a TCLP value greater than 0.2 mg/l (USEPA, 1992). Mercury-contaminated wastes that exceed this value generally must be treated to meet the Universal Treatment Standard (UTS) of 0.025 mg/l or less prior to disposal in a landfill.

In addition, some states may set criteria that define hazardous wastes given the total metal concentration such as California's Total Threshold Limit Concentration (TTLC) of 20 mg/kg for mercury (Randall and Chattopadhyay, 2004). Moreover, according to the European Economic Community (EEC) Landfill Directive Draft of 1991 (Directive 91/689/EEC, 1991) mercury hazardous waste is defined as any waste that has a DIN 38414-S4 test value greater than 0.02 mg/l of mercury in the leachates (Bayar et al., 2009). The Basel Convention stipulated that all wastes having mercury, mercury compounds and mercury vapour are hazardous wastes (Basel Convention, 1989). Furthermore, detailed classifications of

hazardous waste in EU countries are available in the publication of the European Environment Agency (EEA, 1999, 2001).

The stricter application and control of previous regulations could help largely to reduce the high levels of mercury pollution in the world. In line with this, over the past decades special attention has been paid to the mercury cell chlor-alkali production process due to the toxic nature of mercury and the significant amount of mercury solid wastes generated from its use (OSPAR, 2005).

1.5. Mercury cell chlor-alkali process

Chlor-alkali manufacturing industry produces chlorine, hydrogen and sodium hydroxide through electrolysis of saline solution. The primary product is Cl_2. There are three main electrolytic production technologies used in the chlor-alkali industry, diaphragm cell, mercury cell and membrane cell (Schmittinger, 1991).

In the mercury cell chlor-alkali process, elemental mercury (Hg^0) is used as a flowing cathode in the electrolytic cells where the process can be divided into three large phases, brine purification, electrolysis and purification of the obtained products (Melián-Martel et al., 2011). The overall electrochemical reaction is as follows:

$$2\,NaCl + 2\,H_2O \xrightarrow{\text{energy}} Cl_2 + H_2 + 2\,NaOH \tag{1.1}$$

The Hg electrolytic cell consists of an electrolyser and a decomposer. In the electrolyser section, a sodium chloride (NaCl) brine solution flows concurrently above the Hg^0 cathode. A high current density is applied between the Hg^0 cathode and metal anodes, and chlorine gas (Cl_2) forms at the anode while a sodium amalgam forms at the Hg^0 cathode. The amalgam is separated from the brine in the discharge end-box and then enters the decomposer, where deionised water is added. In the decomposer, the amalgam becomes the anode to a short circuited cathode of graphite pellets yielding hydrogen (H_2) gas and sodium hydroxide (NaOH) plus liberation of Hg^0. The Hg^0 is then recycled to the inlet end-box, where it re-enters the electrolyser (Kinsey et al., 2004).

In the electrochemical process, mercury solid wastes are formed in the brine purification stage before passing through the electrolytic cells. Several compounds are added to the brine solution as a precipitation agent (sodium hydroxide and carbonate) to remove calcium and magnesium followed by a filtration step. After the filter is washed, the mud with water goes to a recirculation pool to keep the sludge in suspension. Next, it is pumped to a decanter and Na_2S is added to stabilize the obtained sludge (Gonzalez, 2004, 2008) by means of HgS formation. It has been reported by Brandon et al. (2001) that also H_2S can be added to aqueous solutions (containing Hg^{2+} ions) to form black HgS (metacinnabar) and it will exist indefinitely at room temperature.

From comparison with diaphragm or membrane processes, mercury cell technology has the advantage that a high purity caustic soda is produced by merely simple brine purification (IPPC, 2001). Nevertheless, it is the most environmental unfriendly technology.

Is well known that for most processes where mercury is used, mercury-free alternatives exist. Consequently, many of the uses of mercury are declining, at least in some regions, as alternative products or processes are adopted (UNEP, 2008). Regarding with this, new trends in the use of this heavy and toxic metal have been coming up.

1.6. Trends in the use of mercury cell chlor-alkali plants

Mercury cell chlor-alkali plants are not anymore considered good industrial practice and the Integrated Pollution Prevention and Control (IPPC) of the European Union has indicated that chlor-alkali installations require obtaining licenses based in the Best Available Techniques (Directive 2008/1/EC, 2008). Membrane cell technology is considered the best available alternative technology. A report from the Euro-Chlor Association (Eurochlor, 2011) revealed a constant decrease, but still significant, emission of mercury from chlor-alkali plants.

In 1990, global anthropogenic mercury releases to the atmosphere from sources associated with incidental pollutant emissions, and the intentional use of mercury in the Chlor-alkali industry were estimated at about 1910 ton. However, in 2005 global emissions inventories estimated a total emission at about 1480 ton (Figure 1.3). The greatest decreases were in Europe, with substantial declines also in North America, reflecting the introduction and wider use of emission control technologies (AMAP/UNEP, 2008).

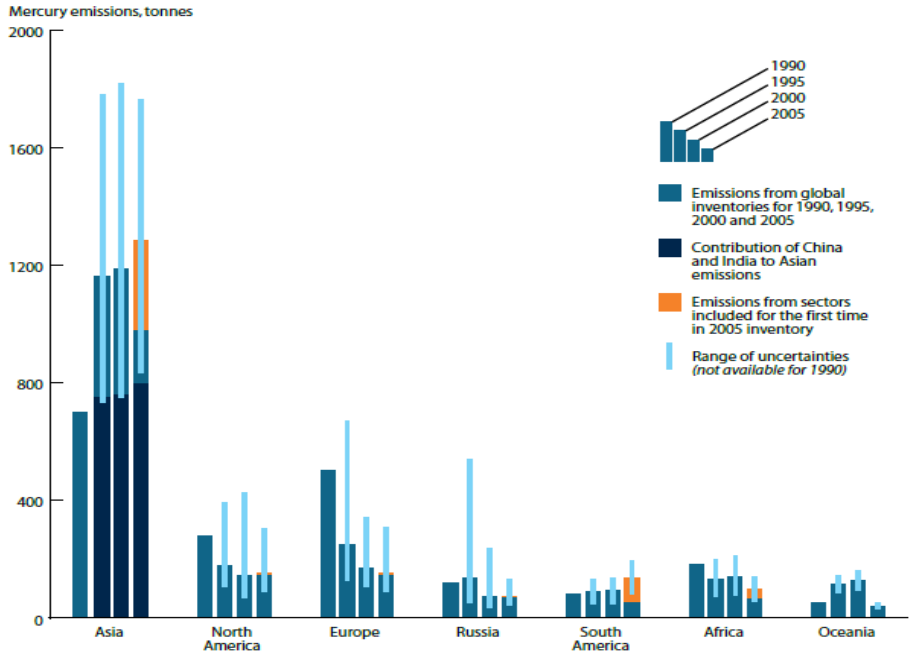


Figure 1.3. Trends in mercury emissions by region from 1990 until 2005 (AMAP/UNEP, 2008)

According to data compiled by the UNEP during the Global inventory of mercury cell chlor-alkali facilities (UNEP, 2009), 100 facilities in 44 countries today have some industrial mercury cell chlorine production capacity. Although fewer and fewer mercury cells will be operating in the future, currently only 12 countries have plan for closure or conversions to non-mercury technology during the period 2010 to 2015 (Table 1.1).

Table 1.1. Countries with the highest mercury production capacities (adapted from UNEP, 2009)

Country	Existing Mercury Cell Facilities	Mercury Chlorine Production Capacity 2010[a]	Plans for Closure or Conversions to Non-Mercury Technology 2010-2015
Germany	6	870	Ludwigshafen (BASF) not specified conversion/closure date in permit. Akzo Nobel (Ibbenburen) conversion or closing estimated between 2010-2015. Evonic (Degussa) not specified conversion/closure date in permit. Akzo Nobel (Frankfurt) - conversion estimated by 2010.
Spain	7	732	All Spanish plants have to submit a plan for conversion or closure by 2011.
France	6	690	Jarrie plant expected to convert in 2012, Solvay Tavaux - 2 out of 4 units use mercury, 1 is being converted in 2010.
United States	4	437	
Belgium	2	420	Tessenderlo and Antwerp plants plan to switch to membrane technology in 2015 and 2012, respectively.
Russia	3	401	
Iran	4	332	
United Kingdom	1	277	
Brazil	4	217	
Cuba[b]	1	7	

Note: [a] In thousands of tons of chlorine capacity. [b] Cuba in comparison.

Although this process seem to be in decline around the world, it still accounts for roughly 15% of the global mercury demand, representing a significant source of local and global mercury pollution (Ulrich et al., 2007; Mahan and Warner, 2009; Reis et al., 2009). The closure or conversion of mercury cell chlor-alkali plants constitutes a huge challenge mainly for developing countries where the change is needed for

environmental reasons but it may not be economically viable. In Cuba, the one mercury facility existing (Table 1.1) represents the major source of mercury pollution in the country and has become a significant concern.

1.7. Mercury pollution in the Cuban context

In Cuba, production of chlorine and caustic soda by using mercury cell technology dates back of the 30s, when a small chlor-alkali facility was installed in Sagua La Grande city, in the central region of the country (Figure 1.4). The industry went through several owners and adopted different trade names over the years.

Due to a growth of the country's population and an increase of the economic and industrial activity after 1959, the capacity of that chlor-alkali plant was found to be insufficient. There was an increase in the import of these products. A new chlor-alkali plant “Elpidio Sosa” (ELQUIM) with higher production capacity was installed. That plant, which currently still is in use, has a daily production capacity of 48 t of chlorine gas and 108 t of caustic soda at 50% concentration.

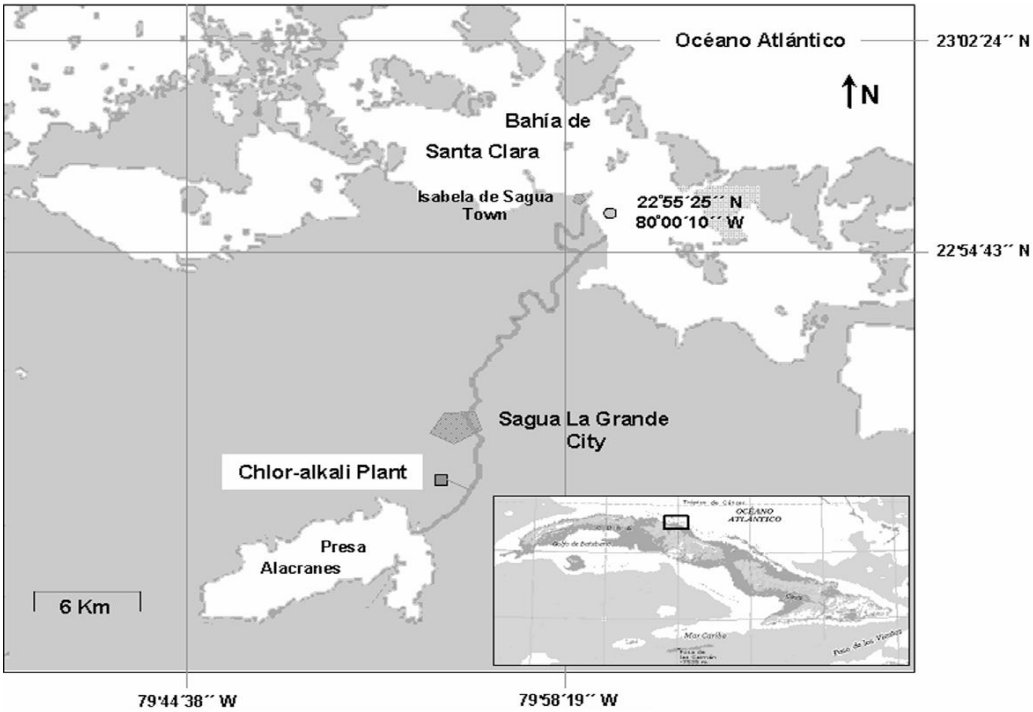


Figure 1.4. Map of Sagua La Grande region (Díaz-Asencio et al., 2009).

Currently, the Electrochemistry “Elpidio Sosa” (Figure 1.5) is the only industry of its kind in the country. It covers the domestic demand for these products, and the surplus is exported to the Caribbean region.

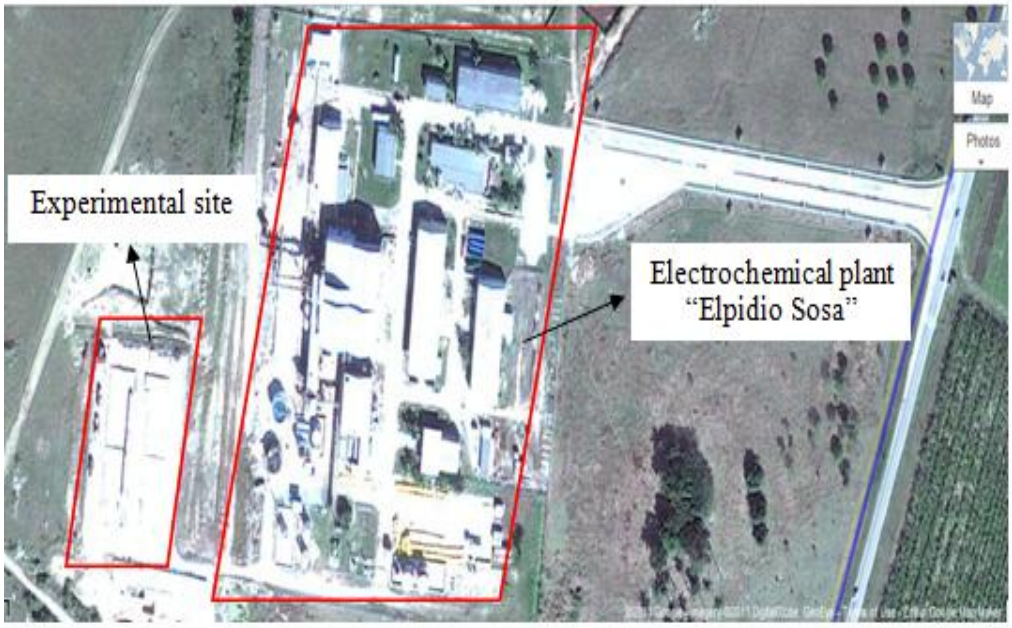


Figure 1.5. Satellite picture of Electrochemical plant "Elpidio Sosa".

1.7.1. Mercury solid waste generated from the chlor-alkali process

Mercury solid wastes from "Elpidio Sosa" chlor-alkali Cuban plant were obtained during the brine purification stage of the electrolytic process as detailed above (section 1.5.). Once the sludge is formed, it is disposed in concrete niches. According to data provided by the plant, the sludge has total mercury contents ranging between 1000-2000 mg/kg. However, concentrations in excess of 5000 mg/kg of total mercury were found (Current work, Chapter 3). Taking in to account the toxicity and volatility of this heavy metal and the higher content found in the sludge, regulations for its proper management, transport and disposal constitute the key to control its damage.

1.7.2. Cuban legislation

In Cuba, the only legislation that sets a regulatory value for Hg is the norm NC 27:1999 "Disposal of residuary waters to soil waters and sewerage. Specifications" (NC 27/1999, 1999) where 0.01 mg/l is set as the average maximum permissible limit (AMPL) for mercury in liquid waste.

According to EPA regulations and due to the chemical characteristic of these mercury contaminated wastes, they can be categorized as hazardous wastes, and in particular as high mercury wastes with more than 260 mg/kg of total mercury. The best demonstrated available technique (BDAT) established by US EPA for a proper management of this sludge require a thermal recovery treatment to reduce or remove completely the mercury from this sludge. However, in Cuba another management of this mercurial sludge has been followed.

1.7.3. Management of mercury solid wastes

Once the sludge is formed (see section 1.5.), it is hand-transported by the plant's workers for disposal in concrete niches (Figure 1.6). The current storage of this waste in concrete niches is inadequate, allowing Hg to leach from the waste. The regular occurrence of natural disasters such as hurricanes (very often in Cuba), inundations and earthquakes aggravates the risks for dispersion of Hg into the environment.

Figure 1.6. Pictures of the concrete niches located around the electrochemical plant.

In 2008 the Cuban government approved plans for a change in technology from mercury electrolytic cells to membrane based technology. While this transition will prevent further production of mercury contaminated waste, thousands of tons of mercurial sludge are currently stored in the surroundings of the plant, constituting a potential hazard to human health and environment. The conversion of this technology into a cleaner technology (membrane) is needed for environmental reasons and it should occur before 2020 in order to comply with the international regulations (UNEP, 2007) and the Cuban environmental strategy. Nevertheless, the required timing to achieve this conversion can not be set with certainty.

Recycling of waste is higher up the "waste management hierarchy" than landfill disposal (Mukherjee, 2004). If economically or environmentally viable, hazardous waste should be recycled, limiting the risk to environment and public health. Several technologies can be applied to treat hazardous mercury wastes such as stabilization/solidification, soil washing, acid leaching, vitrification and thermal treatment. This will be reviewed in Chapter 2.

Many studies and technological treatments over the world have been developed to treat mercury contaminated wastes efficiently. Nevertheless, in Cuba, no research has been conducted to treat the hazardous mercury wastes generated by the electrochemical Cuban plant.

1.8. Objectives and general outline

The present study focuses on development a thermal treatment technology for decontamination of mercury containing wastes from the chlor-alkali Cuban industry. In order to fulfill the main objective five specific objectives are developed.

The research objectives are:

1- To evaluate the efficacy of the current treatment applied by the chlor-alkali Cuban plant to immobilise the mercury in the sludge matrix.

2- To evaluate the potential of thermal treatment by retortion for decontamination of mercury containing wastes generated by the chlor-alkali industry in Cuba.

3- To identify mechanisms and kinetics of chemical reactions of mercury during retortion.

4- To propose treatment technology at the pilot plant scale for decontamination of mercury containing wastes from the chlor-alkali Cuban industry considering technical, economical and environmental factors.

5- To compare the current treatment applied by the chlor-alkali Cuban plant (existing scenario) and the proposed thermal treatment technology (future scenario) from technical, economical and environmental points of view.

The present research is structured in eight chapters. After the General introduction and conceptual framework, **Chapter 2** reviews remediation technologies applied to treat soil, sediments and wastes contaminated with heavy metals. Technologies applicable for mercury contaminated solid wastes such as stabilization/solidification, soil washing, acid extraction, vitrification and thermal treatments are discussed in more detail. Major attention was given to the thermal treatment process and mercury retorting reactions. Furthermore, the criteria for upscaling and installation design as well as technical, economical and environmental definitions used for the proposed technology were also reviewed.

Chapter 3 reports the results of the leaching behaviour of mercury from solid waste generated by chlor-alkali industry. The potential release of mercury from the solid waste was studied at the laboratory scale. Moreover, the potential mercury mobility of the highly contaminated solid waste was observed. These results are reported and discussed in **Chapter 4.** In this chapter, also aspects on toxicity characteristic and environmental impact of the mercurial sludge are addressed.

In **Chapter 5** the potential of thermal treatment for decontamination of mercury containing wastes from chlor-alkali industry was evaluated. Although the experiments were performed under suboptimal conditions of temperature and time, the treatment efficiency parameters were positive and therefore mercury kinetic reactions during thermal treatment were further investigated in **Chapter 6**. Residual mercury levels and mercury leachability were assessed as a function of time at two different temperatures.

Based on these experimental data and simulation software, a kinetic reaction mechanism of mercury removal from the solid waste was developed.

The thermal treatment technology at pilot plant scale for decontamination of mercury solid waste from a chlor-alkali plant was elaborated in further detail in **Chapter 7**, along with a technical, environmental and economic assessment. A techno-economical and environmental comparison between the current treatment applied by the chlor-alkali Cuban plant (stabilisation and disposal of the mercury wastes) and the proposed technology (thermal treatment for mercury recovering) was evaluated. The plant layout of the proposed technology and its 3D representation were also achieved.

To conclude this research, in **Chapter 8** the insights from the previous chapters are incorporated in a general discussion, after which the major conclusions from this study are drawn and future perspectives presented.

REMEDIATION TECHNOLOGIES FOR MERCURY CONTAMINATED WASTES

In this chapter remediation technologies to treat mercury contaminated wastes are reviewed and compared to select the most suitable technology to treat the high mercury contaminated wastes generated by the chlor-alkali Cuban industry. The selected treatment technology is further explored to gain insights into the prevailing reactions of mercury and their kinetics during the treatment. Important definitions for the design and upscaling of a chemical process (specifying in reactor/electric furnace equipment) using modelling and simulation methods are also detailed. Finally, the main techno-economic and environmental criteria that need to be considered to develop the selected technology at the pilot plant scale are identified.

2.1. Remediation techniques for heavy metals contaminated soils and wastes

In response to a growing need to address environmental contamination, many remediation technologies have been developed to treat soil, leachate, wastewater, and groundwater contaminated by various pollutants (Riser-Roberts, 1998). Biological, physical/chemical and thermal remediation technologies may be used independently or in a combination to reduce the contamination to a safe and up to standard levels (Reddy et al., 1999). The most commonly used techniques for soil, sediment and wastes contaminated by heavy metals are listed in Table 2.1.

Even though many technologies are available for the treatment of contaminated sites, their selection depends on contaminant and site characteristics, regulatory requirements, costs, and time constraints (Riser-Roberts, 1998; Reddy et al., 1999).

Table 2.1. Technologies for remediation of heavy metals contaminated soils, sediment and wastes (Table based on Marques et al., 2009; Khan et al., 2004; Mulligan et al., 2001; FRTR, 1999a; 1999b; 1999c; 1999d; USEPA, 1995a)

Remediation Technology	Description
Phytoremediation	Uses plants to remove, transfer, stabilize, and destroy contaminants in soil and sediments. *Limitations:* High concentrations of hazardous materials can be toxic to plants.
Electro kinetic	Removes contaminants by application of a low-intensity direct current through the soil. *Limitations:* Maximum effectiveness occurs if the moisture content is between 14 and 18%.
Soil flushing	Soil flushing is accomplished by passing the extraction fluid through in-place soils, using an injection or infiltration process. *Limitations:* Extraction fluids must be recovered from the underlying aquifer and heterogeneous soils are difficult to treat.
Soil washing	The soil washing process separates fine soil (clay and silt) from coarse soil (sand and gravel), where the contaminants tend to bind and sorbs. *Limitations:* Since soil washing does not destroy or immobilize the contaminants, the resulting soil must be disposed of carefully and the wash water needs to be treated before its final disposal.
Stabilization/solidification	Reduce the mobility of the heavy metal contaminants by addition of an agent that solidifies and then immobilizes the metals. *Limitations:* Sometimes result in a significant increase in volume and leaching analysis of the contaminants must be carefully monitored.
Vitrification	Uses a powerful source of energy to melt soil or other earthen materials at extremely high temperatures (1600 to 2000 °C). By this most inorganic are immobilized into a chemically inert, stable glass product and organic pollutants are destroyed. *Limitations:* Costs can be high and the efficiency can decrease with high organic contents.
Encapsulation	Physical isolation and containment of the contaminated material. The impacted soils are isolated by low permeability caps or walls to limit the infiltration of precipitation. *Limitations:* The efficiency of encapsulation decreases with time and cannot be considered a permanent remedy.
Thermal Desorption/Retorting	The contaminated soil is excavated, screened, and heated to such temperatures that the boiling point of the contaminants is reached, and they are released from the soil. The efficiency of desorption can be greater than 99%. *Limitations*: Clay and silty soils and high humic content soils increase reaction time as a result of binding of contaminants, increasing the operational costs.

2.2. Remediation techniques for mercury contaminated wastes.

According to USEPA (2007), stabilization/solidification, soil washing, acid extraction, vitrification and thermal treatment (thermal desorption/retorting) are the most suitable remediation technologies recommended to treat mercury contaminated solid wastes. An overview of these mercury treatment technologies is shown in Table 2.2.

Table 2.2. Overview of mercury treatment technologies (adapted from USEPA, 2007)

Remediation Technology	Description
Solidification/Stabilization	Physically binds or encloses contaminants within a stabilized mass and chemically reduces the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms.
Vitrification	High-temperature treatment that reduces the mobility of metals by incorporating them into a chemically durable, leach-resistant, vitreous mass. The process also may cause contaminants to volatilize, thereby reducing their concentration in the soil and waste.
Soil Washing/Acid Extraction	Uses the principle that some contaminants preferentially adsorb onto the fines fraction of soil. The soil is suspended in a wash solution and the fines are separated from the suspension, thereby reducing the contaminant concentrations in the remaining soil. Acid extraction uses an extracting chemical, such as hydrochloric acid or sulphuric acid.
Thermal Desorption/Retorting	Application of heat and reduced pressure to volatilize mercury from the contaminated medium, followed by conversion of the mercury vapours into liquid elemental mercury condensation. Off-gases may require further treatment through additional air pollution control devices such as carbon units.

2.2.1. Stabilization/Solidification (S/S)

These methods have long been used to stabilize hazardous wastes. S/S methods are especially useful for the treatment of heavy metal by bearing sludge and inorganic wastes (Chang et al., 1993). S/S methods involve the occurrence of chemical reactions between the stabilizing agent and the contaminants to reduce their mobility (stabilization) and physically binding or enclosing contaminants within a stabilized mass (solidification) (FRTR, 2001a). The process may also include addition of pH adjustment agents, phosphates, or sulphur reagents to reduce the setting or curing time, increase the compressive strength, or reduce the leachability of contaminants (Osborne-Lee et al., 1999; Bishop et al., 2002). Hazardous waste materials can be encapsulated in two ways, microencapsulation or macroencapsulation (Randall and Chattopadhyay, 2004). Microencapsulation involves mixing the waste together with the encasing material before solidification occurs. Macroencapsulation involves pouring the encasing material over and around a larger mass of waste, thereby enclosing it in a solidified block.

Studies of S/S have been applied for reducing the mobility of mercury contaminants in the environment by employing additives to trap or immobilize contaminants within solid wastes through both physical and chemical means (USEPA, 1994; Bhatty and Presbury, 1996).

In a S/S process, the Hg-contaminated solid wastes (Camacho et al., 1995; USEPA, 1997b) are mechanically mixed with a stabilizing agent, such as trisodium salt of trimercapto-*s*-triazine (TMT) (Yin et al., 1997), sulphur (Oji, 1998), fly ash (Mangialardi et al., 1999), Portland cement (PC) (Cullinane et al., 1986), lignin derivatives (Zhuang and Lam, 2002; Zhuang et al., 2003a), polymers (Matlock et al., 2001) or other wastes (Meng et al., 1998; Zhuang et al., 2003b; Yardim et al., 2003). Thus, Hg-

contaminants may be immobilized through a chemical bonding (Zhuang et al., 2003a; 2003b) by the additive, or be enclosed with an S/S additive or binder.

The main advantage of the Stabilization/Solidification technology is that it is one of the most cost effective treatment alternatives. According to Boyce et al. (1999) the estimated cost varies from 40 to over 2000 $/ton. This technology, with processing rates of up to 40 ton/d, is capable to stabilize mercury wastes obtaining mercury concentration levels below the TCLP limit (0.2 mg/l) (USEPA, 2007). Furthermore it requires relatively simply technological equipment, operating efficiently at room temperatures and pressures (Boyce et al., 1999).

However, the use of S/S has also some disadvantages. The applicability of S/S depends on the mobility of mercury which in turn depends on its oxidation state, the pH of the waste disposal environment, and the specific mercury compound contained in the waste (Bishop et al., 2002). This mobility is usually measured by testing the leachability of mercury under acidic conditions. Typically, the leachability of mercury increases with a decrease in pH. Therefore, acidic environments may increase the mobility of mercury in stabilized waste. Some studies also suggest that soluble compounds of mercury, such as mercurous sulphate and mercuric sulphate, may occur at a higher pH (Randall and Chattopadhyay, 2004). The optimal pH range for chemical fixation of mercury compounds to the highly insoluble solid form, mercuric sulphide (HgS), is 4-8 (Clever et al., 1985; Wagh et al., 2000). At high pH the more soluble solids e.g. mercurous sulphate (Hg_2SO_4), mercuric sulphate ($HgSO_4$), and mercury sulphide hydrogen sulphide complex ($HgS[H_2S]_2$) are formed depending on the redox conditions. At a low pH, hydrogen sulphide gas may escape from the waste. Due to the complex behaviour of mercury in various disposal environments, the S/S technology requires a pre-treatment of the waste with reagents such as Na_2S to convert mercury to a less soluble form (e.g. HgS) before stabilization (Bishop et al., 2002; Mattus, 2003; Bowerman et al., 2003). Other additives that also can be used include pH buffers, catalysts such as platinum, H_2S, K_2S and NaHS (Darnell, 1996; Wagh and Jeong, 2001). It results in a significant increase in volume (up to double the original volume) of the contaminated materials (DOE, 1999).

Another disadvantage is that, as an immobilization technique, this technology is not capable for full decontamination because it renders mercury more stable and less leachable but not reduces or eliminates the total mercury content of the waste. Instead, it reduces the leachability of mercury, yielding a product that still may require disposal in a landfill (DOE, 1999). Moreover, stabilization/solidification is not suitable for direct treatment of mercury concentrations greater than 260 mg/kg (high mercury subcategory) or wastes containing elemental mercury contaminated with radioactive materials (USEPA, 2008a).

2.2.2. Vitrification

Vitrification is a high-temperature treatment technology that is designed to immobilise contaminants by incorporating them into the vitrified end product, which is chemically durable and leach resistant (FRTR, 1999c; Dermatas and Meng, 2003). It has been used to treat mercury contaminated soil and sediments *in situ* and *ex situ* (USEPA, 2007).

In situ vitrification technology involves the use of electrical current to heat (melt) and vitrify the treated material in place. Electric current is passed through the soil by an array of electrodes inserted vertically into the surface of the contaminated zone. As current flows between the electrodes, the temperature of the surrounding soil is raised through Joule heating (Jacobs et al. 1992; Dunbar et al. 1993). Eventually, the temperature exceeds the soil melting point. Soil near the surface melts first and with time the electrodes are pushed down into the melt, which penetrates to depths equal to the bottom of the electrodes. When the desired melting depth is reached, power to the electrodes is terminated and cooling begins. The melted material solidifies to a glassy end product (USEPA, 1997b).

As soil has a low electrical conductivity, a chemical frit must initially be placed in a criss-cross pattern between all the electrodes (Acar and Alshawabkeh, 1993). This frit acts as a starter path for current flow. A hood also must be placed over the electrodes to capture any off-gases and direct them to a secondary off-gas treatment system. The temperature of the contaminated soil could reach between 1600 and 2000 °C (USEPA, 2002). Joule heating is not the only useful method capable of inducing *in situ* melting. An alternative and promising method that involves using a plasma arc torch as an energy source has been studied by several authors (Camacho 1988; Circeo et al. 1996; Celes and Mayne 2000). In this alternative, the plasma itself acts as a resistive heating element able to reach much higher temperatures, between 4000-7000 °C (Fox et al., 2001).

Ex situ vitrification technology involves heating contaminated material in a melter or furnace. The heat can be typically generated by combustion of fossil fuel (coal, natural gas, and oil) or input using electrical energy by direct Joule heat, arcs, plasma torches, or microwaves (USEPA, 1997b). The melter or furnace is lined with refractory material, which resists chemical and physical abrasion, and has a high melting point providing a high degree of insulation (USEPA, 2004; DOE, 1998).

According to USEPA (2007) only one full-scale *in situ* (FRTR, 1995) and two pilot-scales *ex situ* (USEPA, 2004; DOE, 1998) vitrification systems have actually been implemented to treat mercury-contaminated soil and sediment thus far. Although in these studies very low Hg TCLP values were obtained after treatment (0.2-0.23 μg/l), the initial Hg concentration of the analysed samples were not very high to start with (2.2-4.8 mg/kg) (FRTR, 1995).

The main advantage of the vitrification technology is that the vitrified final product is monolithic, impermeable and virtually non leachable if the process is well conducted (Johnson, 2002). It can also

increase the density of treated material, thereby reducing its volume. In some cases, the vitrified product can be reused or sold (USEPA, 2004). Furthermore, the combustion of the organic content of the waste liberates heat, reducing the external energy requirements (USEPA, 2007). Therefore, this process may be advantageous in the treatment of wastes that contain a combination of mercury and organic contaminants or for the treatment of organo-mercury compounds.

The use of *in situ* or *ex situ* vitrification technology also has some important disadvantages. According to USEPA (1995b) *in situ* vitrification treatment of soil with high organic content (> 7% weight) may cause excessive heating of the melt, damaging the treatment equipment. In addition, the depth of the contaminants (> 20 feet) may limit the process and innovative techniques need to be applied (Khan et al., 2004). Furthermore, high metals content (> 25% weight) may result in pooling of molten metals at the bottom of the melt, causing electrical short-circuiting (USEPA, 1995b). As such, high concentrations of mercury in soil or sediment may limit the performance of this process USEPA (1997b). Mercury may be difficult to treat because of its high volatility and low solubility in glass (< 0.1% weight), but may be effectively treated at low concentrations (USEPA, 1997b).

On the other hand, in the *ex situ* vitrification treatment the materials must be dewatered before treatment (USEPA, 2004). In addition, the presence of chlorides, fluorides, sulphides, and sulphates may interfere with the process, resulting in higher mobility of mercury in the vitrified product (USEPA, 1997b). Dioxins and furans may also form when excess of chlorides are present and enter the off-gas treatment system. Khan et al. (2004) highlighted that long-term monitoring is often necessary to ensure that the contaminants actually remain immobilized. If insufficient glass-forming materials (SiO_2 > 30% weight) and combined alkali (Na + K > 1.4% weight) are present in the waste, the vitrified product may be less durable (USEPA, 1995c).

These two technologies, S/S and Vitrification, have been successfully used to treat mercury contaminated wastes. As the mercury is not removed from the solid matrix the efficiency of immobilization need to be proven with studies at long-term to ensure that the contaminants are actually immobilized. Due to this fundamental limitation, extraction technologies for mercury removal such as soil washing, acid extraction and thermal treatment are preferred.

2.2.3. Soil washing

Soil washing is a water-based *ex situ* process that uses a combination of physical particle size separation and aqueous-based chemical separation to remove metals from contaminated soils, sludge and sediments (FRTR, 2001c; USEPA, 1997b). It has been reported by FRTR (1999a) that soil washing treatment removes contaminants from soils by two mechanisms: physical separation and chemical extraction.

- *Physical separation (PS):* metal contaminants are concentrated into a smaller volume of soil by exploiting differences in physical characteristics (size, density, magnetism, and hydrophobic surface properties) between the metal bearing particles and soil particles.
- *Chemical extraction (CE):* metal contaminants are solubilised from the soil with an extracting aqueous fluid containing chemical reagents such as acids or chelating agents.

The selection of one removal mechanism or another largely depends on the chemical form of the metals and the characteristics of the solid matrix. Physical separation is primarily applicable when metal contaminants are under particulate forms (discrete particles or metal-bearing particles), while chemical extraction is primarily suitable for ionic forms adsorbed on soil or non-detrital metals (Dermont et al., 2008). However, since metals present in soils or sediments are mostly in sorbed forms, physical separation is often associated with chemical procedures to enhance metal removal (Dermont et al., 2008).

Soils or sediments with CEC of 5-10 $cmol_+$/kg, particle sizes of 0.25-2 mm and a solubility of the contaminant in water higher than 1000 mg/l, can be successfully cleaned by soil washing technique (Hazardous Waste Consultant, 1996). A general description of soil washing technology involves a first screening of the contaminated soil to remove oversized particles and then homogenizing. The soil is then mixed with a wash solution of water or water enhanced with chemical additives such as leaching agents, surfactants, acids, or chelating agents to help remove heavy metals. Particles are separated by size (cyclone or gravity separation, depending on the type of contaminants in the soil and the particle size), concentrating the contaminants with the fines particles. The resulting concentrated fines or sludge usually require further treatment because the soil washing process removes and concentrates the contaminants but does not destroy them. The coarser-grained soil is generally relatively “clean,” requiring no additional treatment. Wash water from the process is treated and either reused in the process or disposed (FRTR, 2001a).

According to Dermont et al. (2008) several projects have been accomplished to treat efficiently mercury contaminated soils and sediments using the soil washing technique based on the physical separation option (PRC, 1996; NATO/CCMS, 2002) where different physical separation units have been used based on soil and metal characteristics such as, magnetic separation, froth flotation, gravity concentration, among others. Other studies have been developed using a combination of physical separation with chemical extraction procedure which use surfactant/chelating and acid agents (BioGenesis 1999; 2005).

The main advantage of the soil washing technology is that the amount of material requiring either mercury recovery or stabilization will be drastically reduced which potentially lowers the cost of cleanup and disposal of the contaminated material (Boyce et al., 1999). Furthermore it can be performed either on or off site and has one of the greatest processing rates (around 25 ton/h) of the technologies recommended

to treat mercury contaminated wastes (Boyce et al., 1999). The average cost for this technology, including excavation, are relatively low (approximately 170 $/ton), depending on site-specific conditions and the target waste quantity and concentration (FRTR, 1999a).

However, soil washing technology has also several disadvantages. Its applicability and effectiveness may be limited for complex waste mixtures, such as metals mixed with organic compounds; that makes it difficult to formulate the appropriate washing solution. On the other hand, soils with high clay content, cation exchange capacity or humic acid content tend to interfere with contaminant desorption and limit the effectiveness of soil washing process (FRTR, 2001b; USEPA, 1997b). Soils with high humic content may require pre-treatment to prevent interference with contaminant desorption (FRTR, 2001c). This process may also have difficulty treating soils with a high (more than 40%) silt and clay fraction. Another drawback of this treatment is that the concentrated waste volume as well as the wastewater volume generated by the process may require treatment prior to discharge (ITRC, 1997). Soil washing is often combined with other technologies (Khan et al., 2004) and has been documented by (USEPA, 2001) that it may not be cost-effective for small quantities of contaminated material.

2.2.4. Acid extraction

Acid extraction (chemical leaching) is an *ex situ* technology that uses an extracting chemical such as hydrochloric acid or sulphuric acid to extract contaminants from a solid matrix (FRTR, 2001b). It has been reported by Tampouris et al. (2001) and Kuo et al. (2006) that several mechanisms contribute to the extraction of metals from soil using a specific acid solution: (1) desorption of metal cations via ion exchange; (2) dissolution of metal compounds; and (3) dissolution of soil mineral components (e.g., Fe–Mn oxides) which may contain metal contaminants.

According to Boyce et al. (1999) and FRTR (2001b) in the acid extraction treatment the mercury contaminated material is first screened to remove coarse solids. Then the extraction agent (e.g. HCl) and the mercury contaminated soil are introduced into the extraction unit. The solid and liquid phases are then separated using hydro cyclones, and the solids are transferred to a rinse system, where they are rinsed with water to remove entrained acid and contaminants. They are then dewatered and mixed with lime and fertilizer to neutralize any residual acid (FRTR, 2001b). The acid extraction fluid and rinse waters are mixed with commercially available precipitants, such as sodium hydroxide, lime, or other proprietary formulations, and a flocculant to remove the heavy metals (FRTR, 2001b). The precipitated solids may require additional treatment or may be disposed in a landfill if they meet a TCLP mercury level of less than 0.025 mg/l. Elemental mercury can be recovered from the residual liquid of the precipitation step (USEPA, 2007).

Several extraction agents can be used to treat mercury contaminated soil and wastes such as acids, surfactant, chelating agents and sodium chloride (USEPA, 2007). For instance, the use of strong acids such as HCl and H_2SO_4 rely on ion exchange and dissolution of soil components/discrete metal compounds to extract metals (Dermont et al., 2008). Chelating agents such as EDTA solubilise metals through a complexation mechanism (Sun et al., 2001; Di Palma and Ferrantelli, 2005). Surfactants such as caustic and acidic surfactant target desorption of metals from soil interface (Mulligan et al., 1999; Chu, 2003; Ehsan et al., 2006). The use of high-concentrations chloride salt solutions (NaCl) at low pH conditions combines the acid leaching action and the formation of metal chlor-complexes to extract metals from soils (Dermont et al., 2008).

Several studies have been developed at pilot scale, demonstrating the efficiency of the acid extraction as a remediation technology for mercury contaminated soils, sediments and wastes (Universal Dynamics, 2004; Selby and Twidwell, 2004; BioGenesis, 2005). From the mercury reduction point of view, promising results were obtained using the patented REMERC technology for the treatment of Hg contaminated soil from a chlor-alkali plant (Universal Dynamics, 2004). The REMERC process based on two extraction steps with NaCl at pH 6 and pH 2 respectively followed by two solid/liquid separation and solids washing and finally mercury recovery on liquid residual using cementation on iron was done, obtaining Hg reduction in the contaminated media near to 99% and Hg TCLP values less than 0.025 mg/l (Universal Dynamics, 2004).

The main advantage of acid extraction treatment is that the hazardous contaminant is separated from soils and sediments, thereby reducing the volume of hazardous waste that will need further treatment (FRTR, 2001b). However, the use of acid extraction has some disadvantages. The acid extraction is limited mainly by the characteristic of the solid contaminated matrix, metal contamination characteristics and extraction reagent characteristics (Dermont et al., 2008). In soils with higher clay content, (> 40%) the extraction efficiency can be significant affected, requiring longer contact time and therefore excessive amount of the extraction reagent (USEPA, 1997b). High cation exchange capacity, or humic acid content, would interfere with the contaminant desorption. Furthermore, the presence of complex, heterogeneous contaminant compositions can make it difficult to formulate a simple extraction solution, requiring the use of multiple sequential extraction steps to remove contaminants (USEPA, 1997b). On the other hand, the knowledge of metal contamination characteristics (type, concentration, fractionation and speciation of metals) plays an important role in order to select the effective acid extraction procedure (Dermont et al., 2008). Besides, extraction tests should be conducted to determine optimal conditions (chemical type and dosage, contact time, agitation, pH, temperature and extraction steps) to meet regulatory requirements before using this technology (Mulligan et al., 2001).

One of the biggest drawbacks to acid leaching is the production of additional waste streams (Boyce et al. 1999). Another disadvantage is that any residual acid in treated soil needs to be neutralized after the process and the wastewater treatment from the process may produce large amounts of toxic sludge that also must be carefully managed (USEPA, 1998; Stepan et al. 1995). It must be also noticed that certain health and safety issues should be considered with the use of this technology associated with possible emissions of extracting agents (surfactants and concentrated acids) during the process (FRTR, 2001b).

2.2.5. Thermal treatment

Thermal treatment is commonly considered as an *ex situ* method that involves the application of heat and reduced pressure to volatilize mercury from the contaminated medium, followed by conversion of the mercury vapours into liquid elemental mercury by condensation (USEPA, 2007). Several studies have been conducted to demonstrate the efficiency of this technology (Stepan et al. 1993; 1995; Washburn and Hill, 2003; Chang and Yen, 2006; Kunkel et al., 2006; Chang et al., 2009). A portable thermal treatment system can process soils contaminated with elemental mercury as well as various mercury compounds such as oxides, sulphides, organometallics and amalgams (Stepan et al., 1995). Bench-scale results showed removal efficiencies greater than 99% and final soil mercury concentration of less than 0.2 mg/kg (Stepan et al., 1995). A thermal treatment at middle-range temperature (540-650 °C) can decrease the concentration of the residual mercury to a lower level below 2 mg/kg and the mercury can be reclaimed with a purity of 99% for sale despite of its different structures and forms (Chang and Yen, 2006).

Although the effectiveness of this technology has been extensively shown, several factors could affect the thermal treatment performance. For instance, finer soils and soils with high humic content require longer processing time, which results in increased unit costs (FRTR, 2001a; Blanchard and Stamnes, 1997). Besides, the presence of large particles in the contaminated medium may impair heat transfer between the heating elements or the combustion gas and the medium (USEPA, 2002). Mercury wastes with moisture content higher than 25% have to undergo pre-treatment, dewatering or mixing with dry materials, before they are loaded into the thermal desorption or retort unit. This pre-treatment can increase the overall processing time and may result in higher treatment costs (Blanchard and Stamnes, 1997). Thermal treatment technologies are energy-intensive (Stepan et al., 1993; Kucharski et al., 2005) and therefore constitute the most expensive technology to treat mercury contaminated wastes. Nevertheless, it is currently the only efficient technology to treat high mercury contaminated wastes, allowing mercury removal rates higher than 99%. In addition, the mercury can be recovered with high purity (George et al., 1995; De Percin, 1995; Cha et al., 1996; Smith et al., 2001).

In general, soil washing and acid extraction (as extraction techniques) are two efficient technologies that can be used to achieve the complete decontamination of mercury contaminated wastes. However,

these techniques have only been shown effective for the treatment of low mercury contaminated wastes (< 260 mg/kg of mercury) (USEPA, 1997b). USEPA (1997b) established that thermal recovery (e.g., thermal desorption/retorting) is the best demonstrated available technology (BDAT) for the treatment of wastes containing more than 260 mg/kg of mercury (high mercury wastes). As the mercury contaminated wastes generated by the chlor-alkali Cuban plant were categorized as hazardous and high mercury contaminated wastes from the characterization analysis (data will be showed in Chapter 3) the most suitable technology to remediate these wastes is the thermal treatment.

2.3. Thermal treatment technologies

Two thermal technologies commonly used to treat mercury-contaminated wastes are thermal desorption and retorting (Kulakow, DU; FRTR, 2001a; Washburn and Hill, 2003). The main difference between both technologies is that the first treatment involves agitation while the second one does not (ITRC, 1998).

2.3.1. Thermal desorption

Thermal desorption involves pre-treatment of the contaminated media, thermal desorption, and post-treatment to treat off-gas and the processed materials (FRTR, 2001a). Thermal desorbers include direct-fired rotary kilns and indirectly heated screw or auger systems. The motion of the rotary drum or auger agitates the waste, promoting mixing and more uniform heating. A typical thermal desorption unit for mercury removal operates at temperatures between 320 and 700 °C (FRTR, 2001a; Washburn and Hill, 2003; PRC, 1996; DOE, 2002). The boiling point of elemental mercury at 1 atmosphere pressure is 350 °C, which renders it suitable for removal by thermal processes (ITRC, 1998; Washburn and Hill, 2003). The high temperatures used in a thermal desorption unit convert mercury into the gaseous or vapour phase, which is collected and further treated. Off-gas generated by the desorption unit is passed through wet scrubbers or fabric filters to remove particulate matter. Mercury in the purified off-gas stream is then condensed and liquid elemental mercury is recovered (Washburn and Hill, 2003).

2.3.2. Retorting

Retorting systems include a retort oven, a condensation unit with a mercury trap and a sulphonated carbon adsorber. Mercury-contaminated material is placed in pans that are stacked in the retort oven. Retorts can be heated either electrically or with fuel burners. In electric retorts, the heating elements are in direct contact with the contaminated medium, while in fuel-fired retorts the burner heats the air surrounding the retort (Washburn and Hill, 2003). The retort chamber typically operates at vacuum at temperatures between 425 and 540 °C to facilitate volatilization of mercury. The resulting off-gas is

passed through condensers to collect liquid elemental mercury. The remaining off-gas is then passed through sulphur-impregnated carbon to capture any residual mercury (Washburn and Hill, 2003).

Although both thermal treatment technologies are equally efficient in removing mercury (Matsuyama et al., 1999; Khan et al., 2004; Kunkel et al., 2006; USEPA, 2007; Huang et al., 2011), retorting treatment normally operates at lower temperatures than thermal desorption, which significantly reduces the capital cost of the process. Several remediation technologies to treat mercury contaminated wastes were described and compared. Thermal treatment using retorting is selected as the most suitable and cost effective treatment technology to remove mercury from the solid wastes. Next sections focus on this approach.

2.4. Retorting treatment of mercury contaminated wastes

Several authors have pointed out that the mercury decontamination level by retorting treatment depends on the solid matrix properties, mercury speciation, treating temperature and treatment time (Davis et al., 1997; Biester et al., 2002b; Sladek et al., 2002; do Valle et al., 2006). A better understanding of these factors has a marked influence in the kinetic behaviour of the mercury removal (retorting efficiency). Moreover, the knowledge of kinetic reaction mechanism allows developing a more efficient design of the retorting technology.

2.4.1. Process variables influencing mercury removal

2.4.1.1. Solid matrix properties

The chemical-physical characteristics and structure of soils or sediments have a marked influence on the speciation and transport of mercury through the solid matrix. Therefore, the chemical-physical characterization of the mercury contaminated waste represents the start point in establishing an effective retorting process. Mercury in the solid matrix can be subjected to several chemically and biologically mediated reactions, including redox reactions, methylation, adsorption and complexation to inorganic ligands (Schuster, 1991). Dissolved ions (Cl^-, OH^-, S^-), organic matter (OM) concentration, pH and redox potential are the dominant parameters in determining Hg speciation in soils or sediments (Lin and Pehkonen, 1999; Ravichandran, 2004). The presence of dissolved ions such as Cl^-, DOC and S^- plays an important role in inorganic mercury-ligand formation. For instance, existence of sulphide is important because it often forms the very insoluble HgS salt (do Valle et al., 2006).

Ramamoorthy and Rust (1978) showed that overall mercury adsorption to mineral and organic particles are correlated to the organic content, cation exchange capacity, and grain size of the soils. In soils or sediments with low organic matter content, most Hg can be found as reactive, ionic Hg species e.g. $HgCl_2$ or $Hg(OH)_2$ which can be transformed easily into more toxic forms such as methyl mercury or

Hg^0 (Skyllberg et al., 2006). The presence of clays may cause poor thermal desorption performance by a heat transfer inhibition (Technical Report, 1998). Besides, the moisture content of soils or sediments should be maintained at less than 25% to avoid difficulties on the retorting process (Morris et al., 1995).

2.4.1.2. Mercury speciation

Several methods have been developed and improved over the years to determine mercury species in solid matrices. Three major techniques can be distinguished: (1) sequential chemical extractions, (2) X-ray absorption spectroscopy analysis (Sladek et al., 2002; Kim et al., 2003; Sladek and Gustin, 2003), and (3) Hg thermo desorption atomic absorption spectroscopy (TDAAS) (Windmoller et al., 1996; Biester and Scholz, 1997). *Sequential chemical extraction/sequential extraction procedure (SEP)* is based on the use of various solutions in sequence to extract Hg with different forms of occurrence and reactivities. This method differentiates Hg compounds according to essentially operationally defined classes, such as water soluble, acetic acid soluble, reducible, etc. (Biester and Scholz, 1997; Bloom et al., 2003). Even though the method does not precisely distinguish the specific species of mercury, the results from SEP are useful to make inferences with respect to relative mobility and bioavailability of the mercury present (Han et al., 2003; Panyametheekul, 2004; Bacon and Davidson, 2008; Lin et al., 2010). As such, sequential extraction is not a speciation method, in that it does not allow to identify specific chemical species. The sequential extraction procedure developed by Neculita et al. (2005) has been extensively used to determine mercury fractions from chlor-alkali contaminated soils and sediments (Zagury et al., 2009; Huang et al., 2011).*X-ray absorption spectroscopy analysis* is a non-destructive technique that uses high energy synchrotron-sourced X-ray radiation to identify specific species, based on scattering patterns. This method is most useful in the identification of specific species (do Valle et al., 2006). However, the identification of Hg^0 is difficult (Sladek and Gustin, 2003) and these methods have high limits of detection (> 100 mg/kg) to the extent that their application in environmental analysis is restricted (Kim et al., 2000; 2003). *Thermo desorption atomic absorption spectroscopy (TDAAS)* method is based on the identification of mercury species by incremental heating and comparison of thermal release patters to a compound database. This method has been used in investigations of Hg compounds in soils and sediments (Biester and Zimmer, 1998; Biester et al., 2000; 2002b; Higueras et al., 2003).

2.4.1.3. Temperature and retorting time

According to Washburn and Hill (2003), time and temperature are the key factors influencing the efficiency of all thermal treatment processes. Mercury species have different desorption temperatures (Biester et al., 1997; Gaona, 2005) (Table 2.3).

Table 2.3. Desorption temperatures for different mercury phases (Navarro et al., 2009)

Phase	Desorption temperature of phase Hg (°C)
Hg^0	< 100
Hg_2Cl_2	170
$HgCl_2$	< 250, 220
HgO	420-550
HgSO4	450-500
HgS (cinnabar)	310-330
Hg in pyrite	> 450
Hg in Sphalerite	600
Hg matrix-bound	200-300

The temperature of the retorting process can be related with the specific Hg form present in the soil or sediment. However, as the properties of the contaminated solid waste and time also influence the retorting process, the final selection of the temperature and retorting time is site specific.

The thermal treatment efficiency significantly increased with temperature, for all thermal treatment times, indicating that the heating temperature is a more important operating parameter than the time (Chang et al., 2009). However, it should be remarked that at lower temperature the influence of the heating time is more pronounced regarding mercury removal efficiency (Massacci et al., 2000).

Retorting has been demonstrated as a viable remediation option to treat polluted sediments from the chlor-alkali industry (Manni et al., 2004). In this study sediment containing 350 mg Hg/kg achieved a Hg content below the Italian regulatory limit of 5 mg/kg for industrial uses after thermal retorting treatment during 3 min at 400 °C. A series of bench, pilot and full-scale experiments have been developed to optimize and evaluate the efficiency of retorting treatment (Chang and Yen, 2006). It was demonstrated that at temperatures higher than 700 °C and retention times of at least 2 h all the soils samples achieved the cleanup criteria of 2 mg/kg. The retorting process reached efficiencies over 97%.

In another study in soils from a former industrial area of a chlor-alkali plant, located in the north of Sweden, significant results were achieved (Taube et al., 2008). A mercury reduction of 95% at around 300 °C was achieved within minutes while at 470 °C and 20 min, a reduction of more than 99% of the mercury was obtained. Furthermore, it was reported that the remaining mercury at temperatures above 300 °C was not affected by the increase in heating time and that the evaporation, at least up to 270 °C,

was controlled by diffusion mechanisms, rather than by chemical and physical properties (e.g. vapour pressure and volatility) of the different mercury species present in the soil.

The treatment of highly contaminated soils from a chlor-alkali process in Taiwan demonstrated that thermal decontamination of these soils at the temperature nearing the boiling point of water was ineffective and could concentrate the Hg in soil (Huang et al., 2011). However, elevating the temperature higher than 170 °C resulted in a decrease of Hg content. In this research, the optimal conditions were found at 400 °C and 15 min, with a mercury removal of 99%. Increasing the heating duration had a small effect on further enhancing Hg removal.

Although important issues have been accounted for regarding the main factors that influence the efficiency of the retorting technology, an improved knowledge about the main reactions of mercury during the retorting process may contribute to improve and optimise treatment of mercury contaminated soils and wastes.

2.4.2. Kinetic model of mercury reactions during retorting treatment

Many researchers have developed kinetic models of homogeneous mercury reactions (gas phase) specifically in the exhaust gases emitted from coal-fired power plants with the aim of studying the mercury transformations (Xu et al., 2008; Agarwal and Stenger, 2007; Yudovich and Ketris, 2005; Galbreath and Zygarlicke, 2000).

Xu et al. (2008) developed a kinetic model which includes the oxidation and chlorination of key flue-gas components, as well as six mercury reactions involving HgO with new reaction rate constants calculated from experimental data. From this study it was concluded that the pathway

$$Hg + ClO \rightarrow HgO + Cl$$

represents a significant reaction in this system, which indicates the necessity of including reactions involving HgO. Studies on the effects of oxygen show that O_2 weakly promotes homogeneous Hg oxidation, especially under the condition of low Cl_2 concentration. Agarwal and Stenger (2007) proposed a reaction mechanism of five reactions to predict homogeneous mercury oxidation obtaining the A (pre-exponential factor) and E (activation energy) values for the Arrhenius rate constant. The main reaction of the mechanism was given by

$$Hg(g) + Cl_2(g) \rightarrow HgCl_2(g),$$

which is considered the main reaction in the oxidation of Hg in a gas stream (Agarwal et al., 2007). Other studies (Aylett, 1975; Schroeder et al., 1991) reported reduction of HgO(g) by reaction with SO_2(g)

and CO(g) as important mechanism of mercury transformation in coal combustion flue gas. The reactions are:

$$HgO(g) + SO_2(g) \rightarrow Hg^0(g) + SO_3(g)$$
$$HgO(g) + CO(g) \rightarrow Hg^0(g) + CO_2(g).$$

However, heterogeneous mercury reactions have been less studied; only thermal decomposition of mercury oxide seems to play an important role in the development of chemistry (L'vov, 1999; L'vov et al., 2004).

The kinetic and thermal decomposition of HgO was studied and a dissociative evaporation scheme was proposed (L'vov, 1999) considering two different HgO decomposition mechanisms. The mechanism of high temperature decomposition (650 K) was described by the reaction:

$$HgO(s) \rightarrow Hg(g) + O$$

where the primary product is not molecular oxygen O_2 but atomic oxygen. On the other hand, at low decomposition temperature it proceeds by the reaction of the lower mercury oxide:

$$Hg_2O(s) \rightarrow 2Hg(g) + O$$

The lower oxide Hg_2O forms, in its turn, in the interaction of Hg vapour with the oxygen atoms produced in decomposition of HgO at the interface between the two solid phases (HgO/Hg_2O). Due to the formation of a film of the solid product (Hg_2O) on the surface of HgO and partial transfer of the energy released in Hg_2O formation to the reactant, HgO decomposition proceeds at a considerably higher rate (L'vov, 1999). The formation of $Hg_2O(s)$ on the HgO surface at low temperatures is in agreement with the previously developed theoretical concepts (L'vov, 1997) of the mechanism of autocatalysis in the presence of a film of a solid product.

Several studies on the mechanism of thermal decomposition of alkaline-earth carbonates metals, in particular $CaCO_3$, have been conducted by L'vov (1997, 2001). At a decomposition temperature of 974 K, the most probable reaction mechanism of thermal decomposition of $CaCO_3(s)$ involves the intermediate hydroxide formation (L'vov, 1997). Nevertheless, the universally accepted mechanism of $CaCO_3$ decomposition is identified by the reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Despite the fact that thermal treatment is a technology widely used to treat sludge or solid wastes highly contaminated with Hg (e.g. sludge generated from the chlor-alkali production), almost all studies

have focused primarily on optimizing best operating conditions of the process at pilot and/or industrial scale. Very few studies have looked into the reactions of mercury during retorting.

Only one significant study related to mercury speciation and soil heating equilibrium calculations was performed, in order to identify potential gas phase mercury species and phase transitions that could explain the experimental findings (Taube et al., 2008). During the equilibrium calculations it was obtained that for a system low on oxygen, the mercury species in the soil was predicted to be Hg(l) or HgS(s) at 20 °C, depending on the amount of chlorine and sulphur available. The Hg(l) and HgS(s) were predicted to be released as Hg^0(g) around 90 °C and 140 °C, respectively. For a system high on oxygen (approximately the same amount as during the thermal treatment experiment) $HgCl_2$(g) and Hg^0(g) were released at temperatures of 90 °C and 350 °C, depending on the amount of chlorine and sulphur available. From higher amount of sulphur, it can be concluded that HgO(s) was vaporized to Hg^0(g) and HgO(g) to a minor extent at 140 °C, and with a maximum around 230 °C and $HgSO_4$(s) starts to decompose into Hg^0(g) and HgO(g) around 270 °C. Comparing the equilibrium results with the results from soil heating, it seems likely that most Hg^0(g) is vaporized in the interval up to 230 °C, and that the vaporization is controlled by diffusion. Furthermore, the equilibrium calculations indicate that the remaining mercury in the soil at around 270 °C most likely is in the form of $HgSO_4$(s). Besides, at thermal temperature of 300 °C, the formation of HgO(g) was excluded. However, in that study, reaction kinetics were not considered.

The few kinetic studies that have been developed to treat mercury wastes from the chlor-alkali process were mainly focused on the global reaction that takes place to obtain metallic mercury at temperature higher than 400 °C (Cruz, 1985; Picazo and Fernandez, 2000):

$$HgS(s) + O_2(g) \rightarrow Hg^0(g) + SO_2(g)$$

However, assuming that the mercury presents in solid waste generated in chlor-alkali plants are only found in the HgS form represents a very limited picture of the whole processes and reactions that actually could be occurring in these types of wastes. Chapter 6 will focus on the reaction mechanisms and kinetics during retorting of the mercury contaminated wastes generated by the chlor-alkali plant in Cuba.

In any chemical process, laboratory scale experiments provide the basic information for the subsequent design and upscaling of the process (Bisio, 1985). The kinetic study carried out at laboratory scale as well as the development of the kinetic reaction mechanism that takes place during the thermal treatment of the sludge under consideration (above mentioned), allows us to develop a more robust and efficient technological proposal for the process design. Nowadays, modern techniques of modelling and simulation processes have being increasingly used to achieve the optimum design of a system.

2.5. Design of the chemical process

Several methods to effectively design a chemical process are known, including the scale-up and mathematical modelling based on the transport phenomena. The first variant by its own is limited by the necessity of a considerable amount of laboratory data which allow increasing the equipment size, from a minor scale. Nevertheless, it has been reported that the use of both methods can significant improve the chemical process design (Perry and Green, 1999; Nauman, 2002).

2.5.1. Mathematical modelling to design chemical process

2.5.1.1. Dynamic modelling

The dynamic model of a process has been defined as the mathematical model that describes its unsteady behaviour (Asprey and Macchietto, 2003). The steady state models, where the accumulation term is zero, have been traditionally used to design and analyse chemical processes. However, in the last decades the use of dynamic models or a combination of both modelling methods has been preferred for achieving a more accurate and integrated control of the process (Roffel and Betlem, 2006; Mikles and Fikar, 2007).A dynamic model is based on differential equations involving the time as independent variable (Mikles and Fikar, 2007). The variables involved in the model are those chemical-physical magnitudes that could change during the operation of the process due to the disturbing effects. These models can generally be represented by a system of nonlinear differential equations, as follows:

$$\frac{dx}{dt} = f(x, d, m, p) \tag{2.1}$$

$$y = h(x) \tag{2.2}$$

where x is the vector of state variables, d and m are the vectors of the input variables; p is the parameter vector and y is the vector of output variables.

In many cases the approach of processes dynamic models leads to a system of equations DAE (differential algebraic equation), by adding to the previous system the following algebraic expressions:

$$g(x, d, m, p) = 0 \tag{2.3}$$

Numerical methods are required to solve DAE systems because analytical solutions are not existing or extremely complex. Nowadays, professional software (MATLAB, MATH and PSI) have been efficiently used to solve differential equation systems obtaining results with minimal programming effort and time investment (Hangos and Cameron, 2001).

2.5.2. Conceptual types of mathematical models

According to Hangos and Cameron (2001) there are four conceptual types of mathematical models that can be used to describe a chemical process:

1. *Mechanistic models*: are based on the system mechanisms such as mass, heat and momentum transfer. Many commonplace models in process engineering applications are derived from knowledge of the underlying mechanisms. However, most mechanistic models also contain empirical parts such as rate expressions or heat transfer relations. Mechanistic models often appear in design and optimization applications. They can be termed "white box" models since the mechanisms are evident in the model description.
2. *Empirical models:* are the result of experiment and observation, usually not relying on the knowledge of the basic principles and mechanisms which are present in the system being studied. They employ essentially equation fitting where the parameters have little or no physical meaning. Empirical models are widely used where the actual underlying phenomena are not known or understood well. These models are often termed "black box" models, reflecting the fact that little is known about the real mechanisms of the process.
3. *Stochastic models:* arise when the description may contain elements which have natural random variations typically described by probability distributions. This characteristic is often associated with phenomena which are not describable in terms of cause and effect but rather by probabilities or likelihoods.
4. *Deterministic models:* are the final types of models characterized by clear cause-effect relationships. In most cases in process engineering the resultant model has elements from several of these model classes. Thus we can have a mechanistic model with some stochastic parts to it. A very common occurrence is a mechanistic model which includes empirical aspects such as reaction rate expressions or heat transfer relationships.

The most common form of model used in process engineering is a combination of mechanistic and empirical parts. Such model is termed "grey box" or phenomenological model as a more accurate method to describe the chemical process by combining experimental data (used to develop kinetic rate equations) with the mass, energy and heat balances.

2.5.3. Phenomenological models

The mathematical model of a process arise from the mass, energy and momentum equations, which are commonly known as the continuity equations. Currently, models that combine empirical equations with equations based on physic-chemical laws are extensively used. Mathematical models that combine empirical equations (black box models) can be used to describe the process dynamics (Hangos and

Cameron, 2001). Nevertheless, the validation range of the model is restricted by the experimentation region.

To develop a dynamic mathematical model of a chemical process, the following aspects need to be defined (Mikles and Fikar, 2007):

1. The modelling environment: is set taking into account the process and its parts.
2. The structure or flow pattern of the process: generally, ideal behaviour is assumed taken into account the modelling environment and if the process is of concentrated or distributed parameters.
3. The kinetics of the process: defined by the controlling steps of the reaction rate. The empirical equations used can be obtained by experiments or based on the kinetic laws developed for the processes of chemical reaction, mass transfer, heat and momentum or by the use of statistical regression models and / or neural networks.
4. The balance equations: if the process is represented by concentrated parameters, these equations result in systems of differential equations to total derivatives and the independent variable is the time. In contrast, if the process is constituted by distributed parameters, the differential equation system is transformed to partial derivates and the independent variables are the time and the spatial variables concerned.
5. The boundary conditions must be defined in the process.

The mathematical model solution will involve checking the fit of the unknown or uncertain parameters and validation in the experimentation region and beyond them, in order to ascertain its predictive potential (Asprey and Macchietto, 2003). Whereas the process flow pattern can be altered with the change of scale, experimentation should be done on the scale closest to prototype or it has to be taken into account for applying the mathematical model at a different scale (Trambouze, 1979).

Continuity equations in a phenomenological model:

For any chemical process the balances of mass, energy and momentum are made considering the terms of input, output and accumulation respectively (Hangos and Cameron, 2001). The general balance expressions can be represented as follows:

- Total mass balance:

$$\frac{d(\rho \cdot V)}{dt} = (\rho_I \cdot F_I)_{input} - (\rho_j \cdot F_j)_{output} \tag{2.4}$$

where V is the volume (m^3), ρ is the density (kg/m^3), F is the flow (m^3/h), i represents the input currents and j represents the output currents.

- Component mass balance:

$$\frac{d(Ca \cdot V)}{dt} = (Ca_I \cdot F_I)_{input} - (Ca_j \cdot F_j)_{output} \pm V \cdot r \pm A_t \cdot J \tag{2.5}$$

where Ca is the component concentration (mol/m^3), V is the volume (m^3), F is the flow (m^3/h), r is the component transformation by chemical reaction (mol/(m^3-h)), At is the transfer area (m^2) and J is the transferred flux (mol/(m^2-h))

- Energy balance:

$$\frac{d(E)}{dt} = (\rho_I F_I h_i)_{input} + (\rho_j F_j h_j)_{output} \pm Q \pm Ws \tag{2.6}$$

where E is the internal energy (kJ), ρ is the density (kg/m^3), Q is the heat transferred (kJ/h) and Ws is the work performed (by or delivered) to the process.

2.6. Scale-up of the chemical process

The main objective of scaling in any process is to obtain an installation of acceptable quality that will correspond with process requirements and conditions used at the experimental scale (Arteaga, 2010). Initially, upscaling from laboratory conditions (the prototype) to pilot or full scale (the model) only focusses on the Similarity Principles (mechanical, chemical and/or thermal). Nevertheless, scale-up by mathematical modelling that combines similarity principles with dynamic modelling could efficiently result in a more secure and optimized design, saving time and resources. Several phases in the upscaling of a process have been reported by Bisio (1985):

- Phase 1: Definition and Formulation:
  - The problem is defined;
  - The data and process information is compiled;
  - Type and modelling technique is selected.
- Phase 2: Preliminary design:
  - The input and output variables of the process are defined;
  - The limitations and assumptions of the model are specified;
  - The required algorithms to develop the model are created.
- Phase 3: Detailed design:
  - The model details are completed from data bank obtained by the experimental results;
  - The sensibility grade of the model is verified developing trials on the model.
- Phase 4: Final checking of the model:

- The robustness of the model is evaluated (Due to changes in to the input variables and operating conditions of the process, which is the output variables behaviour).

2.7. Simulation for designing, upscaling and optimising chemical processes

Simulation of a process using software tools is a highly useful aid for the design, characterization, monitoring and optimization of industrial processes. There are a variety of commercial simulators, some of which are powerful computational tools, with huge databases and methods of analysis to study and create new systems (Arteaga, 2010).

The process simulators can be divided into the following types:

Sequential modular simulators

Global or oriented to equations simulators

In *sequential modular simulators* the calculation method is programmed as a simulation diagram strategy. The advantages and disadvantages are:

1. Flow diagrams can be effectively constructed because the units are individually calculated;
2. The simulation can be understood by engineers “not experts in simulation”;
3. The calculations are made using robust convergence methods such as Direct Substitution and Wegstein;
4. The information entered by the user is easy to interpret and check.

Disadvantages include:

1. Convergence problems in flow diagrams with many recycle streams;
2. Very slow when working with large flow diagrams whit many recycle streams and complex design specifications.

The *global or oriented to equations simulators* are mathematical models that represent a process by a large set of algebraic equations that usually are nonlinear. The advantages are:

1. Optimal convergence of flow diagrams that have many recycle streams;
2. Safe behaviour in convergence.

Disadvantages include:

1. Requires large storage spaces;
2. Presents difficulty in finding errors;
3. Initial values need to be specified;
4. In complex processes results may be less reliable, and convergence problems may be encountered (solutions without physical sense).

2.7.1. Methodology to simulate a chemical process

For simulating equipment, a process section or a whole chemical plant, the following methodology developed by Herbert (2005) has been recommended:

- To formulate the problem which includes to select the software and the hardware and to specify the essential information;
- To develop the flow diagram;
- To define the chemical components;
- To select from thermodynamic models;
- To calculate or complete the binary mixtures data;
- To provide physicochemical data of pure substances;
- To specify the streams of the process;
- To specify the unit operations (measured units);
- To establish the relationship between streams and units.

2.7.2. Sequential modular simulators

Commercial sequential modular simulators used in process industry include Aspen Plus (Aspen Technology, USA), HYSYS (Hyprotech, Canada), CHEMCAD (Chemistations, USA), Pro II (Simulations Sciences, USA) and DESIGN II (Advanced Engineering Software).

The Aspen Plus and HYSYS have been extensively used in the simulation of chemical processes because of the robustness and the large databases including physicochemical data for over 10 000 compounds. Despite the potential of these simulators, the lack of modules for the furnace simulation entails that specific furnace modules need to be created. On the other hand, ASPEN and HYSYS are effective simulators for the simulation of processes that involve conventional kinetic (kinetic that follows a Power Law behaviour). Since the system under study (thermal decomposition of mercurial sludge using retorting furnace) is represented by a complex and multicomponent kinetic (nonconventional kinetic behaviour), these simulators were not further considered.

The PSI (Van den Bosch, 1997) software, which corresponds to an oriented to equations simulator is a wide flexible and less complex simulator which is competent to create a furnace module. Moreover, a simplified computational method that represents the dynamic behaviour of a furnace, including a nonconventional kinetic behaviour can be efficiently simulated using PSI software. For these reasons, PSI simulator software was selected to carry out the present research.

2.8. Indicators used to evaluate a technology

In any chemical process, for the proper selection of best treatment alternative, techno-economic and environmental analyses need to be done. Several tools have been used (Evans et al. 2009; Sankaranarayanan et al. 2010; Casas, 2012) to evaluate the sustainability of existing and new technologies or processes. In this sense, the assessment and finally proper selection of a technology could be made through different analysis tools:

- Technical criteria
- Economic parameters based on process feasibility (dynamic indicators: annual net profit, payback period, net return of investment, etc)
- Environmental impact (Life cycle assessment)

2.8.1. Techno-economic methods

Techno-economic methods are based on the use of profitability and efficiency indicators in which through economic and technological parameters the proper selection of the treatment alternative can be done (Peters et al., 2003). For the specific case of the thermal treatment technology three techno-economic criteria can be considered:

1. Criteria of mercury removal efficiency
2. Criteria of energy efficiency
3. Economic dynamic indicators: Net Present value (NPV), Payback period (PP) and Internal Rate of Return (IRR).

2.8.2. Environmental methods

Environmental methods are based on the Environmental Impact Assessment (EIA) of a treatment, process or project in general. To evaluate the environmental impact of a treatment or process, several qualitative (Leopold and Conesa Matrix) and quantitative (Externalities Calculation and Battelle-Columbus method) methods have been developed (Conesa, 2000). Nowadays, the methodology of Life Cycle Impact Assessment (LCIA) is regarded as the most efficient method to evaluate qualitative and quantitatively the environmental impact with a comprehensive analysis of the proposed technology.

2.8.2.1. Life Cycle Assessment (LCA) methodology

Life Cycle Assessment is an objective procedure for evaluating energy and environmental loads corresponding to a process or activity that is done by identifying materials, energy use and emissions to the environment. The evaluation is performed on the complete life cycle of the process or activity,

including mining and processing of raw materials, manufacturing, transportation, distribution, use, recycle, reuse and final clearance (Iglesias, 2005).

Since the last decades, this methodology has been established as a highly appropriate tool to quantify emission sustainability indicators of development (Ness et al. 2007; Heijungs et al. 2010). Life Cycle Assessment has been performed for the pulp and paper industry (Ross and Evans, 2002), the waste field (Lunghi et al. 2004; Moberg et al. 2005; Finnveden et al. 2009), as well as a multitude of other products and processes. Mostly research reports regarding to environmental impact assessment of mercury employing LCA methodology have been focused on its use in lamps (Eckelman et al., 2008; Garrett and Collins, 2009). The mercury flows in Europe and the world as well as the impact of decommissioned chlor-alkali plants was studied by Concorde (2004). Nevertheless, a lack of surveys about using LCA to evaluate the environmental impact of current or future technologies to remediate mercury contaminated wastes from chlor-alkali plants have been observed.

The technical framework for the Life Cycle Assessment methodology has been standardized by the International Standards Organization (ISO). According to ISO 14040, LCA consists of four phases (UNEP, 2003) that can be presented as follows:

1. **Goal and scope definition:** the product(s) or service(s) to be assessed are defined, a functional basis for comparison is chosen and the required level of detail is defined.
2. **Inventory analysis:** the energy carriers and raw materials used, the emissions to atmosphere, water and soil, and different types of land use are quantified for each process, then combined in the process flow chart and related to the functional basis.
3. **Impact assessment:** the effects of the resource use and emissions generated are grouped and quantified into a limited number of impact categories which may then be weighted for importance.
4. **Interpretation:** the results are reported in the most informative way possible and the need and opportunities to reduce the impact of the product(s) or service(s) on the environment are systematically evaluated.

Life Cycle Assessment (LCA) represents an important tool in the decision making process. A wide range of relevant environmental factors need to be provided in understandable format requiring the use of Eco indicators (Aloma, 2011). Several Eco indicators such as the CML 1992, Eco indicator 95 and Eco indicator 99 have been developed to evaluate a wide range of environmental impacts (Aloma, 2011). Nowadays, the Eco-indicator 99 method has been preferred as it considers a wide range of impacts such as resource depletion, land use and ionizing radiation which are not included in the previous one (Contreras, 2007). In order to carry out Life Cycle Assessment (LCA) software tools of data processing are required such as Eco-it, GaBi 4 Software System and Database, and Sima Pro. The latter, developed

by Pré Consultants (Netherlands), is a suitable tool that allows to make conclusions for the production process optimization (costs, resources, technology, energy saving, etc.) (Contreras, 2007).

CHAPTER 3

LEACHING BEHAVIOUR OF MERCURY FROM HAZARDOUS SOLID WASTE GENERATED BY CHLOR-ALKALI INDUSTRY

Through the conventional chlor-alkali production process, highly mercury (Hg) contaminated waste sludges are produced. Improper handling and disposal of this sludge may constitute an environmental hazard. The leaching behaviour of Hg of land disposed mercurial sludge, originating from a chlor-alkali plant that still is in operation, was investigated using the German DIN 38414-S4 test. Total Hg content of samples was above 1500 mg/kg, allowing the material to be classified as 'hazardous' and 'high mercury waste'. Concentrations of Hg in the leachates for both samples were higher than 0.02 mg/l stipulated by the 1991 EEC Landfill Directive Draft as a maximum limit for a waste that is to be landfilled. The high Hg concentrations, especially for Sample 2 in comparison to Sample 1, suggested the presence of rather soluble Hg species such as $HgCl_2$. The more limited release of Hg from Sample 1 might reflect an ageing effect and to some extent a better quality in the stabilization process done by the factory. However, it still represents a risk for the environment and human health. Results indicate the approach used to stabilize the sludge has not been sufficiently effective, and warrant caution about existing disposal sites and future management of these Hg containing wastes.

3.1. Introduction

Mercury-cell chlor-alkali plants (MCCaP) produce chlorine (Cl_2) and caustic soda (NaOH) by electrolysis of brine, using mercury (Hg) as the cathode. Although this process is based on 19th century technology, MCCaPs around the world still account for roughly 15% of the global Hg demand, and are a significant source of local and global Hg pollution (Ulrich et al., 2007; Mahan and Warner, 2009; Reis et al., 2009). These processes are not any more considered good industrial practice and the Integrated Pollution Prevention and Control (IPPC) of the European Union (EU) has indicated that chlor-alkali installations require obtaining licenses based in the Best Available Techniques (Directive 2008/1/EC, 2008). The technology for production of Cl_2 and NaOH should be replaced by other technologies more compatible with the environment, such as those involving the use of diaphragm and membranes cells. Accordingly, the chlor-alkali industry has moved away from MCCAP since the early 1970's in favour of safer, more economical membrane-based process in which a semi-permeable membrane separates the sodium and chlorine during production, eliminating the need for Hg. Switching to Hg free technology is often economically beneficial, since the newer membrane process uses less energy and has fewer potential occupational exposure problems (Mahan and Warner, 2009).

The USEPA predicts that global use of Hg in manufacturing will continue to decline because of the decline in chlorine production using mercury cell chlor-alkali plants (USEPA, 2007). Many plant owners in Europe and USA have already announced plans or indicated an ability to decommission by 2020. Only about 50 plants have not announced plans or are not required to decommission by 2020 (Mahan and Warner, 2009). Their combined production is quite small, and thus converting these remaining plants is feasible. Still, a global inventory of Hg cell chlor-alkali facilities reported around 100 facilities in 44 countries that have Hg cell-based chlorine production capacity (UNEP, 2009).

In Cuba, the production of chlorine and caustic soda started in the mid 1930's in Sagua La Grande City in central Cuba. The plant has a daily production capacity of 48 ton of chlorine gas and 108 ton of caustic soda at 50% concentration. Currently, the Electrochemistry "Elpidio Sosa", the only industry of its kind in the country, covers the domestic demand for these products and the surplus is exported to the Caribbean region. In 2008 the Cuban government approved plans for a change in technology from Hg electrolytic cells to membrane based technology. While this transition will prevent further production of Hg contaminated waste, thousands of tons of mercurial sludge are currently stored in the surroundings of the plant, constituting a possible hazard to living beings and environment.

In evaluating environmental risks, leaching tests can provide information on anticipated mobility/availability of hazardous metals through water and groundwater, soil, sediments and solid wastes. Two types of laboratory leaching tests are distinguished to determine the heavy metal mobility in the samples, single batch tests and dynamic, multiple extraction/flow-through leaching tests (Cappuyns and Swennen, 2008).

Single batch extraction tests typically involve mixing a sample with a specific amount of leaching solution without renewal of the leaching solution (Washington State Department of Ecology, 2003; Bayar et al., 2009). In dynamic leaching tests, where time is also an important variable, a specific amount of leaching solution and test material are mixed and the leaching solution is periodically or continuously renewed. The mixing is performed over a relatively long time period (days to months) compared to single batch extraction tests (Fytianos and Charantoni, 1998; Washington State Department of Ecology, 2003).

The leaching test DIN 38414-S4 is a dynamic leaching method for environmental impact assessment. It was developed by the German Institute of Standardization (DIN) in 1984. It is commonly used to evaluate the leaching of metals from landfill disposal (Viguri et al., 2000; Kazi et al., 2005; Bayar et al., 2009; Reis et al., 2009). According to Quevauviller et al. (1996) the DIN test is a simple method for evaluating the most weakly bound, easily mobilizable or bioavailable fraction in samples of solid waste or contaminated soil. The permissible limit of mercury in the leachates is 0.02 mg/l according to the European Economic Community (EEC) Landfill Directive Draft of 1991 (Bayar et al., 2009).

The Hg containing solid wastes in the Cuban factory are generated after mixing the exhausted mercury of the electrolytic cell with sodium sulphide (Na_2S) in a first step, and with sodium chloride (NaCl), calcium carbonate ($CaCO_3$), magnesium hydroxide $Mg(OH)_2$ and diatomaceous earth in a second step. This sludge is currently unsafely disposed in concrete niches. Contact with ground water or rain may cause Hg to leach and contaminate the soil and underground water. Moreover, studies on the leaching behaviour of mercurial sludge from chlor-alkali industry are not available. In the present chapter, the DIN S4 leaching test was used to assess Hg release from this contaminated sludge in order to corroborate the actual environmental risk that this mercurial sludge represents.

3.2. Material and Methods

3.2.1. Site description

Mercurial sludge was sampled from a site near an electrochemical plant that produces chlorine and soda, located in the north of the central region of Cuba. The mercurial sludge generated from

the electrolytic process is buried in concrete niches that are scattered around the factory. The niches are 9.5 m long, 4.5 m wide and 3.5 m heigh. They allow storage of 150 m^3 of sludge.

In the region where the electrochemical plant is located, annual medium temperature is between 24 °C in the plains to 26 °C and more on the eastern coast. On average, the temperature ranges between 20 and 22 °C in January (winter) and between 26 and 28 °C in July (summer). There are two seasons, the rainy season from May to October and the dry season from November to April. The accumulated annual average in 2010 was 932 mm of rain (Weather data archive of Villa Clara province, 2011). Typically, nearly 80% of the yearly rain falls during the rainy season

3.2.2. Sampling and sample preparation

Two samples were collected from different filled niches. Sample 1 has been one year and four months in the niche while Sample 2 has been only four months in the niche before sampling. Each sample was prepared as a composite sample from equal amounts of sludge taken from three different points on a diagonal line, at 20 cm of the two extremes of the niches and in the centre point, as well as at three depths, 0 - 20, 20 - 40 and 40 - 60 cm (Buduba, 2004). Immediately upon arrival at the laboratory, samples were air-dried for seven days, hand-crushed in a mortar, passed through a 2 mm sieve and thoroughly mixed.

3.2.3. Sample characterization

The pH of the solid waste was measured after 18 h using an Orion model 520 pH meter (Orion, Boston, MA, USA) in a suspension of 50 ml of distilled water with 10 g of waste sludge (Cottenie et al., 1982). Organic matter was estimated by weighing before and after ashing 1 g of the sample at 400 °C for 2 h (Van Ranst et al., 1999). Carbonate content was determined by back-titrating an excess of 0.50 M H_2SO_4 added to 0.25 g of the sample with 0.50 M NaOH (Nelson, 1982). Cation exchange capacity (CEC) at neutral pH was determined by the ammonium acetate method (Ross, 1996) using 5 g of mercurial sludge sample. To determine the chloride content 1 g of sludge sample was suspended in 50 ml of 0.15 mol/l HNO_3 and shaken for 30 min. The filtrate was titrated with 0.05 mol/l $AgNO_3$ with potentiometric end-point detection (Van Ranst et al., 1999) using a Metrohm 761 Compact IC potentiometer (Metrohm, Herisau, Switzerland).

Total mercury content was determined by cold vapour atomic absorption spectrometry (Mercury Analyzer MAS-50, Coleman, Oak Brook, Illinois, USA) after a specific destruction as reported by Cottenie et al. (1982). The destruction procedure involved adding 0.05 g of V_2O_5, and 10 ml of concentrated HNO_3 to 0.5 g of sample and digestion for 30 min at 160 ºC. After the samples were cooled down 15 ml of concentrated H_2SO_4 was added and the digestion was completed for 2 h without extra heating. A standard solution of 0.25 mg/l Hg was prepared from 1000 mg/l stock

solution (Mercury Standard Solution, MERCK, Darmstadt, Germany). The calibration curve was obtained by measuring transmittance after injection of different volumes (0, 0.5, 1, 2, 4 and 8 ml). Pseudo total metal content was determined after destruction in aqua regia (Ure, 1990), followed by metal determination using Inductivity Coupled Plasma Optical Emission Spectrometry (ICP-OES, Vista MPX CCD Simultaneous, Varian, Mulgrave VIC, Australia). Each determination was carried out in triplicate and all reagents used were of analytical grade.

3.2.4. DIN 38414 S4 leaching test

Leachability of Hg from the mercurial sludge was assessed using the DIN 38414-S4 leaching test (DIN 38414-S4, 1984). The liquid to solid ratio (L/S) is the ratio of the mass of leaching agent to the mass of waste during leaching. The cumulative L/S ratio ranged from 10 to 40.

Five grams of solid waste were transferred to a centrifuge tube (100 ml volume) with screw cap and suspended in 50 ml of distilled water as leaching agent. This corresponds to a L/S ratio of 10. The suspensions were shaken continuously using an end over end mechanical shaker at 30 rpm. After 24 hours, the samples were centrifuged (Megafuge 1.0, Heraeus Instruments GmbH, Heraeus, Germany) during 12 min at 3000 rpm to allow settling of suspended materials. The supernatant solution was decanted and filtered through a 0.45 μm pore membrane filter (CM, Porafil, Macherey-Nagel, Düren, Germany). Fresh leaching agent was added, and the extraction procedure was repeated until four fractions were collected. After determination of pH and electrical conductivity the leachate sample was acidified to a pH below 2 with concentrated HNO_3 to store the sample before mercury analysis. All extractions were carried out in triplicate.

Electrical conductivity was measured in the extracts using a Microprocessor Conductivity Meter (LF 537, Weilhem, Germany). The pH was determined potentiometrically using an Orion model 520 pH meter (Orion, Boston, MA, USA). Measurement of Ca and Mg was performed using ICP-OES (Vista MPX CCD Simultaneous, Varian, Mulgrave VIC, Australia). Flame photometry (ELEX 6361, Eppendorf, Hamburg, Germany) was used to determine Na and K.

Total concentration of Hg in the leachates was determined using cold vapour atomic absorption spectrometry (Mercury Analyzer MAS-50, Coleman, Oak Brook, Illinois, USA). An aliquot of 20 ml of sample solution, 10 ml of concentrated HNO_3 and 15 ml of concentrated H_2SO_4 were added in 250 ml volumetric flask and diluted to volume using deionised water. Calibration was performed as outlined before. The limit of detection (LOD), defined as three times the standard deviation of the blanks, was 0.02 mg/l. All analysis was carried out in triplicate

3.3. Results and Discussion

3.3.1. Chemical characteristics of the solid waste

The mercurial sludge exhibited an alkaline pH of 9.3-9.4 (Table 3.1). This is caused by the presence of calcium carbonate and magnesium hydroxide, two components added during the stabilisation of the waste product. Carbonate contents were in the order of 60-70%, whereas pseudo total analysis revealed high Ca and Mg concentrations (Table 3.2).

Table 3.1. Chemical characteristics of the mercurial sludge[a]

Parameter	Sample 1	Sample 2
pH-H_2O	9.3 (0.03)	9.4 (0.03)
Organic Matter (g/kg)	158 (5.1)	102 (5.8)
$CaCO_3$ (g/kg)	667 (5.8)	733 (5.8)
Chloride (g/kg)	57.2 (0.4)	60.5 (1.8)
CEC [b] (cmol/kg)	11.8 (0.4)	7.8 (0.3)

Note: [a] Values in parenthesis are standard deviations of three replicates. [b] Cation exchange capacity.

Table 3.2. Pseudo-total metal content of the mercurial sludge[a]

Metal contents	Sample 1	Sample 2
Ca (g/kg)	223 (1)	275 (3)
Mg (g/kg)	32 (0.2)	18 (0.2)
Fe (g/kg)	10 (0.1)	10 (0.4)
Hg (g/kg)	5.6 (0.2)	1.5 (0.1)
Pb (mg/kg)	44 (1.4)	58 (4.4)
Zn (mg/kg)	177 (1)	181 (0.5)
Ni (mg/kg)	31 (0.3)	23 (1)
Cu (mg/kg)	169 (1)	455 (4)
Cr (mg/kg)	40 (0.4)	27 (1)
Cd (mg/kg)	1.8 (0.1)	2.6 (0.1)
Mn (mg/kg)	235 (1)	232 (2)

Note: [a] Values in parenthesis are standard deviations of three replicates.

In addition, about 300 g diatomaceous earth is used for the production of 1 kg mercurial sludge. It also contributes carbonate to the final waste product. Diatomaceous earth also contains about 6% (w/w) of organic matter and about 2% (w/w) of Fe (Antonides, 1998). This explains the relatively high Fe concentrations in the mercurial sludge. Elevated chloride levels, in the order of 50 g/kg, were found, indicating the presence of a substantial amount of soluble salts.

Between the samples, mercury total contents differed by a factor of three, pointing to a marked variability in the production of mercurial sludge. In both samples, mercury concentrations were much higher than 260 mg Hg/kg, allowing the materials to be classified as hazardous high mercury wastes according to US EPA: LDR (USEPA, 2008a). Other potentially toxic trace elements were present in levels that were higher than normal ranges present in soils (Kabata-Pendias and Pendias, 1984).

3.3.2. Actual leachability

The DIN S4 leaching test provides indications on the release of elements when the contaminated material is contacted with increasing amounts of leaching agent. High pH values of the leachates (Table 3.3) result from the presence of free hydroxides provided by the $Mg(OH)_2$ used during the preparation of the sludge. For both samples pH further increased in the second fraction. This increase may reflect a kinetic effect, where the initially dry sludge would interact slower with the added leaching agent than the wet sludge in subsequent extraction steps.

Table 3.3. pH and electrical conductivity in the fractions of the DIN S4 leaching test[a]

	L/S ratio			
Samples	**10**	**20**	**30**	**40**
		pH		
1	9.49 (0.06)	9.92 (0.05)	9.97 (0.03)	9.97 (0.01)
2	9.51 (0.03)	9.84 (0.05)	9.8 (0.05)	9.65 (0.02)
		Electrical Conductivity (mS/cm)		
1	19.1 (0.2)	2.45 (0.04)	0.58 (0.01)	0.25 (0)
2	19.7 (0.11)	2.19 (0.02)	0.48 (0)	0.18 (0)

Note: [a] Values in parenthesis are standard deviations of three replicates.

High values of electrical conductivity in the first fraction reveal the presence of significant amounts of soluble salts. This leachate is classified as highly saline according to FAO (Rhoades et al., 1992). This may mostly be NaCl as suggested by the very high levels of Na compared to other cations in the extracts (Table 3.4, note that Na is in g/l). Sodium is used at different points in the chlor-alkali production process, as raw material (NaCl) in the electrolytic cell process and as Na_2S added to the residual sludge to stabilize Hg in the sludge.

Table 3.4. Metal concentration in the fractions of the DIN38414-S4 leaching test [a]

L/S ratio	10	20	30	40
		Sample 1		
Na (g/l)	3.75 (0.09)	0.44 (0.01)	0.092 (0.02)	0.041 (0.01)
K (mg/l)	23.6 (0.87)	3.8 (0)	1.73 (0.23)	1.13 (0.12)
Ca (mg/l)	2.41 (0.18)	1.61 (0.07)	1.04 (0.04)	1.19 (0.04)
Mg (mg/l)	10.2 (1.76)	0.93 (0.12)	0.27 (0)	0.29 (0.05)
		Sample 2		
Na (g/l)	4.05 (0.12)	0.4 (0.003)	0.074 (0)	0.031 (0.004)
K (mg/l)	9.67 (2.67)	1.67 (0.23)	0.73 (0.23)	0.67 (0.12)
Ca (mg/l)	2.51 (0.05)	1.65 (0.03)	1.2 (0.05)	1.66 (0.09)
Mg (mg/l)	8.56 (0.54)	0.71 (0.03)	0.27 (0)	0.4 (0.01)

Note: [a] Values in parenthesis are standard deviations of three replicates.

The rapid decline in electrical conductivity with increasing cumulative L/S ratio indicated the removal of soluble salts during the consecutive steps of the leaching test. Unlike Na, K and to a lesser extent Mg, the concentrations of Ca were more constant in the subsequent fractions (Table 3.4). This observation is consistent with the limited solubility of calcium carbonates.

The concentrations of Hg in the fractions of the DIN test differed greatly, by more than one order of magnitude, between both samples (Figure 3.1). Overall, Hg concentrations decreased in subsequent fractions of the DIN leaching test, although Sample 2 exhibited a pronounced increase, by a factor of three, in mercury concentration in the second fraction compared to the first. It is difficult to explain the different behaviour between sludges considering that chemical characteristics of both sludges were similar (Table 3.1). As Sample 1 was one year older, the more limited release of Hg from that sample, despite its higher total Hg content (Table 3.2), might be attributed to an ageing effect. However, it might also reveal a significant variability in the quality of stabilization applied to the sludge. Regular sampling and testing of the produced sludges would be required to ascertain the variability in the production.

The cumulative leaching of mercury from the sample can be described by a logarithmic equation, according to:

$$CMR_1 = 2.00 \ln (L/S) - 2.97 \qquad R^2 = 0.9950 \qquad (3.1)$$

$$CMR_2 = 64.2 \ln (L/S) - 129 \qquad R^2 = 0.9904 \qquad (3.2)$$

where: CMR represent the cumulative mercury leaching in mg/kg dry sludge, and L/S represents the liquid/solid ratio. Subscripts represent sample numbers. Similar equations were used by Cappuyns and Swennen (2008) to describe the lixiviation of mercury from contaminated soils. The

slope of each equation can be considered as a measure of the Hg leaching intensity, and represents a tendency of the Hg to be released from the sludge matrix. The cumulative leaching of Hg over the entire leaching test amounted to less than 0.1% for Sample 1, but was in the order of 7.0% for Sample 2, which exhibited a lower total Hg content but a much more intensive leaching.

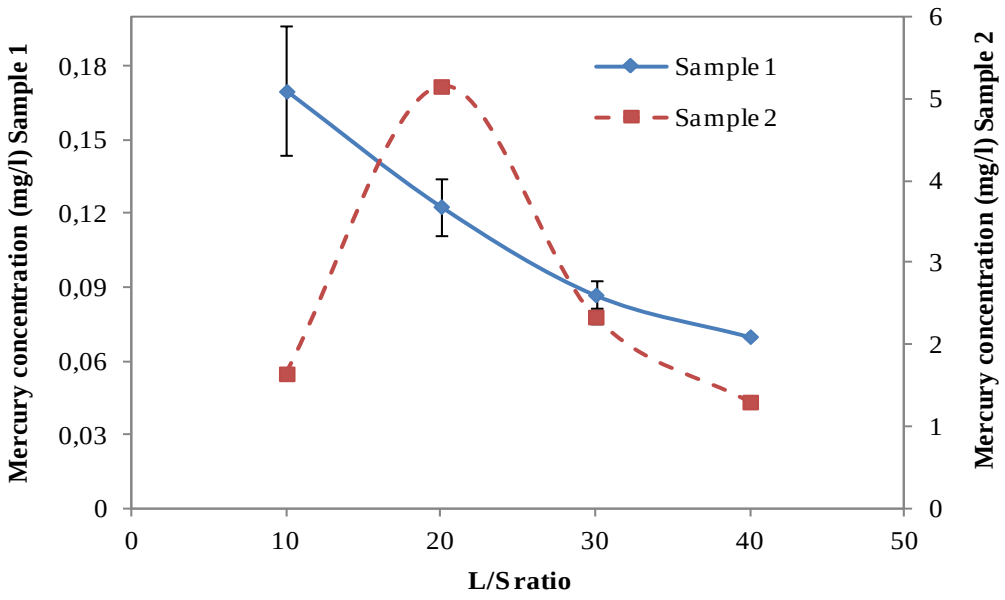


Figure 3.1. Mercury concentration in the DIN S4 leaching test fractions at increasing L/S ratio for the two mercurial sludge samples (Note different scales for each of the samples).

The Council Directive 91/689/EEC on hazardous waste is widely used for the characterization of waste prior to landfilling to the environment. The directive establishes when a waste can be considered a “hazardous waste”. Also, it defines the limit concentration values for each hazardous constituent and the applicable test methods (Directive 91/689/EEC, 1991). According to this directive, the DIN38414-S4 test is normally used to characterize the leaching behaviour of compounds in the sample.

The limit value for mercury concentration in the leachate is 0.02 mg/l (Bayar et al., 2009). The mercury concentrations in all fractions of Sample 2 by far exceeded this permissible limit (Figure 3.1.). Although Sample 1 showed a much slower release of Hg, the concentrations in all fractions were still hundredfold above the permissible limit. This causes the studied material to be classified as a hazardous waste.

It is clear from the leaching test data that the current treatment of the mercury waste is not sufficiently effective to stabilize the mercury. Long term leaching and migration of contaminants from improperly disposed wastes can result in contamination of both surface and ground water

(Maskell and Thornton, 1998). Long term leaching test are necessary to evaluate the potential release of mercury from the sludge matrix. However, it is well known that the leachability and bioavailability of trace metals in soils and sediments depend on their chemical and physical associations (Bubb and Lester, 1991; Tack and Verloo, 1993; Ma and Rao, 1997). Metals in soils and sediments may form specific mineral phases, be loosely bound on exchangeable sites, co-precipitate, be adsorbed onto mineral phases, be fixed by organic matter and sulphides or be structurally bound in alumino-silicate structures (Belzile et al., 1989). The fate, transport and bioavailability of the mercury in the sludge are dependent upon the species in which it is present (Liu et al., 2006).

HgS is polymorphic, existing as the common red (α) form known as cinnabar and the black metastable (β) form, metacinnabar. Both forms are highly insoluble in water (Brandon et al., 2001). Black HgS (metacinnabar) is formed by the addition of H_2S or Na_2S to aqueous Hg^{2+} ions and will exist indefinitely at room temperature with no formation of cinnabar (Brandon et al., 2001). The stabilization of the mercurial sludge using Na_2S aims to convert mercury into insoluble HgS.

The high concentrations of Hg observed in the DIN test fractions, especially for Sample 2, indicate the presence of more soluble mercury forms. $HgCl_2$ has a practical solubility in water of 70 g/l. Bollen et al. (2008) reported that a high mercury concentration in the leachate of contaminated soils was mainly due to the presence of $HgCl_2$. However, also the solubility of sulphidic mercury forms may be higher than expected by the extremely low solubility constants of the compounds, considering the high pH of the mercurial sludges. At high pH, an increased solubility of HgS results from the formation of polysulphide mercury forms such as HgS_2^{2-} and $Hg(S_x)_2^{2-}$ (with S_x^{2-} x=3-6) (Paquette and Helz, 1997; Jay et al., 2000). In addition, oxidation of mercury sulphides during the leaching process may contribute to enhance mercury mobility (Barnett et al., 2001; Holley et al., 2007).

3.4. Conclusions

The leaching test carried out in the present chapter constitutes the first evidence that the stabilization process applied to the mercurial sludge did not allow preventing significant leaching of Hg. In this sense, a well stabilization procedure should be stress the formation of black HgS (metacinnabar) by the addition of Na_2S. Nevertheless, the high concentrations of Hg observed in the DIN test fractions, especially for Sample 2, indicate the presence of more soluble mercury forms such as $HgCl_2$. The sludge may therefore be stored only in thoroughly sealed disposal sites. Historical disposal sites may not meet the strict requirements needed to guarantee safe storage of highly hazardous waste material.

In our study case, remedial actions are definitely needed to prevent further dispersion of Hg from these sites into the surroundings. Remedial actions may involve treatment of the sludges to remove the Hg or to reduce the leachability to acceptable levels. Alternatively, the material may need to be disposed in tightly sealed and thoroughly controlled dedicated disposal sites. Better techniques to stabilize the generated mercurial sludges may also contribute toward a safe handling and storage of the waste. More research on long term leaching, Hg speciation including treatment technologies is needed to develop adequate managing waste strategies. Fortunately, the trend to shift towards other, non Hg based technologies will decrease and eventually eliminate the production of these mercurial waste sludges.

CHAPTER 4

MERCURY MOBILITY AND AVAILABILITY IN HIGHLY CONTAMINATED SOLID WASTES FROM A CHLOR-ALKALI PLANT

Chlor-alkali industries generate large amounts of high mercury containing waste sludges. The mobility and availability of mercury is determined by the chemical forms of occurrence of the metal in the sludge. High values of total mercury content (2320 ± 40 mg/kg) in the sludge sample as well as in the extract of the Toxicity Characteristic Leaching Procedure (TCLP) (0.46 ± 0.02 mg/l) were observed. More than half of the total Hg (52.2 ± 1.5%) was recovered in the most mobile fractions of the sequential extraction procedure (F1+F2). The water-soluble fraction (F1) alone accounted for 13.7 ± 0.8% of the total Hg. This reflects the presence of water-soluble and exchangeable mercury compounds such as $HgCl_2$, $HgSO_4$ and HgO, and indicates a high risk of Hg mobilisation if the waste is not stored in tightly sealed disposal conditions. The mercury fractionation clearly shows that the current stabilization procedure for the waste sludge is inadequate. As this study provides insights into the different mercury compounds presents in the waste sludge, it can contribute in the design of a suitable technology to decontaminate that mercurial sludge at Cuban conditions.

Redrafted from:

Busto, Y., Tack, F. M. G., Cabrera, X. 2012. Mercury mobility and availability in highly contaminated solid wastes from a chlor-alkali plant. *Int. J. Environment and Sustainable Development* **11** (1): 3-18.

4.1. Introduction

Environmental impact studies in soils and sludge that are highly contaminated with mercury require the identification of the mercury species being involved. The species in which a contaminant is present determine its fate, transport and bioavailability in soil (Barnett et al., 1997; Wallschläger et al., 1998a; 1998b). Differentiation of the total contents in fractions of different reactivities enables the prediction and explanation of their mobility, bioavailability and toxicity (Issaro et al., 2009).

In many cases possibilities for determination of the true speciation in an environmental sample are limited, because of the large numbers of possible species present, and because of analytical limitations in procedures of sampling, sample preservation and analysis. Fractionation by using a sequential extraction constitutes an operationally defined procedure that allows to identify various classes of species of an element and to determine the sum of its concentrations in each class (Buffle et al., 1997).

Fractionation have been defined by the International Union of Pure and Applied chemistry as the process of classifying an analyte or a group of analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties (Templeton et al., 2000). The concept of fractionation emphasizes the concept of subdividing the “total content” (Tack and Verloo, 1995).

Evaluating the environmental impact of an element may sometimes be achieved without determining its speciation by the use of a fractionation process even though the fractions are only operationally defined (Templeton et al., 2000). According to Liu et al. (2006) the mercury fractionation in soil and sediment may be defined operationally (e.g. water soluble, exchangeable, and organo-chelated Hg fractions).

Sequential extraction procedures (SEPs), thermal desorption analysis, and spectroscopic techniques are three major approaches to determine Hg speciation in soil. Sequential extraction is a widely used method for Hg speciation and can provide useful information related to the environmental behaviour of Hg in soil, such as solubility, mobility, and bioavailability (Biester and Scholz, 1997; Han et al., 2003; Panyametheekul, 2004). Thermal desorption analysis has also been used for the analysis of Hg species in solid samples offering the advantages of being simple, fast, and cost-effective (Bombach et al., 1994). Spectroscopic techniques, such as X-ray absorption fine structure spectroscopy or X-ray microprobe spectroscopy, can provide a direct indication of Hg speciation. The application of this approach is however limited by its relatively poor detection limit (Kim et al., 2000; Kim et al., 2003). Sequential extraction procedures (SEPs) are frequently used to determine the partitioning of contaminants associated with different categories of soil constituents,

and to elucidate the transfer potential and thus the availability and mobility according to the extractability by various solvents (Sánchez et al., 2005).

Standardization studies performed in the framework of the Standards, Measurement and Testing Program of the European Union resulted in a three-step Sequential Extraction Procedure (BCR EUR 14763 EN). The so-called BCR protocol (Ure et al., 1993; Quevauviller, 1998) was recommended for the study of heavy metals distribution in sediment samples. However, mercury was not included among the elements investigated in the range of standardization tests. A modified BCR procedure was established after a systematic study of the potential sources of uncertainty in the previous BCR procedure (Sahuquillo et al., 1999) and was later applied to mercury in sediments (Sahuquillo et al., 2003). A wide range of sequential extraction protocols have been developed for the fractionation of mercury in soils and sediments (Issaro et al., 2009). These include the procedures of Di Giulio and Ryan (1987), Panyametheekul (2004), Han et al. (2006), Neculita et al. (2005) among others. The procedure of Neculita et al. (2005) has been widely used for mercury fractionation in highly contaminated soils from chlor-alkali plants (Rodriguez et al., 2000; Bernaus et al., 2006) and was selected for this work.

The chlor-alkali industry, which produces caustic-soda, hydrogen and chlorine by the mercury technology, has been one of the biggest mercury users and emitters. It accounted for 90 % of the global mercury utilisation prior to 1980 (Lacerda and Salomons, 1998), and has been one of the main sources of mercury pollution throughout the world (USEPA, 1997c). Several studies have been carried out in the last decades to assess the impact of chlor-alkali plants on the environment (Maserti and Ferrara, 1991; Biester et al., 2002a; 2002b; Neculita et al., 2005; Zagury et al., 2006; Ulrich et al., 2007, Reis et al., 2009; 2010)

The amounts of mercury used in chlor-alkali plant have been decreasing due to improvements in the process (Eurochlor, 2011) and conversion to the membrane process, which avoids the use of mercury. However, the effects of the mercury pollution will be observed for a long time after production plants have closed down (Turner and Lindberg, 1978; Parks, 1984; Maserti and Ferrara, 1991).

In Cuba, the Electrochemistry plant “Elpidio Sosa” (ELQUIM), located in the central region of the country, constitutes the main source of mercury pollution. This factory has been producing mercury solid wastes for more than forty years and has caused a widespread contamination with mercury in the surrounding environment (Gonzalez, 1991). In 2008 the Cuban government approved the conversion from technology based on the use of mercury cells to a membrane based production process. Nevertheless, the negative impact to the environment and human health could persist for much longer due to the existence of 7668 ton of mercury wastes buried in 52 niches

(values provided by workers of the chlor-alkali Cuban plant/May 2012), unless a properly management policy of these wastes is implemented. The sludge containing mercury is produced by mixing the exhausted mercury of the electrolytic cell with sodium sulphide in a first step and with sodium chloride, calcium carbonate, magnesium hydroxide and diatomaceous earth in a second step. This sludge is currently unsafely disposed in concrete niches. Contact with ground water or rain may cause mercury to leach and contaminate the soil and underground waters.

The elevated mercury content of this mercurial sludge as well as the high toxicity levels have been previously reported by Busto et al. (2011). Leaching tests showed that the stabilization process applied to the mercurial sludge did not prevent significant leaching of mercury, and suggested the presence of rather soluble mercury species such as $HgCl_2$. While Hg fractionation studies are available from soils contaminated by chlor-alkali plants, no information currently exists on the different mercury-bindings forms in the waste itself. The aim of the research was to study the fractionation of Hg in the highly contaminated solid wastes generated by the chlor-alkali Cuban factory. Such information contributes to assessing mobility and availability of mercury in the waste, and thus to an adequate risk assessment while investigating suitable management options for the waste sludge.

4.2. Material and Methods

4.2.1. Sampling and sample preparation

Mercurial sludge was sampled from the Chlor-alkali plant “Elpidio Sosa” located in the north of the central region of Cuba (Sagua La Grande city). It was collected from the niche that was open at the sampling time. A composite sample was prepared from equal amounts of sludge taken from three different points on a diagonal line as well as at three depths (Buduba, 2004). Immediately upon arrival at the laboratory, the sludge was dried and crushed following the procedure outlined in Chapter 3.

4.2.2. Physico-chemical analysis

The pH of the solid waste was measured after 18 h using a pH meter (ORION 520A, Laboratory Extreme, Kent, Michigan, USA) in a suspension of 50 ml of distilled water with 10 g of waste sludge (Cottenie et al., 1982). Electrical conductivity (EC) was determined in a saturation extract (Jackson, 1965) with a Microprocessor Conductivity Meter (LF 537, Weilhem, Germany). The extract was obtained from a suspension of 50 ml of distilled water with 10 g of waste sludge. The suspension was stirred for 30 min and filtered using 0.45 μm pore membrane filters (CM, Porafil, Macherey-Nagel, Düren, Germany). Carbonate content was determined by back-titrating an excess

of 0.50 M H_2SO_4 added to 0.25 g of the sample with 0.50 M NaOH (Nelson, 1982). Organic matter was estimated by weighing before and after ashing 1 g of the sample at 400 °C for 2 h (Van Ranst et al., 1999).

4.2.3. Total mercury determination

Total mercury content was determined by cold vapour atomic absorption spectrometry (Mercury Analyzer MAS-50, Coleman, Oak Brook, Illinois, USA) after a specific destruction as reported by Cottenie (1982). The destruction procedure involved adding 0.05 g of V_2O_5, and 10 ml of concentrated HNO_3 to 0.5 g of sample and digestion for 30 min at 160 ºC. After the samples were cooled down 15 ml of concentrated H_2SO_4 was added and the digestion was completed for 2 h without extra heating. A standard solution of 0.25 mg/l Hg was prepared from 1000 mg/l stock solution (Mercury Standard Solution, MERCK, Darmstadt, Germany). The calibration curve (correlation factor of 0.9981) was obtained by measuring transmittance after injection of different volumes (0, 0.5, 1, 2, 4 and 8 ml). Pseudo total metal content was determined after destruction in aqua regia extract (Ure, 1990), followed by metal determination using Inductivity Coupled Plasma Optical Emission Spectrometry (ICP-OES, Vista MPX CCD Simultaneous, Varian, Mulgrave VIC, Australia). Each determination was carried out in triplicate and all reagents used were of analytical grade.

4.2.4. TCLP leaching test

Mercury leachability in the mercurial waste was evaluated according to the EPA TCLP Procedure (USEPA, 1992). The extraction fluid used depends on the alkalinity of the sample. According to the TCLP procedure, pH (1) value was measured by mixing 5 g of sludge sample and 96.5 ml of deionized water in a 250 ml beaker after stirring for 5 min. This value offers information about the acidic or alkaline properties of the waste. The value of pH (2) is tested after adding 3.5 ml 1 mol/l HCl to the suspension, followed by heating to 50 ºC for 10 min. This provides an indication on the alkalinity of the solid waste. For the analyzed sample, pH (2) was above 5. Accordingly, extractant fluid 2 composed of 5.7 ml glacial CH_3CH_2OOH in 1l deionized water was to be used (USEPA, 1992).

For the TCLP test, 1 g of the sample was introduced in a 100 ml centrifuge tube, and 20 ml of extractant fluid 2 was added. The suspension was agitated during 18 h in an end over end shaker operating at approx. 30 rpm. After agitation, the pH after extraction (pH (3)), was measured. The TCLP leachate was filtered using 0.45 µm membrane filters (CM, Porafil, Macherey-Nagel, Düren, Germany). The filtrate was acidified to pH < 2 using concentrated HNO_3 and stored at 4 °C before analysis. Analysis of Hg determination was carried out by CVAAS as described before.

4.2.5. Sequential extraction

The fractionation of Hg was performed according to the procedure outlined by Neculita et al. (2005). The procedure consists of four steps (Table 4.1).

Table 4.1. Extractants and Hg fractions defined in the sequential extraction procedure of Neculita et al. (2005)

Fraction ID	Extractant	Extractant(ml): sludge(g) ratio	Hg Fraction
F1	Deionized water	20:2	Water soluble
F2	0.5 mol/l NH_4-EDTA (pH 8.4)	20:2	Exchangeable
F3	0.2 M NaOH and 4% CH_3COOH	20:2	Organic

The extraction was performed using 2 g of accurately weighed sludge sample mixed with 20 ml of solvent in a 100 ml centrifuge tube. The tubes were thoroughly shaken for 2 h at 20 ± 2 ºC using the end over end shaker. The supernatant was obtained between each extraction and rinse step, by centrifuging at 3000 rpm for 15 min at 10 ºC followed by filtration using 0.45 μm pore membrane filters. Rinsing steps consisted of washing the leached residues twice with deionised water (20 and 10 ml) for 15 min. Rinses were always subsequently added to the solvent extract from the same sample. The resulting combined supernatant from the first three extraction steps was analyzed for total Hg content by CVAAS. Residual Hg was extracted by adding the same reagents as for total Hg determination in the sludge sample directly in the original 100 ml centrifuge tube. The sample was then transferred into a 100 ml standard volumetric flask. The digestion was performed using the same procedure as previously described for total Hg in the sludge sample.

Total mercury content was determined by cold vapour atomic absorption spectrometry (Mercury Analyzer MAS-50, Coleman, Oak Brook, Illinois, USA) after a specific destruction as reported by Cottenie (1982). The destruction procedure involved adding 0.05 g of V_2O_5, and 10 ml of concentrated HNO_3 to 0.5 g of sample and digestion for 30 min at 160 ºC. After the samples were cooled down 15 ml of concentrated H_2SO_4 was added and the digestion was completed for 2 h without extra heating. A standard solution of 0.25 mg/l Hg was prepared from 1000 mg/l stock solution (Mercury Standard Solution, MERCK, Darmstadt, Germany). The calibration curve was obtained by measuring transmittance after injection of different volumes (0, 0.5, 1, 2, 4 and 8 ml). Pseudo total metal content was determined after destruction in aqua regia extract (Ure, 1990), followed by metal determination using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Vista MPX CCD Simultaneous, Varian, Mulgrave VIC, Australia). Each determination was carried out in triplicate and all reagents used were of analytical grade.

4.3. Results and Discussion

4.3.1. Chemical characteristics of the mercurial sludge

The mercurial sludge exhibited an alkaline pH of 9.9 ± 0.01. This is mainly due to the presence of calcium carbonate and magnesium hydroxide, two components added during the stabilisation of the waste. Carbonate content was in the order of the 60% (Table 4.2), whereas pseudo total analysis revealed high Ca and Mg levels (Table 4.3).

Table 4.2. Chemical characteristics of the mercury solid waste[a]

Parameter	Sample
pH-H_2O	9.9 (0.01)
Organic Matter (g/kg)	163 (2)
$CaCO_3$ (g/kg)	633 (8)
EC [b] (mS/cm)	48 (1)

Note: [a] Values in parenthesis are standard deviations of three replicates. [b] Electrical conductivity.

The presence of carbonates may also be partly due to the use of diatomaceous earth, another component of the mercurial sludge. As reported by Antonides (1998), this compound also contributes with the organic matter content in a 6% (weight).

The high value of electrical conductivity (EC) would allow us classifying the sample as highly saline according to FAO (Rhoades et al., 1992). This value for EC indicates a significant presence of soluble salts which can be linked with the high content of K and Na obtained from the ICP-OES analysis. Relatively high values of Fe were found. This would be linked to the input of diatomaceous earth as an important component of the sludge (291 g/kg of sludge). As reported by Antonides (1998) diatomaceous earth includes normally about 2% (weight/weight) of Fe.

Table 4.3. Pseudo total metal content and total Hg content [a]

Metal content	Sample
Ca (g/kg)	207 (1)
Fe (g/kg)	114 (1)
Al (g/kg)	73 (1)
Na (g/kg)	67.4 (3)
Mg (g/kg)	21 (1)
Cu (g/kg)	2.8 (0.3)
Hg (g/kg)	2.3 (0.4)
K (g/kg)	1.6 (0.2)
Mn (mg/kg)	223 (2)
Zn (mg/kg)	157 (1)
Pb (mg/kg)	128 (2)
Cr (mg/kg)	33 (1)
Cd (mg/kg)	32 (2)
Ni (mg/kg)	24 (1)

Note: [a] Values in parenthesis are standard deviations of three replicates.

Other potentially toxic trace elements were analysed to assess whether they could also be of environmental concern. Contents of these trace elements were elevated compared to normal ranges present in soils (Kabata-Pendias and Pendias, 1984).

4.3.2. Mercury contents and leachability

The total mercury content was above 260 mg Hg/kg of sludge (2320 mg/kg), allowing the material to be classified as 'hazardous high mercury waste' according to US EPA: LDR (USEPA, 2008a). Mercury leaching from the sample more than doubled the EPA TCLP limit of 0.2 mg/l. Consequently, the waste is classified as 'toxic waste' according to US EPA regulations (USEPA, 1992). According to USEPA (2008a) this sludge has to be treated (thermal treatment) for its final disposal in a safe way.

4.3.3. Evaluation of the environmental risk (mercurial sludge fractionation)

The sum of the sequentially extracted fractions amounted to 95.8 ± 1.8% of the total content, indicating a good recovery. Mercury recoveries lower than 100% can be explained by the loss of volatile Hg species during the manipulation (Neculita et al., 2005). The different fractions are represented in Figure 4.1 as percentage of the total content. The distribution among the different fractions followed the order F4>F2>F1>F3. The residual fraction, F4, represented the largest

fraction, including 42.7 ± 1% of the total content. Neculita et al. (2005) in the fractionation study carried out in highly contaminated soils from a chlor-alkali plant, linked the residual fraction to the presence of HgS.

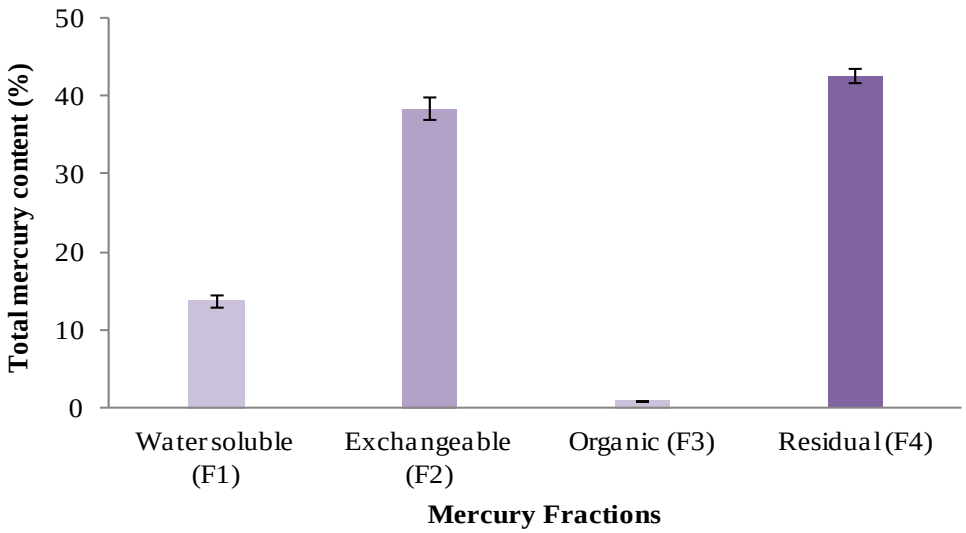


Figure 4.1. Mercury fractionation in contaminated solid waste from chlor-alkali Cuban plant using sequential extraction procedure (error bars mean ± standard deviations, n = 4)

In the chlor-alkali Cuban plant, where the mercury in the wastes is present as $HgCl_2$, the precipitation reaction with Na_2S promotes the formation of HgS. For this reason, in this chapter the residual fraction of mercury was correlated with the presence of HgS in the sludge sample. It is well known that the black HgS (metacinnabar) form can be obtained by the precipitation reaction from $HgCl_2$ solution using Na_2S solution (Biester et al., 2002b). The second main group of mercury species was extracted within the "exchangeable phase" (F2) representing 38.5 ± 1.3% of the total mercury content. This fraction can be correlated with soluble species of mercury in the oxic layer of the sludge matrix. The water-soluble fraction (F1) represented 13.7 ± 0.8% of total Hg and it is recognized as very important from an environmental risk point of view due to its easy availability in environmental weathering conditions (Bloom et al., 2003). This fraction should be treated with caution because its mercury content (318.8 mg/kg) exceeded the permissible limit established by the USEPA regulation LDR: 40 CFR Part 273 (USEPA, 2008a) by 22.6%. Mercurial wastes which contain more than 260 mg Hg/kg of total mercury content must be treated before final disposal (USEPA, 2008a).

Although the mercury content present in the fraction F3 (organic) only accounts for 0.9 ± 0.1% of the total Hg content, it still represents a significant amount (21.2 mg/kg) and therefore an environmental concern. This result can be correlated with the 16.3% of organic matter obtained in

the sludge sample (Table 4.1). The affinity of Hg for organic matter and especially for S-containing groups of organic molecules is well known (Xia et al., 1999; Yu et al., 2006). Nevertheless, several studies developed in polluted soils near chlor-alkali plants (Hempel et al., 1995; Bloom et al., 2003; Neculita et al., 2005) demonstrated that high organic carbon content do not entail a high proportion of methylmercury. For instance, it was reported by Neculita et al. (2005) that in CAP contaminated soils with an organic carbon content of 18.2 g/kg the methylmercury only accounted for 0.00008% of total Hg. A significant environmental concern arises from the high Hg levels recovered in fractions F1 and F2 in this sludge. These fractions include water-soluble and exchangeable mercury compounds such as $HgCl_2$, $HgSO_4$ and HgO, and thus represent a mobile Hg fraction that can easily be leached from the sludge (Neculita et al., 2005; Bernaus et al., 2006). The sum of the mobile Hg fractions (F1 + F2) corresponded with 52.2 ± 1.5% of the total Hg, clearly indicating an elevated risk for Hg mobilisation.

4.4. Conclusions

The high mercury content in the studied sludge, the TCLP result as well as the mercury fractionation analysis suggest highly significant potential mercury mobility via the sludge solution, thus representing a significant environmental hazard if not disposed in tightly sealed conditions. The high total mercury content (2320 mg/kg) and the high concentrations in the TCLP extract allow to classify the sample as a toxic waste according to US EPA regulations. The fractionation revealed that a major fraction of the total Hg was insufficiently stabilized, as only 42% of the total Hg was associated with the residual fraction. The mobile Hg fraction (F1 + F2) represents the major fraction of the total mercury found in the sample (52.2%) indicating a high risk of Hg mobilisation by the presence of water soluble and exchangeable mercury compounds such as $HgCl_2$, $HgSO_4$ and HgO.

CHAPTER 5

POTENTIAL OF THERMAL TREATMENT FOR DECONTAMINATION OF MERCURY CONTAINING WASTES FROM CHLOR-ALKALI INDUSTRY

Old dumps of mercury waste sludges from chlor-alkaline industry are an environmental threat if not properly secured. Thermal retortion can be used to remove mercury from such wastes. This treatment reduces the total mercury content, and also may reduce the leachability of the residual mercury. The effects of treatment temperature and treatment time on both residual mercury levels and mercury leachability according to the US EPA TCLP leaching procedure were investigated. Treatment for 1 h at 800 °C allowed to quantitatively removing the mercury. Treatment at 400 °C and above allowed decreasing the leachable Hg contents to below the US EPA regulations. The ultimate choice of treatment conditions will depend on requirements of further handling options and cost considerations.

Redrafted from:

Busto, Y., Cabrera, X., Tack, F. M. G., Verloo, M. G. 2011. Potential of thermal treatment for decontamination of mercury containing wastes from chlor-alkali industry. *Journal of Hazardous Materials* **186**: 114-118.

5.1. Introduction

High mercury-containing wastes can constitute a significant environmental threat when not handled properly. The amount of Hg in wastes only in the EU has been estimated at about 990 metric tonnes (Mukherjee, et al., 2004). An important industrial source of high mercury waste is the electrochemical production of chlor-alkali from cells with mercury cathodes (Zhuang et al., 2004; Neculita et al., 2005; Bernaus et al., 2006; Taube et al., 2008). Although at present membrane cell and diaphragm cell processes are replacing Hg cell technology, there are hundreds of tons of Hg contaminated wastes accumulated and buried. This research concerns mercury waste disposed in the central region of Cuba Island. The current storage of the waste in concrete niches is inadequate, allowing Hg to leach from the waste. The regular occurrence of natural disasters such as hurricanes, inundations and earthquakes aggravates the risks for dispersion of Hg into the environment.

Recycling of waste is higher up the "waste management hierarchy" than landfill disposal (Mukherjee et al., 2004). If economically or environmentally viable, hazardous waste should be recycled, limiting the risk to environment and public health. Technologies applied for removal or stabilization of Hg in contaminated solid waste or soil include solidification/stabilization (Zhuang et al., 2004; Piao and Bishop, 2006; USEPA, 2007; Svensson and Allard, 2008; Xiong et al., 2009), soil washing (Dronen et al., 2004; USEPA, 2007; Lesa et al., 2009), thermal treatment (Washburn and Hill, 2003; Kunkel et al., 2006; Chang and Yen, 2006; USEPA, 2007; Chang et al., 2009), and vitrification (USEPA, 2007).

Soil washing and acid extraction are used for ex situ treatment of mercury-contaminated soil and sediment. These technologies have been implemented at the full scale and pilot scale. In soil washing, the contaminants are preferentially adsorbed onto the fines fraction of the soil or sediment. The separated fines must be further treated to remove or immobilize the contaminant. In acid extraction, the process depends on the solubility of the contaminants in the acidic extraction solution. Spent extraction solution may require further treatment (USEPA, 2007).

Vitrification is a high-temperature treatment technology designed to immobilize contaminants by incorporating them into the vitrified end product, which is chemically durable and leach resistant. This treatment requires a large amount of energy to achieve vitrification temperatures. Also, the wastes with high concentrations of mercury, chlorides, fluorides, sulphides, and sulphates may limit the performance of this process (USEPA, 2007).

Stabilization/Solidification (S/S) are applied for reducing the mobility of mercury contaminants in the environment by employing additives to trap or immobilize contaminants within solid wastes through both physical and chemical means (Zhuang et al., 2004). The stabilizing agents more used

are trisodium salt of trimercapto-s triazine (TMT), sulphur, fly ash, pozzolan, Portland cement, lignin derivatives, polymers and other wastes (Zhuang et al., 2003a; 2003b).

Thermal treatment processes (thermal desorption or retorting) are physical methods to remove mercury from contaminated medium where heat is supplied under reduced pressure to the contaminated soil or waste, to facilitate volatilization of mercury. The off-gas is treated by condensation to generate liquid elemental mercury (USEPA, 2007). The main difference between retorting and thermal desorption process is that first one does not involve agitation. Retorting is a thermal treatment method involving distillation or dry distillation (Washburn and Hill, 2003). It is a method recommended by US EPA to treat high mercury content waste (> 260 mg/kg) (USEPA, 2008a).

The present Chapter aims to investigate the potentialities of the thermal treatment to decontaminate mercury containing wastes from the chlor-alkali Cuban production process. The effects of temperature and exposure time on the efficiency of mercury reduction of this mercury waste are assessed. The effect of the treatment is evaluated based on reduction in total contents and reduction in leachability according to the US-EPA Toxicity Characteristic Leaching Procedure (USEPA, 2008b).

5.2. Material and Methods

5.2.1. Mercury waste sampling and preparation

The solid waste samples used in this chapter were collected from two different niches following the collected procedure explained in previous chapters. These samples were combined in order to obtain two composite samples representative for each niche. Immediately upon arrival at the laboratory, the sludge samples were prepared for the further analyses following the same method explained in Chapter 3. The samples are referred to as Sample A and Sample B.

5.2.2. Sample characterization

Cation exchange capacity (CEC) at neutral pH was determined by the ammonium acetate method using 5 g of mercurial waste (Van Ranst et al., 1999). To determine the chloride content 1 g of sediment was suspended in 50 ml of 0.15 mol/l HNO_3 and shaken for 30 min. The filtrate was titrated with 0.05 mol/l $AgNO_3$ using potentiometric end-point detection (Van Ranst et al., 1999) by potentiometer Metrohm, 761 Compact IC, Switzerland. Organic matter was estimated through the loss on ignition (LOI) method as reported by Heiri et al. (2001) for organic matter determination in soils. In this test 5 g of the sludge sample was heating during 1 h at 400 °C. The weight loss was determined and assumed to represent the organic matter content in the sludge. Pseudo-total metal

content and pH-water were determined using the methods described in Chapter 4. All analyses were carried out in triplicate.

5.2.3. Mercury determination

Total mercury content was determined by Cold Vapour Atomic Absorption Spectrometry (Mercury Analyzer MAS-50, Coleman, IL, USA) following the method explained in Chapter 4. To measure Hg, the digest was transferred to a mercury reduction vessel. After addition of $SnCl_2$, the solution was purged and the gasses were introduced into the mercury analyzer. Peak absorbance was recorded. A standard solution of 0.25 mg/l Hg was prepared from 1000 mg/l stock solution (MERCK, Darmstadt, Germany). The calibration curve was obtained by injecting different volumes of this 0.25 mg/l stock solution (0, 0.5, 1, 2, 4 and 8ml) into the Hg reduction vessel. The calibration was used only when a correlation better than 0.99 was achieved. All reagents used were analytical grade.

5.2.4. TCLP tests

Mercury toxicity levels in the mercury waste and the ashes resulting from the thermal treatments were evaluated according to the EPA TCLP Procedure (USEPA, 1992). As was explained previously in Chapter 4, the extraction fluid used depends on the alkalinity of the residual solid phase. According to the TCLP procedure, pH (1) value was measured by mixing 5 g of sludge sample and 96.5 ml of deionized water in a 250 ml beaker after stirring for 5 min. This pH-value provides an indication of the acidic or alkaline properties of the waste. The value of pH (2) is tested after adding 3.5 ml 1mol/l HCl to the suspension, followed by heating to 50 °C for 10 min. This provides an indication on the alkalinity of the waste solids. If pH (2) is below 5, an acetic acid/acetate buffer solution is used (extraction fluid #1). Otherwise, a more acidic extractant fluid #2 composed of 5.7 ml glacial CH_3CH_2OOH in 1 l deionized water, must be used. Both samples required the use of the latter extracting solution.

For extraction, 1 g of the sample was introduced in 100 ml high density polyethylene (HDPE) extraction vessels, and 20 ml of extractant fluid 2 was added. Suspensions were agitated during 18 h in the end over end shaker operating at approx. 30 rpm. After agitation, the final pH, pH (3), was measured. The TCLP leachates were filtered using 0.45 μm pore membrane filters (CM, Porafil, Macherey-Nagel, Düren, Germany). The filtrates were acidified to pH < 2 using concentrated HNO_3 and stored at 4 °C before analysis. Analysis of Hg determination was carried out by CVAAS as described before.

5.2.5. Thermal treatment

Experiments at different temperatures and times were carried out at the laboratory scale to simulate the retorting conditions. A muffle furnace (Carbolite type P330 Controller, Nabertherm, Bremen, Germany) located inside a fume cupboard Model Potteau, Belgium, was used. Each test involved ashing 5 g of dried and ground mercury waste in a porcelain crucible in different conditions. In a preliminary test series, mercury removal after treatment at 600 and 800 °C during 30 and 60 min was evaluated. No replicates were done. In a second test series, temperature was varied between 100 and 800 °C in increments of 100 °C. Retorting time was 1 h. These tests were triplicated.

5.3. Results and Discussion

5.3.1. Chemical and physical characterization of samples

The wastes reveal themselves as grey powders. The pH in water is high, at about 10. This would suggest the presence of lime compounds (CaO, MgO) next to lime stone ($CaCO_3$, $MgCO_3$). Compounds where limestone dominates would exhibit a pH between 7.5 and 8.5 (Lindsay, 1979). No organic carbon determination is available, but for soils and sediments, loss on ignition at 400 °C can provide a good estimate of organic matter (Heiri et al., 2001). Although this estimate is less precise for waste materials, weight loss of the waste at 400 °C may indicate organic matter levels in the order of 8-10%. The wastes exhibit some cation exchange capacity, although it is small and comparable to typical light textured soils (Brady and Weil, 1990). As such, it is not expected to be capable of retaining significant amounts of cations on the sorption complex. Differences in CEC between the samples could be related mostly to differences in organic matter content, which is a prime component contributing CEC to a soil (Brady and Weil, 1990).

The mercury wastes contained high levels of Ca, Mg, and Na (Table 5.1). The presence of Na is associated with the brine used for electrolysis, the use of Na_2CO_3 and NaOH used for the purification of the brine, and the use of Na_2S for precipitation of Hg. The presence of Ca and Mg is explained by to the use of calcareous products such as $CaCO_3$ and $Mg(OH)_2$ to increase pH and stabilize the sludge. Significant amounts of Na^+ are explained by the use of NaCl in the electrolytic process and the high Fe values are provided by diatomaceous earth composition, which also contributes to stabilization of the wastes. The typical chemical composition of diatomaceous earth includes about 2% iron (Antonides, 1998).

Table 5.1. Properties and metal contents of mercury sludge samples (means ± standard deviations, n = 3)

Parameter	Sample A	Sample B
pH-H_2O	9.96 (0.01)	9.98 (0.02)
Chloride (g/kg)	178 (1)	94 (2)
Org Matter Content (g/kg)	85 (9)	100 (8)
CEC ($cmol_c$/kg)	3.2 (0.3)	6.7 (0.4)
Total Metal Content (g/kg DM)		
Ca	156.19 (5)	125 (1)
Mg	46.5 (0.1)	36.3 (0.3)
Na	128 (3)	36 (0.7)
Fe	4.97 (0.05)	4.93 (0.03)
K	1.01 (0.001)	0.54 (0.003)
Total Metal Content (mg/kg DM)		
Cd	1.06 (0.02)	1.99 (0.01)
Cr	15.0 (0.6)	19.0 (1.3)
Cu	63 (3)	170 (2)
Mn	132 (1)	136 (0.1)
Ni	10.4 (0.4)	10.6 (0.3)
Pb	15.1 (0.06)	26.9 (0.6)
Zn	159 (2)	121 (2)
Hg	505 (17)	1205 (16)

As expected, the waste materials contain significant amounts of Hg, at 505 mg/kg dry matter for the first sample and 1205 mg/kg for the second. Considering levels that naturally occur in soils (< 0.4 mg/kg) as a worldwide average in soils as is reported by Kabata-Pendias and Pendias (1984), these concentrations are extremely high. With Hg total contents exceeding 260 mg/kg, the waste is characterized as high mercury waste according to the US Land Disposal Restrictions. This result is consistent with previous one obtained in Chapters 3 and 4. Important differences in Hg contents and other properties between the samples reflect the two different niches, where sediment from different batches and time periods were disposed. Unfortunately, there is no record on the exact time of disposal in these niches.

Other potential toxic trace elements were analyzed to assess whether they could also be of environmental concern. Chromium, Mn, Ni, and Pb were well within levels normally present in soils (Brady and Weil, 1990), and thus are not expected to pose any problem. Contents of Cd, Cu and Zn were somewhat elevated compared to normal ranges in soils, but still in the same order.

Hence, no significant issues are anticipated also with these elements, although a final conclusion would require further testing.

Table 5.2. pH and Hg concentrations in extracts according to the TCLP leaching test (mean ± standard deviation, n = 3).

Sample	A	B
pH (3)	7.84 (0.16)	8.07 (0.07)
Hg (mg/l)	3.85 (0.24)	0.32 (0.05)

Note: Mercury content by USEPA Regulations: 0.20 mg/l.

Mercury leaching from both samples exceeded the EPA TCLP limit of 0.2 mg/l (Table 5.2). Hence, the waste is classified as toxic waste according to USEPA regulations. The significant difference in leachability between samples, an order of 10, reflects the different nature of the waste in the various niches, and the variability in composition and behaviour of wastes generated at different times. Surprisingly, the waste with the higher total mercury content (waste B) is the one with the least Hg leaching. This could partly be explained by a higher buffering capacity, which is reflected in a higher pH after the extraction. Theoretically, $Hg(OH)_2$ solubility is expected to decrease by a factor 100 for each unit increase in pH (Lindsay, 1979). As such, a pH difference of only 0.25 units is very important with respect to leaching behaviour.

5.3.2. Thermal treatment

Table 5.3 shows ash rest and mercury removal efficiency at 600 °C and 800 °C, for 30 min and 1 h. Efficiency was calculated as the difference between mercury content in the sludge sample before and after the treatment divided by the mercury content before the retorting treatment. The lowest values of ash content and average Hg content in the remaining ash were consistently obtained at higher temperature and exposition time. The effect of temperature was much stronger than the effect of time. In a follow up experiment, the exposure time of 1 h was adopted, and the effect of temperature was investigated in more detail.

Table 5.3. Effects of time and temperature on residual ash content, residual Hg content and Hg removal efficiency

Temp. (°C)	Time (min)	% ash		Residual Hg (mg/kg)		Treatment efficiency (%)	
		A	B	A	B	A	B
600	30	86.4	81.4	12.4	11.8	97.6	99.0
800	30	74.0	68.7	1.25	0.52	99.7	100.0
600	60	85.0	80.1	9.9	8.6	98.0	99.3
800	60	71.9	65.9	0.18	0.11	100.0	100.0

Figure 5.1 reveals the decrease in ashes residue with temperature. Although weight loss of both samples followed the same trend, sample A exhibited less decrease in weight than sample B. Organic matter content and loss of crystalline bound water mostly explain weight decreases up to 400-500 °C. Above that temperature, carbonate compounds increasingly will decompose to oxides, e.g. CaO and MgO (Heiri et al., 2001). This is observed by the additional decrease in ash residue above 500 °C.

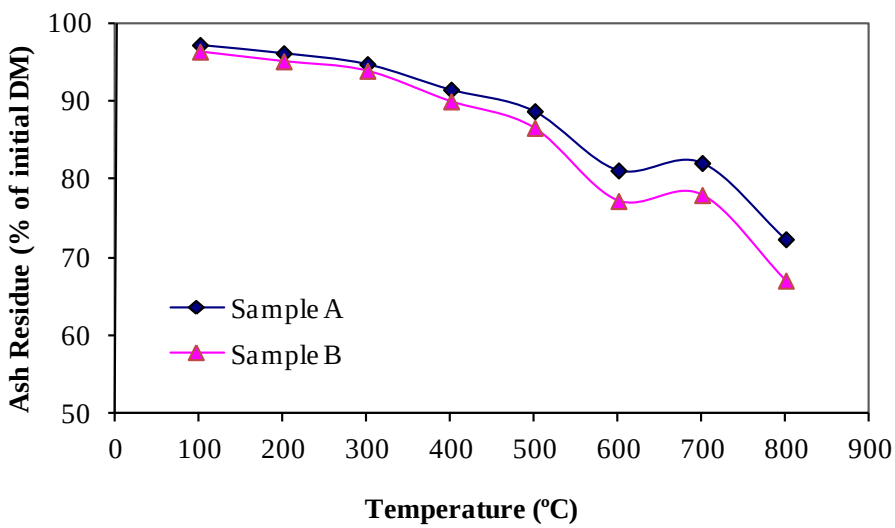


Figure 5.1. Influence of retorting temperature during 1 h on the residual ash, expressed as percentage of the initial dry mercury sludge.

Up to 300 °C the removal of Hg was low, below 50% (Table 5.4). Similar results were obtained by Taube et al. (2008) but working with mercury contaminated soils. Mercury removal became highly efficient (more than 90% removal) when temperature was higher than 300 °C. Similar results were reported by Chang and Yen (2006). Samples behave with differences between them at low temperatures (< 400 °C) and in similar way above 600 °C.

Table 5.4. Total mercury and mercury removal efficiency remaining after thermal treatment of the mercury sludges as a function of treatment temperature.

Temp. (°C)	Residual Hg content (mg/kg on ash)[a]		Hg removal efficiency (%)	
	A	B	A	B
20	505 (17)	1205 (16)	-	-
100	489 (23)	1473 (190)	3.1	-
200	236 (34)	814 (34)	53.3	32.5
300	40 (3)	47 (6)	92.1	96.1
400	31 (3)	33 (3)	93.8	97.3
500	20.0 (0.7)	20.0 (0.8)	96.1	98.4
600	10.1 (0.9)	11.2 (2.1)	98.0	99.1
700	3.1 (1.2)	2.1 (0.9)	99.4	99.8
800	0.1 (0.07)	0.1 (0.01)	100.0	100.0

Note: [a] Average and standard deviation of three replicates.

5.3.3. Leachability of the treated wastes

Figure 5.2 shows the final pH after extraction as a function of temperature. Considering that the initial pH of the extracting solution is 2.88, the high pH values after extraction reveal the large buffering capacity of the wastes. The extraction fluid used consisted of 0.1 mol/l acetic acid. In the conditions of the extraction, at most 0.1 g of $CaCO_3$-equivalent can be neutralized. The excess of calcareous materials therefore determines the pH after extraction.

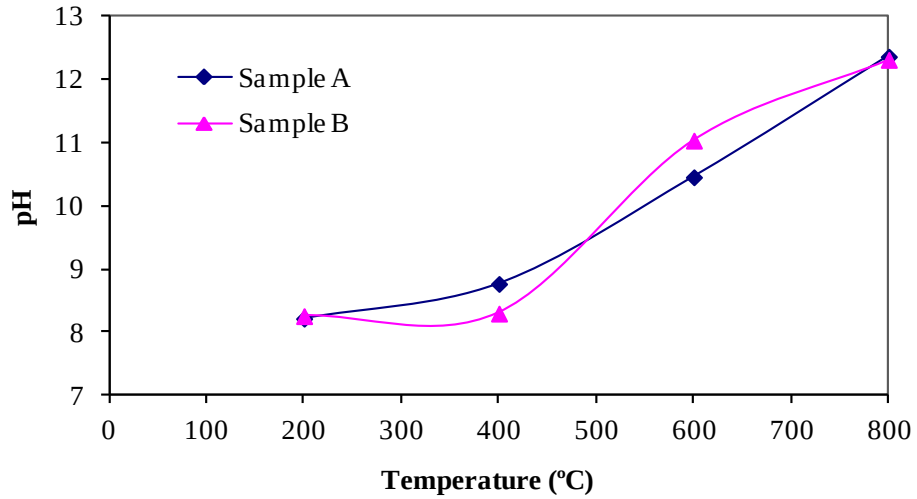


Figure 5.2. Final pH of the TCLP extract of mercury sludges, treated during 1 h at increasing temperatures.

The increase in final extraction pH above 500 °C reflects the increasing conversion of carbonates to oxides during the retorting process. Whereas carbonate compounds governed the final pH under 500 °C, increasingly hydroxides governed the final pH at increasing temperatures. Figure 5.3 reveals a decrease in TCLP leachable Hg with temperature. Treatments at temperatures above about 350 °C allowed to decrease Hg leachability in the residue to below the TCLP reference value, and would cause the product not anymore to be classified as toxic waste. Current experiments reveal that technically, the thermal treatment allows decreasing total mercury contents, and consequently also achieves to reduce leachability to values below the threshold value.

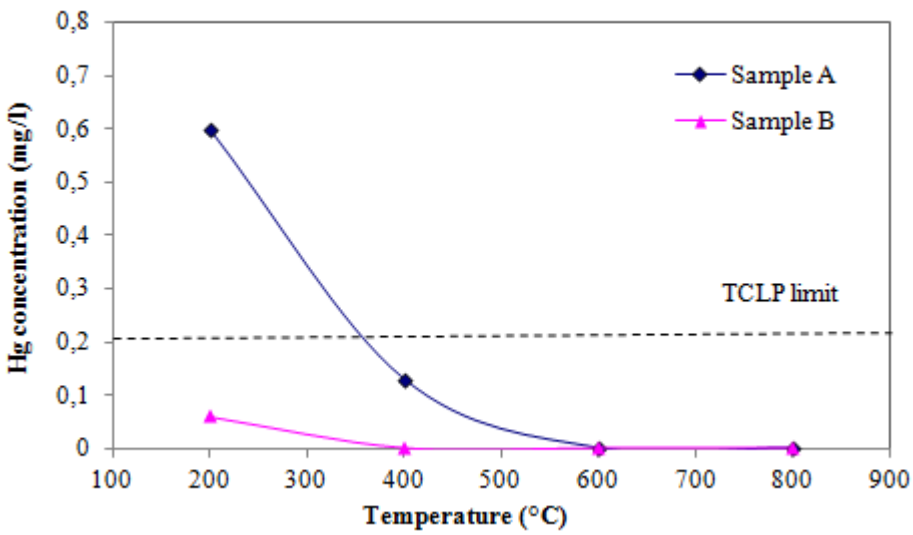


Figure 5.3. Mercury concentrations in TCLP extracts of mercury sludges, treated at increasing temperatures.

The optimal operating conditions for the retorting operations will depend on subsequent handling options for the treated waste. Provided total contents of other elements are not a limiting factor, the material may be considered for reuse in construction or landscaping. This would require retorting conditions that reduce total mercury contents to below limits considered acceptable for this type of use. In case the treated material is to be disposed again, milder conditions for retorting could be used, that decrease mercury leaching to below the threshold level, without eliminating all total mercury contents. While the first option would lead to an elimination of this waste problem, associated costs might be prohibitive. Economic considerations in combination with different requirements for different handling options e.g. reuse or disposal, will ultimately determine the optimal treatment conditions of the retortment process.

As an element, mercury is never destroyed in any waste treatment process, but only transferred. The retorting process, which is based on volatilization and subsequent condensation of the mercury vapour, results in the recovery of metallic mercury (Washburn and Hill, 2003; Chang and Yen,

2006). As such, 1000 m^3 of mercury sludge would yield about 0.125 m^3 of metallic Hg, assuming a bulk density of 1700 kg/m^3 for the sludge. The recovered metallic mercury has a purity of 99% (Chang and Yen, 2006) and could be recycled or be disposed in smaller containers depending of the industrial management interest. These aspects require further investigation, preferably based on pilot scale studies.

5.4. Conclusions

Regarding with the results obtained in the present Chapter, the waste sludge of chlor-alkali industry that was studied is considered as a toxic waste, based both on total contents and leachability of Hg. The current storage in poorly confined niches constitutes a significant risk for Hg dispersion into the surrounding environment. Moreover, it was demonstrated that Thermal treatment is very effective to remove mercury from wastes sludge generated by chlor-alkali industry considering the high mercury removal efficiency, close to 100% obtained in this survey. Leachability according to the US EPA TCLP leaching test decreases below the threshold value of 0.2 mg Hg/l after treatment at a temperature of 400 °C or higher. Optimal operating conditions will depend on the requirements of further handling options and cost considerations.

CHAPTER 6

KINETIC MODELLING OF MERCURY REMOVAL FROM CONTAMINATED SOLID WASTE GENERATED BY CHLOR-ALKALI PLANT USING THERMAL TREATMENT

A kinetic model to describe mercury removal from solid waste generated by the chlor-alkali process using thermal technology was developed. The isoconversional method of kinetic analysis was used to calculate the kinetic parameters that best describe mercury thermal decomposition in the solid waste. A mechanism involving 6 heterogeneous and homogeneous reactions was proposed to represent the behaviour of mercury compounds in the solid matrix during thermal treatment. The proposed model was compared to nine models previously reported in literatures to elucidate the controlling reaction mechanism. Fitting each of these to the experimental data of thermal decomposition of the mercurial sludge sample, confirmed the hypothesis that not a single mechanism is ruling the process. The D_1-diffusion mechanism could be considered the controlling step of the process at high retention times while at low thermal decomposition times (< 15 min) the diffusion mechanism (D_1) as well as the third order reaction mechanism (F_3) could be controlling the process. Nevertheless, as a first depth-in to the knowledge of this polydisperse and multicomponent system (mercurial sludge), the diffusion mechanism (D_1) can be considered the overall controlling stage as an increase of temperature smooths the progress of the chemical reactions involved.

6.1. Introduction

Mercury (Hg) is a globally spread pollutant due to its low melting and boiling points, conversions between chemical forms and its involvement in biological cycles (Hylander and Meili, 2003). The US Environmental Protection Agency (US EPA) reported 290 sites included in the National Priorities List showing Hg contamination and from them 173 were of mercury contaminated soils (USEPA, 2007).

Anthropogenic emissions of mercury are leading to a general increase in mercury pollution at local, regional and global scales (Reis et al., 2009). Mercury represents a huge environmental threat since it is highly toxic, persistent, bio-accumulative and can cause neurological damage (Zhang et al., 2009). Among the primary sources of mercury anthropogenic emissions are those where mercury is emitted as an unintentional 'by- product'. Such emissions come from sectors that involve coal or oil combustion, pig iron and steel production, non-ferrous metals production, and cement production (Streets et al., 2005; Pacyna et al., 2006). On the other hand, the three largest secondary sources of mercury anthropogenic emissions include artisanal and small-scale gold mining (ASGM) (Telmer and Veiga, 2008), the production of vinyl chloride monomer (VCM) with the use of mercuric chloride as catalyst and the chlor-alkali industry (Swain et al., 2007).

In 2000, the chlor-alkali industry was, with an emission of 40.4 ton/y responsible for about 17% of the total anthropogenic mercury emissions in Europe (Pacyna et al., 2006). The amount of mercury in wastes from chlor-alkali productions has been estimated at about 990 ton in the EU only (Mukherjee et al., 2004).

Over the last decades, increased awareness of the negative impact of mercury for the environment and human health has led to stronger regulations against its emissions (Schroeder and Munthe, 1998). Mercury cell chlor-alkali plants are not anymore considered a good industrial practice and the Integrated Pollution Prevention and Control (IPPC) of the European Union has indicated that chlor-alkali installations require obtaining licenses based on the Best Available Techniques (Directive 2008/1/EC, 2008). The best available technique for mercury cell chlor-alkali plants is considered to be the conversion to membrane cell technology.

In the United States, only five mercury plants were kept in operation by late 2008. In Europe, mercury cells accounted for 43% of the mounted capacity in 2006 and Western European producers have been committed to closing or converting all remaining chlor-alkali mercury plants by 2020 (UNEP, 2007). This technology seems to be in decline. Nevertheless, the potential risk represented by thousands of tonnes of mercury wastes generated by this process will remain for a long period of time even after the shutdown or conversion to cleaner technologies of these chlor-alkali plants.

Cuba as a developing country still uses mercury cell technology to produce gaseous chlorine and caustic soda. It currently hosts more than 7000 tons of mercury contaminated wastes buried in concrete niches. Mercury wastes generated by the electrochemical Cuban plant were characterized as 'high mercury waste' (total Hg content exceeding 260 mg/kg) according to the US Land Disposal Restrictions (USEPA, 2008a) (Chapter 5, Busto et al., 2011). According to (USEPA, 1997d), thermal treatment represents the most suitable technology for ‘high mercury wastes’. The potential of this approach to decontaminate the mercury containing wastes from the chlor-alkali industry in Cuba has been explored in Chapter 5.

Despite the fact that thermal treatment, specifically by retorting method, is a widely used technology to treat solid wastes highly contaminated with mercury (e.g. mercury wastes from the chlor-alkali process), almost all studies have focused so far mainly on achieving the best operating conditions at pilot and industrial scale that increases the mercury removal efficiency of this treatment (De Percin, 1995; Smith et al., 2001; Chang and Yen, 2006; Chang et al., 2009; Huang et al., 2011). In contrast, very few studies have been published on the kinetic reaction mechanism representing mercury behaviour during the thermal treatment (Taube et al., 2008).

Many kinetic models exist for homogeneous mercury reactions in the gas phase. These have been studied specifically in the context of exhaust gases emitted from coal-fired power plants (Galbreath and Zygarlicke, 2000; Agarwal and Stenger, 2007; Xu et al., 2008). Many studies have been dedicated to unravel the reaction mechanisms of homogeneous mercury oxidation (Sliger et al., 1998; 2000; Senior et al., 2000; Edwards et al., 2001; Niksa et al., 2001; Xu et al., 2003; Li et al., 2003; Zheng et al., 2005; Krishnakumar and Helble, 2007; 2012). An elementary reaction mechanism for homogeneous Hg^0 oxidation with an emphasis on major interactions among Cl^- species and other pollutants in coal derived exhausts has been proposed and evaluated (Niksa et al., 2001). The kinetic mechanism of mercury oxidation, by *ab initio* calculations of quantum chemistry has been studied and the rate constant calculated using the transition state theory (Zheng et al., 2005). Recently, using the transition state theory, rate constants for the 8-step homogeneous Hg-Cl reaction mechanism that describe mercury oxidation in combustion systems have been determined (Krishnakumar and Helble, 2012).

Heterogeneous mercury reactions have been less studied, only thermal decomposition of mercury oxide seems to play an important role in the knowledge of the mercury solid phase reactions (L´vov, 1999; 2007; L´vov et al., 2004). The kinetic and thermal decomposition of HgO was studied and a dissociative evaporation scheme which includes two different HgO(s) reactions at high (> 650 K) and low decomposition temperature was developed (L'vov, 1999). Moreover, an investigation of the retardation effect of oxygen on the evaporation rate of HgO concluded that the

dissociative evaporation of HgO proceeds with the release of atomic oxygen as a primary product of decomposition (L'vov et al., 2004). The mechanism of thermal decomposition of $Mg(OH)_2$ has been studied (L'vov et al., 1998; L'vov and Ugolkov, 2004) and several studies on the mechanism of thermal decomposition of alkaline-earth carbonates metals, in particular, $CaCO_3$ have been carried out (L'vov, 1997; 2001; 2007). Nevertheless, based on a literature survey, there are no kinetic and thermodynamic studies about the mechanism of mercury removal during thermal treatment which includes homogeneous and heterogeneous reactions and the behaviour of the other compounds present in the solid matrix. The purpose of this study is to properly formulate a kinetic reaction mechanism that describes mercury removal by thermal treatment, using retorting method. The proposed reaction mechanism considers both homogeneous and heterogeneous mercury reactions, the species of mercury present in the sludge matrix as well as the chemical-physical properties of the mercurial sludge. The thermodynamic and kinetic parameters that best describe the kinetic model of mercury thermal decomposition in the solid waste are determined and the controlling reaction mechanism is investigated comparing the proposed model with nine previously reported in literature.

6.2. Material and Methods

6.2.1. Sampling and chemical analysis

The mercurial sludge sample used for the experiment was collected from a filled niche, located around the chlor-alkali Cuban factory. Sampling, sample preparation and chemical analysis has been described in Chapter 5.

6.2.2. Thermal treatment set-up at bench scale

Thermal treatment was performed at the laboratory scale using a ceramic muffle furnace (L9/11/SKM/P330 Model, Nabertherm, Germany, Bremen) which has a temperature control accurate to ±1 °C. The oven was located inside a fume cupboard (Model Potteau, Belgium) to avoid pollution with mercury vapours.

The thermal decomposition of the sludge sample was studied in a flowing air atmosphere. For the kinetic study of mercury removal in the solid waste, total mercury content determinations for retorting temperatures of 250, 350 and 450 °C and for treatment times of 5, 10, 25, 30, 40, 50, 60, 90, 120 and 150 min were conducted. The test was carried out by ashing 3 g of dried and ground mercury waste in a porcelain crucible. Total mercury content in the original sample and in the ashes obtained from the retorting experiment was determined in order to assess mercury removal. From thermal analysis at retorting temperatures of 250, 350 and 450 °C and for treatment times of 5, 25,

60, 120 and 150 min, the resulting samples were subjected to a TCLP test in order to evaluate the influence of the retorting temperature on the toxicity level of the sample.

6.2.3. Thermodynamic analysis

Thermodynamic analyses were performed using Mondeja's Methodology (Smith, 1991) which is based on Kirchhoff's Equation. This equation expresses the temperature dependence of the thermal quantities associated with a chemical reaction through the difference in heat capacities between the products and reactants taking into account their stochiometric coefficients in the reaction equation (Aleksander, 1979).

To obtain the thermodynamic parameters through Mondeja's Methodology, the following equations were considered:

$$\Delta Cp = \Delta\alpha_i \cdot T + \Delta\beta_i \cdot T^2 + \Delta\gamma_i \cdot T^3 \tag{6.1}$$

$$\Delta H_j = IH_j + \Delta\alpha_i \cdot T + \frac{\Delta\beta_i}{2} \cdot T^2 + \frac{\Delta\gamma_i}{3} \cdot T^3 \tag{6.2}$$

$$IH_j = \Delta H^0 - \Delta\alpha_i \cdot Tr - \frac{\Delta\beta_i}{2} \cdot Tr^2 - \frac{\Delta\gamma_i}{3} \cdot Tr^3 \tag{6.3}$$

$$\Delta G_j = IH_j - \Delta\alpha_i \cdot T \cdot \ln(T) - \frac{\Delta\beta_i}{2} \cdot T^2 - \frac{\Delta\gamma_i}{6} \cdot T^3 - IK_j \cdot R \cdot T \tag{6.4}$$

$$IK_j = \frac{(IH_j - \Delta\alpha_i \cdot Tr \cdot \ln(Tr) - (\frac{\Delta\beta_i}{2}) \cdot Tr^2 - \frac{\Delta\gamma_i}{6} \cdot Tr^3 - \Delta G^0}{R \cdot Tr} \tag{6.5}$$

$$\ln Ke_j = \frac{-IH_j}{R \cdot T} + \frac{\Delta\alpha_i \cdot \ln(T)}{R} + \frac{\Delta\beta_i \cdot T}{2R} + \frac{\Delta\gamma_i \cdot T^2}{6R} + IK_j \tag{6.6}$$

where α_i, β_i and γ_i are the coefficients of the empiric model with polynomial adjust which correlate the heat capacity (Cp) with the temperature (T); T_r, Ke_j, IK_j and IH_j are the reference temperature (298 K), equilibrium constant (Ke_j) and the integration constants for the heat of formation (ΔHs_j) and the Gibbs free energy (ΔG_j) of each reaction, respectively. In principle this methodology determines ΔH_j, ΔG_j and Ke_j considering that the heat capacity changes for each reaction with the temperature (ΔCp).

A scheme that involves 6 homogeneous and heterogeneous reactions (Table 6.1) was proposed considering the chemical and physical composition of the sludge sample, the mercury fractionation study previously reported (Chapter 4, Busto et al. 2012), in which the presence of $HgCl_2$, HgS and $HgSO_2$ in the sludge matrix was suggested and the mercury reactions reported by Patnaik (2003) and O' Neil et al. (2001). Thermodynamic data to determine the $\Delta H°$ and $\Delta G°$ (reference values at

298 K) for all reactions were obtained from Green and Perry (2007). Values of ΔCp for each chemical reaction were calculated using Equation (6.1). The parameters alpha (α_i), beta (β_i) and gamma (γ_i) were obtained from the literature (Dean, 1968; Green and Perry, 2007) for some species ($HgCl_2$, SO_2, HgO, CaO, $CaSO_4$, Cl_2, Fe, FeS). For the remaining species, these values were calculated correlating Cp values at different temperatures obtained experimentally by other researchers (Dean, 1968).

Table 6.1. The reaction scheme representing the mercury removal of the mercury waste generated from the chlor-alkali process using thermal treatment

Number	Reaction	Reference
1	$HgS_{(c)} + \frac{3}{2}O_{2(g)} \rightarrow HgO_{(g)} + SO_{2(g)}$	(Patnaik, 2003)
2	$HgO_{(g)} \rightarrow Hg_{(g)} + \frac{1}{2}O_{2(g)}$	(O' Neil et al., 2001)
3	$HgS_{(c)} + CaO_{(c)} \rightarrow Hg_{(g)} + \frac{3}{4}CaS_{(c)} + \frac{1}{4}CaSO_{4(c)}$	(Patnaik, 2003)
4	$HgSO_{4(c)} \rightarrow Hg_{(g)} + SO_{2(g)} + O_{2(g)}$	(Patnaik, 2003)
5	$HgS_{(c)} + Fe_{(c)} \rightarrow Hg_{(g)} + FeS_{(c)}$	(Patnaik, 2003)
6	$HgCl_{2(aq)} \rightarrow Hg_{(g)} + Cl_{2(g)}$	(Patnaik, 2003)

6.2.4. Kinetics of thermal decomposition of the solid mercury waste

Reactions involving a wide range of mercury compounds such as metallic Hg, $HgCl_2$, HgO, $HgSO_4$ and HgS, were modelled using the Simulation PSI Software (Van den Bosch, 1997). For calculations, we considered that the Muffle furnace works as a "Perfect Mix Reactor". This was assumed since the internal temperature gradients in the oven were negligible due to the high temperature of the oven, its design characteristic and the high velocity of the gas (Nabertherm, 2012). Since the thermal treatment was carried out at batch operation conditions, the kinetic parameters for each reaction were obtained by a non-steady state material balance of each species.

The kinetic study of mercury behaviour (mercury content) at different thermal conditions was carried out using the Flynn, Wall and Ozawa (FWO) integral isoconversional method (Vyazovkin and Dollimore, 1996). This method yields the effective activation energy (E) and pre-exponential factor (A) which are the Arrhenius parameters for each given conversion (α). The general kinetic equation can be expressed as follow:

$$\frac{d\alpha}{dt} = A \cdot \exp(-\frac{E}{RT}) \cdot f(\alpha) \tag{6.7}$$

where t, R, T are the time, the universal gas constant and the retorting temperature respectively and α is the conversion of the species that contains mercury (unitless). It represents the fraction between the converted moles of mercury and the initial moles of mercury and can be calculated as follows:

$$\alpha = \frac{n_0 - n}{n_0} \tag{6.8}$$

where n_0 and n represent the initial and final moles for each reaction.

Moreover, from Equation (6.7) f(α) represents the mathematical function of α and can be determined adjusting the experimental data of mercury conversion with temperature. Besides, dα/dt is the variation of mercury conversion with the time and it can be calculated as follows:

$$\frac{d\alpha}{dt} = \frac{-1}{n_0}\frac{dn}{dt} \tag{6.9}$$

In order to calculate the values of the activation energy (E) for each reaction, Equation (6.7) was transformed into a logarithmic form, allowing to assess the E values from the slope of ln(dα/dt) versus 1/T for each of the α values. Once the E value has been determined it is possible to find the kinetic model which best describes the measured data set.

Additionally, a model-fitting analysis was performed to determine the most probable f(α) kinetic model consistent with the isoconversional kinetic results, following the methodology outlined (Vyazovkin and Wight, 1997). Table 6.2 shows the commonly used alpha (α) functions for solid state thermal decomposition reactions which were considered in this analysis (Vyazovkin and Wight, 1997; Galwey and Brown, 1998).

Table 6.2. Empirical kinetic model (α) functions for solid state thermal decomposition reactions (Rodriguez et al., 2009).

Rate mechanism	Symbol	F(α)
(1) Sigmoid α-T curves		
(a) Prout –Tompkins equation	B_1	$\alpha(1-\alpha)$
(1.1) Nucleation and nuclei growth		
(a) Random nucleation –Avrami –Erofeev equation I	A_2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
(b) Random nucleation –Avrami –Erofeev equation II	A_3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
(c) Random nucleation –Avrami –Erofeev equation III	A_4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
(2) Acceleratory α-T curves		
(a) Exponential law	E_1	α
(3) Deceleratory α-T curves		
(3.1) Reaction order		
(a) First order- Unimolecular decay law	F_1	$(1-\alpha)$
(b) Second order	F_2	$(1-\alpha)^2$
(a) Third order	F_3	$0.5(1-\alpha)^3$
(3.2) Diffusion mechanisms		
(a) Parabolic law, one-dimensional diffusion	D_1	$0.5\alpha^{-1}$
(b) Valesi, two-dimensional diffusion	D_2	$[-\ln(1-\alpha)]^{-1}$
(c) Jander, three-dimensional diffusion, spherical symmetry	D_3	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
(d) Ginstling-Brounshtein, three-dimensional diffusion, spherical symmetry	D_4	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$
(3.3) Phase-boundary reaction		
(a) Two-dimensional (cylindrical geometry)	R_2	$2(1-\alpha)^{1/2}$
(b) Three-dimensional (spherical geometry)	R_3	$3(1-\alpha)^{2/3}$

6.2.4.1. Equations rate simulated using the PSI software

The kinetic behaviour of the mercurial sludge thermal decomposition was simulated using the PSI software. Initial data and the main design operational parameters of the simulated furnace are listed in Table 6.3. The general expressions of the material balance were established as follows:

- Total material balance in the solid matrix (mercurial sludge):

$$\frac{dmT}{dt} = Vlf \sum n_{ij} \cdot R_j \cdot Pm_i \tag{6.10}$$

- Material balance by component:

$$\frac{dn_i}{dt} = Vlf \sum (\pm) n_{ij} \cdot R_j - F_i \tag{6.11}$$

where mT, Vlf, n, R are the sludge mass (g), furnace volume (m^3), moles and the rate expression (min^{-1}) respectively, Pm is the molecular weight (g/mol) and F is the outlet molar flux (mol/min) of the process. The subscript (i) represents the components and the subscript (j) corresponds to ID number of the chemical reactions involved.

i = $O_{2\,(g)}$, $SO_{2(g)}$, $H_2O_{(g)}$, $Hg_{(g)}$, $N_{2(g)}$, $H_2O_{(aq)}$, $HgCl_{2(aq)}$, $Hg_{(c)}$, $HgS_{(c)}$, $HgSO_{4(c)}$.

j = 1, 3, 4, 5, 6, 7, 8, 9, 10, 11.

$F_i = 0$ (in aqueous and solid phase).

The general expression used to determine the kinetic rate for solid phase reactions was represented as follow:

$$R_{jfs} = k_j \cdot f(\alpha) \tag{6.12}$$

where: R_{jfs} is the kinetic reaction rate of each reaction (thermal decomposition of mercury compounds in the solid phase) and k_j represents the kinetic constant. The f(α) was defined in Table 6.2 for the different mechanisms tested during the calculations.

Table 6.3. Initial data and design parameters used in the thermal decomposition process (operating conditions of the simulated laboratory furnace).

Nomenclature	Symbols	Values	Units
Initial data from chemical –physical analyses			
Sludge mass inlet to the laboratory furnace	mT_0	3	g
Sludge humidity	hT_0	0.032	g
Mass fraction of HgS	xMs_0	0.429	g HgS/g total Hg
Mass fraction of $HgCl_2$	$xMcm_0$	0.502	g $HgCl_2$/g total Hg
Mass fraction of metallic Hg	xMm_0	0.031	g Hg^0/g total Hg
Mass fraction of $HgSO_4$	$xMsu_0$	0.022	g $HgSO_4$/g total Hg
Total initial Hg content in the sludge/g of sludge	xMT_0	$1.32 \cdot 10^{-3}$	g total Hg/g sludge
Organic matter content/g of sludge	xMO_0	0.144	g Org. Mat./g sludge
Carbonate content/g of sludge	xCa_0	0.633	g Carbonate/g sludge
Design parameters of the simulated Muffle furnace			
Length of the furnace	l	0.24	m
Width of the furnace	w	0.24	m
Height of the furnace	h	0.17	m
Number of electric resistance strip	nut	75	-
Length of the strip	lt	0.79	m
Length of the hot strip	lct	0.69	m
Power of the simulated furnace	kwe	0.09	kW/cm of steel
Air humidity	hair	65	%
Retorting time	t	150	min

An integration-optimization procedure was implemented to obtain the rate expressions that better describe the process kinetics. The mass balance Equations (6.10-6.11) were solved for the same conditions that the experiments (Table 6.3) and all f(α) in Table 6.2 for the solid phase were explored.

On the other hand, the simulation equations used to determine the kinetic rate for gas phase reactions expressions R_1 and R_4 (Table 6.1) were represented as follows:

$$R_1 = k_1 \cdot pHgS \cdot pO_2^{\frac{3}{2}} \tag{6.13}$$

$$R_4 = k_4 \cdot pHgSO_4 \tag{6.14}$$

where pHgS and pO_2 are the partial pressure of HgS and O_2 (atm).

6.2.4.2. Kinetic model adjustment

The kinetic constant and reaction order (k_j, n_r) at each retorting temperature were calculated by a nonlinear optimization method of Hooke and Jeeves (Mayo, 1998) using as fitting criteria the difference between experimental conversion data and model values at different times and temperatures (250, 350 and 450 °C):

$$F_{obj} = \min \sum_t \left(\alpha_{f\,mod} - \alpha_{f_{exp}}\right)^2 \tag{6.15}$$

where t, $\alpha_{f\,mod}$, $\alpha_{f\,exp}$ are the retorting time, the final conversion obtained from the developed model and the final conversion from the experimental data.

A statistical analysis using two non-parametric statistical tests (Ranksum and Kruskalwallis) were applied using Matlab 10.0 to evaluate the goodness of fit of the model to the experimental data.

6.3. Results and Discussion

6.3.1. Mercurial sludge characterization

In Table 6.4 the main values obtained from mercurial sludge characterization are shown. The chemical-physical characteristics were in the same range of values presented in previous Chapters.

Table 6.4. Properties and metal contents of mercurial sludge sample (mean ± standard deviations, n = 3).

Parameters	Mercurial sludge sample
pH-H_2O	9.5 (0.06)
Carbonate content (g/kg DM)	633 (6)
Org Matter content (g/kg DM)	144 (4)
EC (mS/cm)	34 (0.1)
Total Metal Content (g/kg DM)	
Ca	191 (2)
Mg	36 (1)
Na	50 (1)
Fe	13 (0.1)
Al	9 (0.1)
Hg	1.3 (0.1)
Total Metal Content (mg/kg DM)	
Cd	2 (0.1)
Cr	24 (0.1)
K	942 (18)
Mn	239 (1)
Ni	20 (1)
Pb	58 (1)
Zn	136 (1)
Cu	243 (13)
Metal concentration in the TCLP leachate (mg/l)	
Hg	2.5 (0.3)

6.3.2. Thermal treatment of the mercurial sludge sample

Figure 6.1 shows the behaviour of mercury in ashes of the sludge sample at different exposure times for three retorting temperatures (250, 350 and 450 °C). We observed that at lower temperatures the influence of the retorting time (until 30 min) is more pronounced than at higher temperatures. This phenomenon could be linked with a change in the controlling reaction mechanism during the thermal process. On the other hand, the behaviour of mercury removal at 350 and 450 °C for the all time series was well correlated.

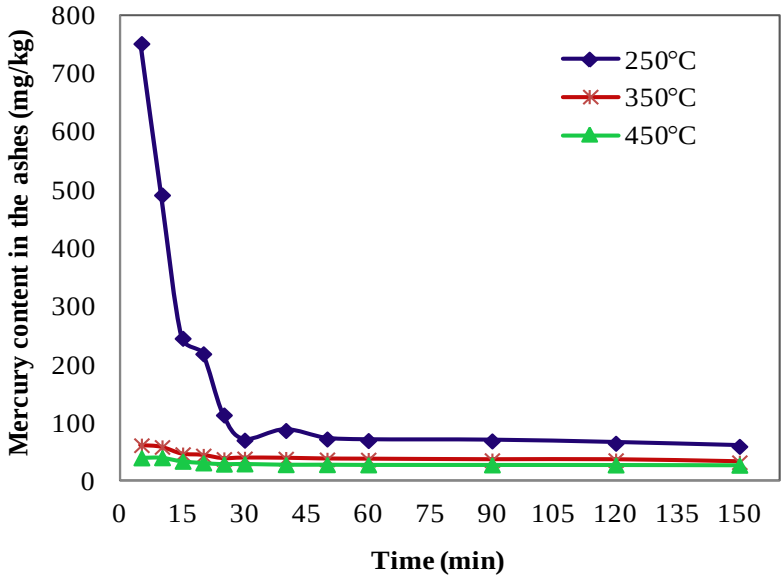


Figure 6.1. Behaviour of mercury content in ashes with the retorting time at three different temperatures.

The efficiency of the thermal treatment in this type of mercury waste has been previously demonstrated. In Chapter 5 it was establish that up to 300 °C the removal of mercury was below 50%, while more than 90% of the mercury was successfully removed after 60 min for treatment temperatures higher than 300 °C. In the present survey, the behaviour of mercury removal followed the same pattern but the lowest values of mercury average content in the remaining ashes of 27 mg/kg (97.98% of mercury removal) was obtained at higher temperature (450 °C) and exposition time (150 min). These differences were attributed to the chemical-physical characteristics of the sludge samples employed in each Chapter. In addition, this study has allowed us to corroborate that the effect of the retorting temperature is much stronger than the effect of the exposure time (Figure 6.1).

The toxicity levels of mercury in the sludge sample at different temperatures and exposure times were evaluated (Figure 6.2). At 250 °C the mercury toxicity level of the sample is above the TCLP permissible limit for the entire range of exposure times. When the sample was heated at 350 °C for 25 min and greater times the TCLP limit was reached. In the same way, when the solid mercury waste was exposed at 450 °C the TCLP limit was always reached regardless of exposure time. Although in Chapter 5 a decrease on mercury concentration in the TCLP extract was observed with an increase of the retorting temperature, which is in line with behaviour found it in the present study, the permissible limit was reached at a little different temperature (400 °C and higher) respect

to results currently obtained. This difference could be related with the chemical-physical properties of each analyzed sample.

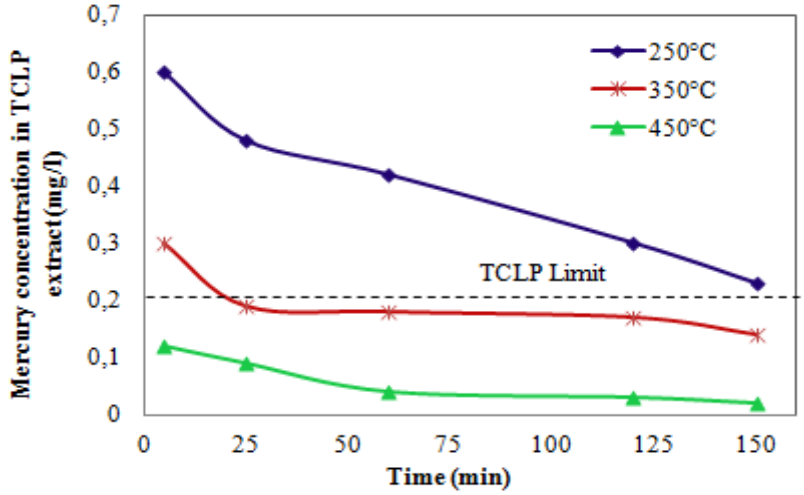


Figure 6.2. Behaviour of mercury concentrations (TCLP test) in ashes with the retorting time at three different temperatures.

6.3.3. Chemical reaction mechanism

To describe the thermal decomposition of the mercurial sludge sample generated by a chlor-alkali Cuban plant, a scheme of six reactions was proposed (Table 6.1). The reasons to select this reactions scheme have been illustrated above (see section 6.2.3). Once a reaction mechanism (reaction pattern) was built, considering also the Gibbs free energy values obtained for each proposed reaction, the kinetic model was adjusted in order to satisfy the experimental results.

The proposed reaction mechanism used in this study is based on the thermal decomposition in the solid phase followed by several gas phase reactions. Thermal decomposition reactions in the solid phase were considered a fast processes influenced by the temperature but limited by the diffusion and particle size of the sludge sample (L'vov, 2001; 2008).

The added value of knowing the mercury reaction mechanism during thermal treatment for the design of a pilot or full-scale process should not be underestimated. At first, it allows elucidating the most significant parameters to be taken into account. For instance, in the present study the process controlling mechanism (reaction and diffusion) mainly rely on solid phase reactions, and for this reason the design of the furnace has to be focussed on maximizing mercury conversion. To this end, a homogeneous temperature inside the furnace (temperature profile), as well as a constant thickness of mercurial sludge layer are of special importance. In second place, the knowledge of the mercury reaction mechanism avoids performing a pure scaled-up by similarity principles which

could be seen as a significant advantage from technical and economical points of view. Likewise, the detailed mass and energy balances can be also solved based on detailed kinetics.

6.3.3.1. Thermodynamic analysis of the reaction scheme

The reaction mechanism was thermodynamically evaluated to verify the probability of occurrence of these reactions by considering the Gibbs free energy values (ΔG). Thermodynamic parameters were determined at the highest working temperature of the furnace (450 °C). Table 6.5 shows the thermodynamic parameters (ΔG_j, ΔH_j and Ke_j) calculated for each reaction using Mondeja's Methodology.

Table 6.5. Thermodynamic parameters (ΔG, ΔH, Ke) of the chemical reaction mechanism.

Reactions	**$\Delta G_{450\,°C}$ (kcal/mol)**	**$\Delta H_{450\,°C}$ (kcal/mol)**	**$Ke_{450\,°C}$**
R_1	$-7.18\cdot10^{1}$	$-8.71\cdot10^{1}$	147.83
R_2	1.15	$3.76\cdot10^{1}$	$9.23\cdot10^{-1}$
R_3	$-1.28\cdot10^{1}$	9.89	2.44
R_4	$-9.87\cdot10^{3}$	$-4.2\cdot10^{4}$	$2.32\cdot10^{298}$
R_5	$-8.07\cdot10^{-1}$	$5.61\cdot10^{1}$	1.06
R_6	$-5.23\cdot10^{1}$	$7.64\cdot10^{1}$	38.12

The analyzed reactions showed spontaneous behaviour where the variation of the Gibbs free energy ΔG ranged from $-8.07\cdot10^{-1}$ to $-9.87\cdot10^{3}$. Reactions R_1 and R_4 are exothermic reactions due to their $\Delta H < 0$ while the other reactions have an endothermic behaviour. On the other hand, the equilibrium constant of each reaction Ke_j showed in all cases that the direct reactions are favoured with $Ke > 1$, except for R_2 which exhibited a low Ke_2. The same behaviour of the R_2 obtained from this study has been previously reported (L'vov, 1999), where the inverse reaction (HgO formation) is favoured. Due to the thermodynamic results obtained for reaction R_2 (mentioned above) as well as its low significance on the kinetic model (corroborated by simulation), this reaction was not further considered. The high equilibrium constant value obtained for reaction R_4, where is highly favoured the Hg, SO_2 and O_2 formation, is in line with previous results reported by Navarro et al. (2009).

This reaction mechanism describes a complex mechanism of five heterogeneous (gas-solid phase and liquid-gas phase) and one homogeneous (gas phase) reactions. It has been assumed that R_1, R_3 and R_5 occur in parallel.

6.3.3.2. Kinetic model for thermal decomposition of mercurial sludge

The kinetic model of the reaction mechanism obtained to explain the thermal decomposition of mercurial sludge sample can be represented by the general function of:

$$f(\alpha) = (\alpha_f - \alpha)^{n_r} \tag{6.16}$$

where α_f is the final conversion when the sludge is exhaust, and n_r is the reaction order. In this expression, α is refers at the total mercury conversion in the solid matrix and n_r is determine by the optimal adjustment of the kinetic model. It has been reported by Kafarov (1977) that Equation (6.16) is well suited for polydisperse systems and/or where a component is separated in different phases. On the other hand, it is very effective when there are changes in the diffusive stage that controls the process (Peralta, 1993).

Chemical reactions R_1, R_3-R_6 were used to obtain the kinetic model for thermal decomposition of the mercurial sludge sample. However, in the kinetic model, to simplify the mathematical procedure, the phase change reactions were analyzed disaggregated. Then the chemical reactions that represent the detailed kinetic model are:

$$HgS_{(g)} + \frac{3}{2}O_{2(g)} \rightarrow HgO_{(g)} + SO_{2(g)} \tag{R_1}$$

$$HgS_{(c)} + CaO_{(c)} \rightarrow Hg_{(g)} + \frac{3}{4}CaS_{(c)} + \frac{1}{4}CaSO_{4(c)} \tag{R_3}$$

$$HgSO_{4(g)} \rightarrow Hg_{(g)} + SO_{2(g)} + O_{2(g)} \tag{R_4}$$

$$HgS_{(c)} + Fe_{(c)} \rightarrow Hg_{(g)} + FeS_{(c)} \tag{R_5}$$

$$HgCl_{2(g)} \rightarrow Hg_{(g)} + Cl_{2(g)} \tag{R_6}$$

$$HgCl_{2(aq)} \rightarrow HgCl_{2(g)} \tag{R_7}$$

$$H_2O_{(aq)} \rightarrow H_2O_{(g)} \tag{R_8}$$

$$Hg_{(c)} \rightarrow Hg_{(g)} \tag{R_9}$$

$$HgS_{(c)} \rightarrow HgS_{(g)} \tag{R_{10}}$$

$$HgSO_{4(c)} \rightarrow HgSO_{4(g)} \qquad (R_{11})$$

From the proposed reactions scheme, the prevalence of reactions containing HgS was observed as this mercury compound appears in the highest proportion in the sludge sample. Furthermore, the thermal decomposition of this sludge including gas-phase and solid-phase reactions allowed a best adjustment of the kinetic model. In Table 6.6 the kinetic parameters (α_f, k_j and n_r) obtained experimentally for each retorting temperature are given.

Table 6.6. Kinetic parameters (α_f, k_j and n_r) obtained by the adjusted kinetic model for each operating temperature.

Kinetic parameters	250 °C	350 °C	450 °C
k_1	$1.56\cdot10^{-22}$	$2.51\cdot10^{-19}$	$5.24\cdot10^{-17}$
k_3	3.59	4.41	10.79
k_4	$1.1\cdot10^{-38}$	$5.84\cdot10^{-30}$	$5.47\cdot10^{-24}$
k_5	0.59	1.54	10.79
k_6	$1.03\cdot10^{-37}$	$2.08\cdot10^{-29}$	$1.69\cdot10^{-23}$
k_7	$5.15\cdot10^{-10}$	$1.18\cdot10^{-8}$	$1.62\cdot10^{-8}$
k_8	$1\cdot10^{-20}$	$1\cdot10^{-14}$	$1\cdot10^{-10}$
k_9	$2.83\cdot10^{-2}$	$5.38\cdot10^{-1}$	$5.73\cdot10^{-1}$
k_{10}	$4.14\cdot10^{-2}$	$7.98\cdot10^{-2}$	$1.15\cdot10^{-1}$
k_{11}	$4\cdot10^{-20}$	$1\cdot10^{-14}$	$1.93\cdot10^{-2}$
α_f	$9.75\cdot10^{1}$	$9.76\cdot10^{1}$	$9.79\cdot10^{1}$
n_r	$7.86\cdot10^{-1}$	1.03	1

As can be noticed from the results in the Table 6.7 at the retorting temperature of 250 °C, the kinetic model obtained by simulation did not result in a suitable adjustment with the experimental values. Contrarily, a very good fit of the experimental conversion with the empirical conversion values (simulated model) were achieved at 350 °C and 450 °C. This phenomenon could be linked with a change in the controlling reaction mechanism during the thermal process. The statistical comparison for two nonparametric tests is discussed in section 6.3.3.5.

Table 6.7. Comparison between maximum conversion values achieved by the experimental data and the simulated model.

Time (min)	$\alpha_{250\ °C}$		$\alpha_{350\ °C}$		$\alpha_{450\ °C}$	
	Experiment	**Model**	**Experiment**	**Model**	**Experiment**	**Model**
15	81.4	61.6	96.5	97.56	97.4	97.95
30	94.7	72.4	97.1	97.57	97.8	97.96
60	94.7	85.1	97.2	97.57	97.91	97.96
90	94.8	91.2	97.3	97.57	97.92	97.96
120	95.1	94.1	97.3	97.57	97.93	97.96
150	95.5	95.48	97.56	97.57	97.96	97.96

6.3.3.3. Kinetic model behaviour- dependence of the temperature

The behaviour of mercury compounds during the thermal decomposition of the sludge sample was obtained for each analyzed temperature. Figure 6.3 represents the conversion profiles followed by the mercury compounds that are present in the sludge matrix at 250, 350 and 450 °C respectively (expressed as converted/desorbed mass). Results show a fast reduction of the mercury compounds (Hg, $HgCl_2$, $HgSO_4$, HgS) mass in the solid matrix (mercurial sludge) for the three temperatures.

This trend is in line with the chemical reaction mechanism proposed which include the phase change reactions. The behaviour of the mercury compounds was strongly dependent of the temperature at 250 °C where the highest conversion was achieved at 120 min. On the other hand, at temperatures of 350 and 450 °C, all mercury compounds showed the same behaviour obtaining the highest conversion in 15 min except for the $HgSO_4$. The result obtained for $HgSO_4$ at 350 °C was expected and is in agreement with the thermal behaviour previously reported (Nakamura et al., 1981; Ahmed et al., 2000) due to the $HgSO_4$ has a temperature of thermal decomposition of 500 °C.

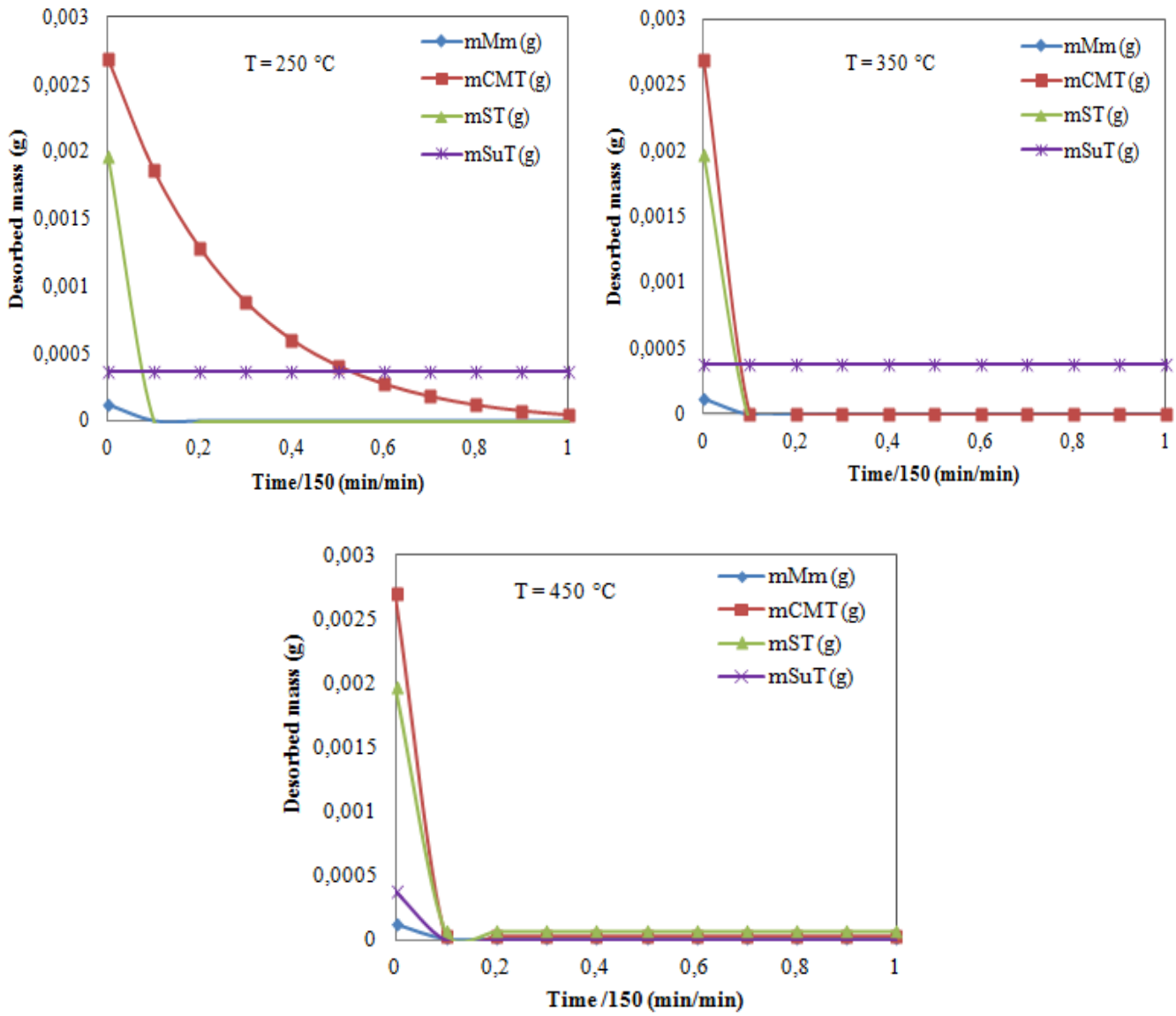


Figure 6.3. Behaviour of the mercury compounds present in the sludge matrix with the time at three different temperatures (250, 350 and 450 °C).

The relationship between each chemical reaction rate and the temperature was established using Arrhenius's Equation. The values of activation energy (E) and pre-exponential factor (A) are shown in Table 6.8.

Table 6.8. Values of Activation energy (E) and Pre-exponential factor (A) of the chemical reactions involved in the proposed reaction scheme.

Kinetic reaction R_j	Activation energy E (kJ mol^{-1})	Pre-exponential factor A (min^{-1})
R_1	199.99	0.015
R_3	208.76	$1.4 \cdot 10^{18}$
R_4	515.44	$9.53 \cdot 10^{13}$
R_5	94.22	$8.36 \cdot 10^{7}$
R_6	508.81	$9.59 \cdot 10^{13}$
R_7	523.39	$9.59 \cdot 10^{13}$
R_8	333.40	$1 \cdot 10^{14}$
R_9	197.09	$1 \cdot 10^{14}$
R_{10}	206.75	$1 \cdot 10^{14}$
R_{11}	524.80	$9.99 \cdot 10^{29}$

Conversion profiles were obtained from the adjusted kinetic model in order to evaluate the influence of the temperature in the thermal decomposition of the sludge sample. A different behaviour was observed from comparing the conversion profiles at 250 °C and 350-450 °C (Figure 6.4).

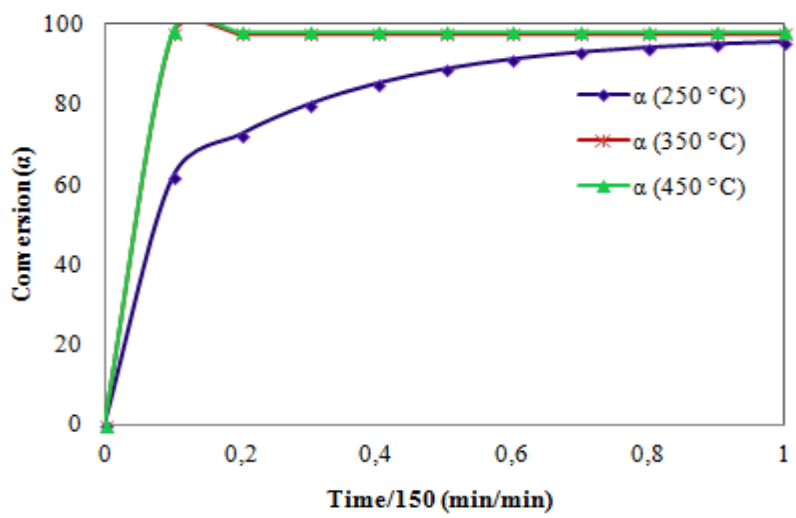


Figure 6.4. Conversion profiles of the kinetic model at the three retorting temperatures. (α values are expressed in %)

These results are consistent with the experimental observations (mentioned above), where the effect of the retorting temperature was much stronger than the effect of exposure time. Nevertheless, the main explanation for the occurrence of this phenomenon could be associated with the controlling reaction mechanism that take place at low (250 °C) and high temperature (350-450 °C).

6.3.3.4. Comparison among nine kinetic reaction mechanisms

The kinetic decomposition behaviour in the solid state can be characterized by sigmoid curves that have decelerator behaviour at the beginning and at the end of the mechanism while an accelerator phase can be observed in the middle of the curve (Halikia et al., 2001). A wide range of reaction mechanisms could take place in the thermal decomposition of a solid sample (Roduit et al., 1996; Guo and Lua, 2001; Rodriguez et al., 2009). In this survey, the reaction mechanisms that represent deceleratory behaviour α-T curves (Table 6.2) were used. The selection of the 9 kinetic mechanisms used for the comparison was based on the experimental conversion curves, as no initial deceleration was observed (Figure 6.4). The study of these reaction mechanisms was carried out in order to understand the difference between mercury conversion at low (250 °C) and high (450 °C) temperatures which involve a possible change of the reaction mechanism of the process. First, the 9 mechanisms expressions were solved together with the mass balance and the results were compared to the experimental data for each temperature. Subsequently, a comparison between conversions values (α) obtained by the current proposal model and the 9 reaction mechanisms was conducted.

The D_1-diffusion mechanism (one-dimensional diffusion as indicates Table 6.2) could be considered the controlling mechanism of the process at high retention times while at low thermal decomposition times (< 15 min) the diffusion mechanism (D_1) as well as the third order reaction mechanism (F_3) could be controlling the process. This behaviour was observed at low (250 °C) and high (450 °C) temperatures by a good fitting of the thermal decomposition data over the whole range of conversions (Figure 6.5). As a first depth-in to the knowledge of this kind of systems, the diffusion mechanism (D_1) can be considered the overall controlling mechanism as an increase of the temperature smooth the progress of the chemical reactions involved. The application of the model – fitting method to the experimental data of thermal decomposition of the mercurial sludge sample confirmed the idea that not a single mechanism is ruling the process.

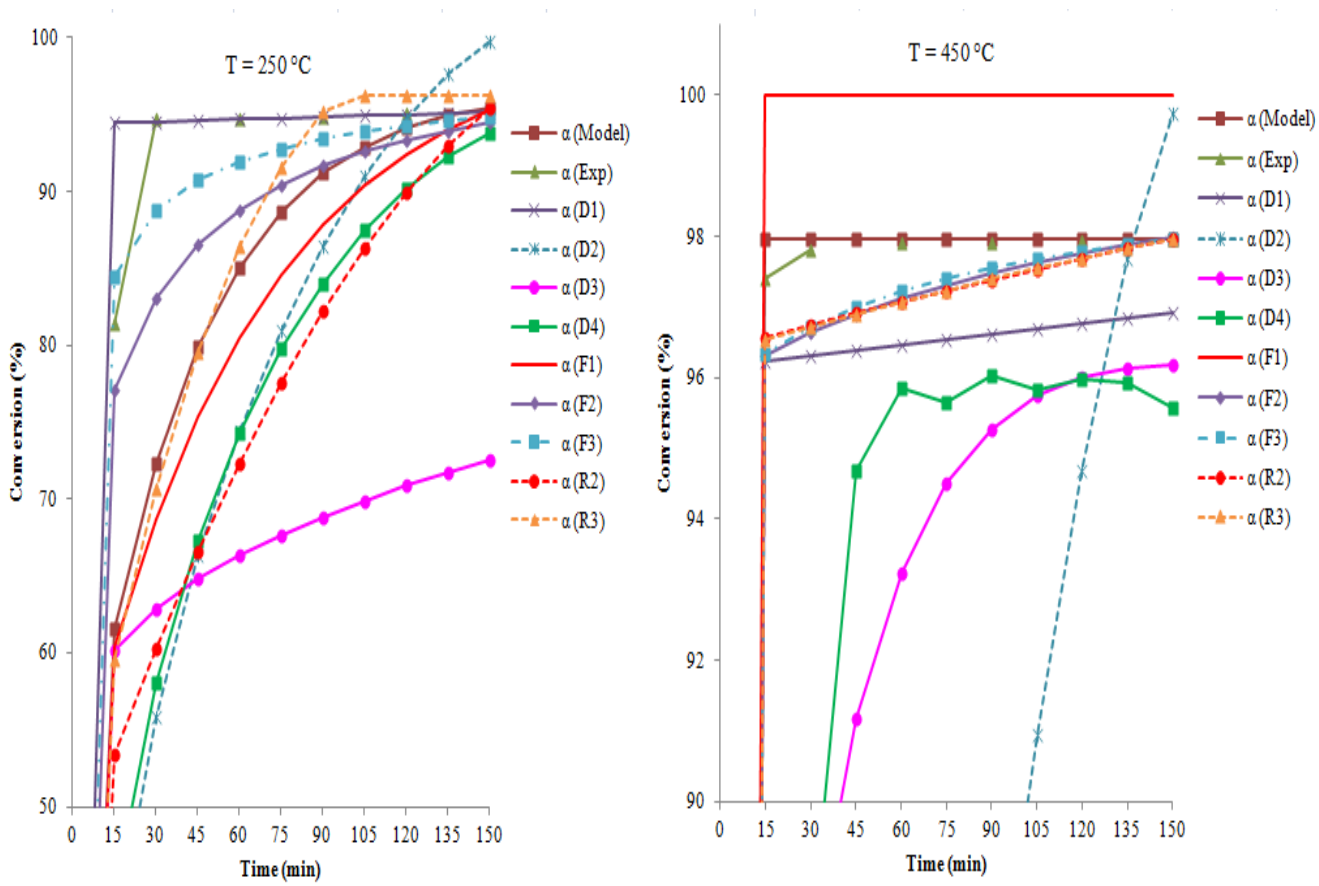


Figure 6.5. Mechanisms comparison to determine the controlling stage for the thermal decomposition of the mercurial sludge sample at low temperature (250 °C) and high temperature (450 °C) (Note different scales for each of the temperatures).

From these results we can stress that the thermal decomposition behaviour of the mercurial sludge show changes in the diffusive phase that control the reaction mechanism. Specifically at the beginning, the external diffusion of the gas through the sludge particle is the controlling mechanism as the compound is diffused in the superficial phase and in outer layers of the sludge particle. With the time, the thickness of the product layer (ashes) will increase and the diffusion through the ashes will become the controlling reaction mechanism. However, it is necessary to remark that the 9 reaction mechanisms used for comparison were established for mono-components and mono-disperse systems, but in our study case, the solid matrix is much more complex (polydisperse and multicomponent).

6.3.3.5. Statistical analysis

As a marked change was observed between the conversion behaviour at 250 and 450 °C, the statistical analysis was done for these operating temperatures. The P values obtained at 250 °C from the Ranksum and Kruskalwallis statistical tests were 0.119 and 0.175 ($P > 0.05$) respectively.

Equally, P values obtained at 450 °C from the Ranksum and Kruskalwallis statistical tests were 0.167 and 0.097 respectively; demonstrating that non-significant differences exist between experimental data and the proposal model.

6.4. Conclusions

In the present Chapter, a kinetic reaction mechanism which describes the mercury removal process by thermal decomposition of mercury solid waste generated by the Chlor-alkali process has been proposed. For the proposed reaction mechanism including 6 homogeneous and heterogeneous reactions, the thermodynamic parameters and the kinetic model were obtained. The experimental kinetic data was reasonably well represented by the simulated kinetic model. The effect of the retorting temperature was much stronger than the effect of the exposure time.

A comparison among 9 kinetic mechanisms of solid-state reactions well established on the literature (deceleratory behaviour α-T curves) was carried out to elucidate the controlling reaction mechanism of the process. The application of these models – fitting method confirmed the idea that not a single mechanism is ruling the process. The D_1-diffusion mechanism could be considered the controlling mechanism of the process at high retention times while at low thermal decomposition times (< 15 min) the diffusion mechanism (D_1) as well as the third order reaction mechanism (F_3) could be controlling the process. This behaviour was observed at low (250 °C) and high (450 °C) temperatures by a good fitting of the thermal decomposition data over the whole range of conversions.

As a first depth-in to the knowledge of this kind of systems (polydisperse and multicomponent), the diffusion mechanism (D_1) can be considered the overall controlling mechanism as an increase of the temperature smooth the progress of the chemical reactions involved. From these results we can stress that the thermal decomposition behaviour of the mercurial sludge show changes in the diffusive phase that controls the reaction mechanism. Specifically at the beginning, the external diffusion of the gas (O_2) through the sludge particle was the controlling mechanism. Nevertheless, as the thickness of the product layer (ashes) increased with time, the diffusion of products through the ashes to the gaseous phase became the controlling reaction mechanism.

CHAPTER 7

TREATING HIGH MERCURY CONTAINING WASTES FROM CHLOR-ALKALI PLANT USING PILOT-SCALE THERMAL TREATMENT TECHNOLOGY: TECHNO-ECONOMIC AND ENVIRONMENTAL ANALYSIS.

A pilot-scale thermal treatment technology to treat high mercury containing wastes generated by the chlor-alkali process was developed. Mass and energy balances at steady-state, the scale-up methods as well as the mercury reaction scheme (developed in Chapter 6) are used for the design of the pilot-scale thermal treatment plant. Two operating alternatives of thermal treatment have been analyzed in this study. In the first alternative, the pilot-scale thermal plant operates to achieve the maximum mercury removal. In the second alternative, the waste is treated to a point where the TCLP leaching limit is reached. Static and dynamic economic indicators have been employed to evaluate both thermal treatment alternatives. The environmental impact assessments for both technological alternatives as well as the current treatment applied by the chlor-alkali Cuban plant (detailed in Chapter 1) have been studied regarding to their impact and damage categories using Life Cycle Analysis (LCA).

The proposed pilot plant with 960 ton of sludge/y of processing capacity is able to recover 639 kg of metallic Hg/y and 479 ton/y of treated sludge (arid) that can be sold. 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 realised. Furthermore, in a period of 4.2 y the total capital investment of the project could be paid with a profitable internal rate of return of 15%. From an environmental point of view, a significant reduction on the human health impact (95.4%), ecosystem quality impact (83%) and impact on resources (78.5%) would be achieved in comparison with the existing treatment applied by the chlor-alkali Cuban plant. The proposed thermal treatment technology (alternative 2) is a project of significant costs, but represents considerable benefits for the environment and human health.

7.1. Introduction

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). Chlor-alkali industry represents the third major mercury user worldwide (AMAP/UNEP, 2008). In this process, very large quantities of liquid mercury are used as a cathode in electrolytic cells to produce chlorine, sodium hydroxide and hydrogen by electrolysis of brine solution (Southworth et al., 2004).

In the United States, mercury cell chlor-alkali plants (MCCAPs) were estimated to be the largest non-combustion anthropogenic source of atmospheric mercury pollution, emitting 6.5 ton/y from the 14 operating plants in 1994-1995 (USEPA, 1997c). In Europe, chlor-alkali industry was responsible in 2000 for about 17% (40.4 ton/y) of the anthropogenic total mercury emissions (Pacyna et al. 2006).

One of the major concerns from the chlor-alkali mercury emissions is the mercury solid waste generated by the process. The amount of Hg in wastes from chlor-alkali productions, only in the European Union were estimated at about 990 ton (Mukherjee, 2004). Although this technology seems to be in decline, as the older plants are shut down or converted into a novel technology of membrane cells, during the remaining life of mercury cell plants measures should be taken to minimize current and future mercury emissions following handling, storage, treatment and disposal of mercury-contaminated wastes (Directive 2008/1/EC, 2008).

The management and ultimate disposal of mercury contaminated hazardous waste is controlled by USEPA regulations known as the Land Disposal Restrictions (LDRs) (40 CFR, Part 268). Under the current LDR program, USEPA (2008a) recommended thermal recovery (e.g., roasting/retorting treatment) as the best demonstrated available technology (BDAT) for treatment of wastes containing more than 260 mg/kg of mercury. For treatment of wastes 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 (USEPA, 2008a).

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 chlor-alkali Cuban plant “Elpidio Sosa” currently hosts more than 7000 ton of mercury contaminated wastes buried in concrete niches. Mercury wastes 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 (USEPA, 2008a) (Busto et al., 2011).

Several studies have demonstrated the efficiency of thermal treatment at pilot and full scale to treat solid wastes highly contaminated with Hg (e.g. mercury wastes from the chlor-alkali process) (George et al., 1995; De Percin, 1995; Cha et al., 1996; Smith et al., 2001; Chang and Yen, 2006; Kunkel et al., 2006; Chang et al., 2009). Despite this fact, so far almost all studies have focused primarily on achieving the best operating parameters (time and temperature) that increase the mercury removal efficiency of the treatment (De Percin, 1995; Smith et al., 2001; Chang and Yen, 2006; Kunkel et al., 2006; Chang et al., 2009; Huang et al., 2011). While investigating operational parameters for thermal treatment of mercury contaminated wastes, no studies have yet considered reactions mechanisms and kinetics of mercury during the thermal treatment.

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 (Chapter 5). Moreover in Chapter 6, the kinetic reaction mechanism which represents the behaviour of mercury and mercury compounds, within the sludge matrix during the thermal treatment was developed. To design a more feasible technology, the reaction mechanism and kinetic of mercury during the thermal treatment should be considered.

The goal of the present work was to propose a technological design of the thermal treatment (retorting) to treat mercury contaminated wastes generated by the chlor-alkali Cuban plant. Specifically, in the present Chapter, we wanted to scale up and design at pilot-scale the main steps of the thermal technology using scaled-up methods (by similarity principle) and process simulation. The proposed design will consider the kinetic reaction mechanism, energy and material balances, equipment design equations as well as techno-economic and environmental analysis.

7.2. Material and Methods

7.2.1. Bench-scale thermal treatment process

In this study we treated mercury containing wastes from the chlor-alkali Cuban plant by a thermal treatment process to recover the mercury. Figure 7.1 shows the flow diagram of the bench-scale thermal treatment process, which includes three main stages: drying, crushing and mercury removal of the mercurial sludge sample.

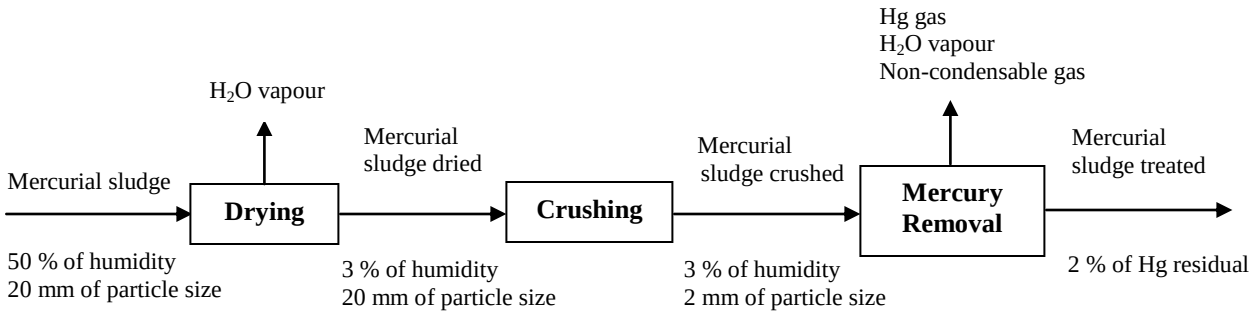


Figure 7.1. Flow diagram of the bench-scale thermal treatment process.

The first stage of the process (drying) has the goal of striping the mercurial sludge sample of its water content from 50% to 3%, in order to facilitate the crushing operation. The second stage (crushing), aims to reduce and homogenize the particle size of the sludge sample from 20 mm to 2 mm, to reduce the diffusional resistances improving the mass and heat transfer in the later stage. In the final stage temperature of the furnace is increased in order to remove the mercury by thermal process.

7.2.1.1. Input variables

The amount of sludge to be processed, the chemical composition of the sample (total mercury content, mercury fractionation results), the moisture content, the particle size of the mercurial sludge sample and the thermal treatment temperature and time were the input variables considered in this treatment. Mercury fractionation data from Chapter 4 (Busto et al., 2012) and total mercury content from Chapter 6 have been used in the present study.

Five grams of mercurial sludge were heated at 45 °C during 24 h in a ceramic muffle furnace (L9/11/SKM/P330 Model, Nabertherm, Germany, Bremen) to determine the moisture content of the sample by weigh deference analysis (Van Ranst et. al., 1999). The initial particle size of the mercurial sludge sample (taken from the niche) was reported by workers at the chlor-alkali Cuban plant.

As shown in Chapter 6, the conversion profile for all mercury compounds present in the sludge matrix followed the same thermal desorption behaviour at 350 °C and 450 °C. Furthermore, it was observed that the Hg remaining in the sludge sample was the same at 350 °C after 3 h of treatment as at 450 °C after 1 h. For the highest treatment temperature, TCLP leachable concentrations of Hg were below the limit for any treatment time. Data from Chapter 5 showed that the TCLP limit can be achieved at 400 °C and higher. According to what was explained above, the best working temperature selected for operating the proposed thermal desorption plant was 450 °C.

The total mercury content of the mercurial sludge sample inside the niche at different depths was determined. Total Hg content was determined using 1 g of sludge sample following the analytical method explained in section 6.2.1. Each determination was carried out in triplicate and all reagents used were of analytical grade.

7.2.1.2. Design parameters at bench-scale

The drying stage was carried out using a heating/drying oven with air forced convection (FD-115 Model, Binder, Germany, Tuttlingen). For the crushed stage (particle size reduction) the sludge 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, Bremen) which has a temperature control accuracy of ±1 °C and 0.24 x 0.24 x 0.17 m of dimensions.

7.2.1.3. Operating conditions at bench-scale

For the drying stage the main operating conditions were the time and temperature. A drying test was carried out using the procedure reported by Perry and Green (1999) to obtain the regimen curve of drying as well as the drying time of the sludge sample. One hundred grams of mercurial sludge 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% (determined by the workers of the Chlor-alkali plant) to 3% (determined experimentally as explained above). Once the moisture content of the samples was tabulated at each 30 min, the values of drying regimen were calculated which represent the decrease rate on the samples moisture content during time (Table 7.1). 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.

Table 7.1 Summary data of the drying test applied to the mercurial sludge sample at bench-scale[a].

Drying curve		
Drying time (min)	**SW_0 (g)-CW(g)**	**X_f (kg of water/kg of dry sludge)**
0	99.76	0.498
30	90.81	0.408
60	82.16	0.322
90	75.01	0.250
120	69.09	0.191
150	65.06	0.151
180	61.09	0.111
210	57.49	0.075
240	53.35	0.034
Drying regimen curve		
ΔX (kg of water/kg of dry sludge)	**ΔT (h)**	**N (Drying regimen)**
0.408	0.5	0.317
0.322	1	0.306
0.250	1.5	0.253
0.191	2	0.213
0.151	2.5	0.143
0.111	3	0.140
0.075	3.5	0.127
0.034	4	0.076

[a] **Note:** SW_0, CW and X_f represent the sludge initial weight, crucible weight and moisture final content, respectively.

7.2.2. Scale-up of the thermal treatment to 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 sludge occurs in this stage. To design the furnace at pilot-scale by scale-up, principles of geometric, chemical and thermal similarity were followed (Bisio, 1985; Perry and Green, 1999; 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 sludge 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 key process influencing furnace performance is heat transfer who affects every other physical or chemical process occurring in the furnace (Richter, 1985). Regarding to this, the scaling-up factor employed to design the pilot plant furnace was calculated considering that the ratio of power consumption to sludge mass was the same for the laboratory furnace (prototype) and the pilot plant furnace (model).

7.2.3. Pilot-scale thermal treatment process

Figure 7.2 shows the schematic diagram of the proposed pilot-scale thermal treatment process, which can be divided into a mercury sludge pre-treatment system, a thermal treatment system, a mercury recovery system and a co-products recovery system. The mercury sludge pre-treatment system includes the sludge extraction from the niche (excavator), an equipment to contain and to feed the mercurial sludge into the trays (feed hopper), an equipment to transport the mercurial sludge to the drying machine (conveyor), an equipment to reduce the sludge moisture content (drying) and a machine for crushing the mercurial sludge (mill).

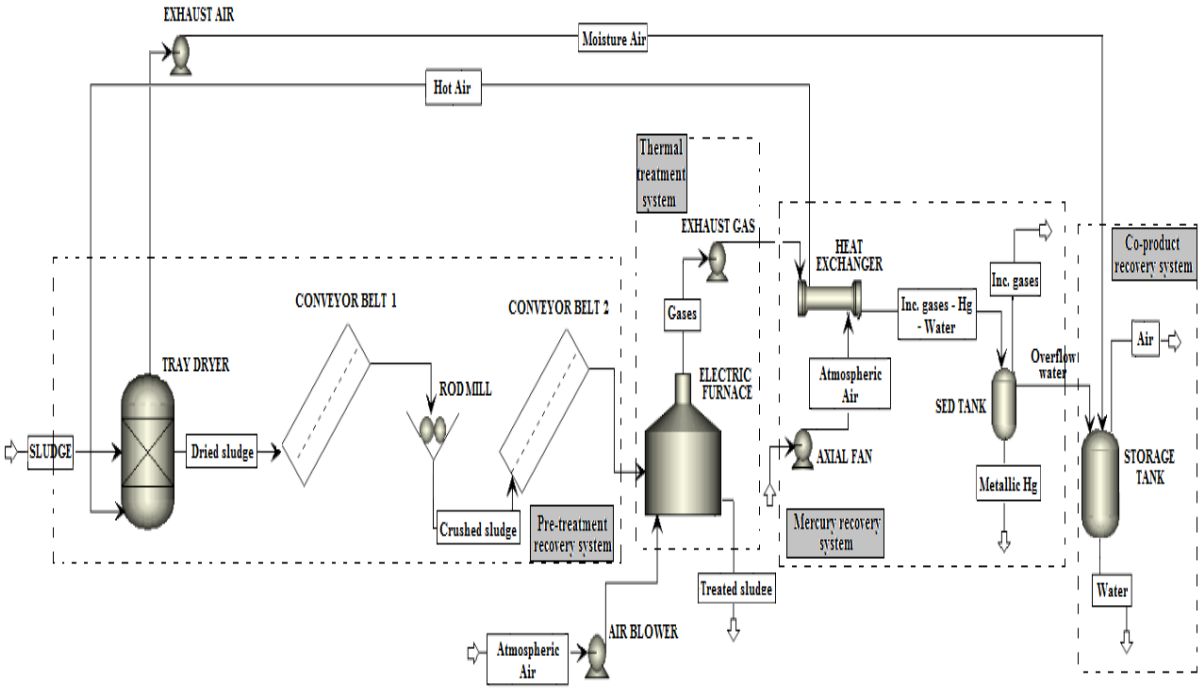


Figure 7.2. Schematic diagram of the proposed pilot-scale thermal treatment plant.

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 sludge recovery system (retention hopper).

7.2.4. Mass and energy balance of the overall process

Mass and energy balances allow selecting and designing efficiently the technological equipment of the process. In each stage of the proposed technology, mass balances in solid, gaseous and/or liquid phase as well as energy balances were developed to determine the unknown streams and parameters of the overall process.

7.2.4.1. Mass and energy balance of mercury sludge pre-treatment system

For this stage, the mass and energy balances were developed on the drying and crushing equipment. For calculations a size reduction efficiency of 100% for the crushing stage (inlet sludge mass equal to outlet sludge mass) was considered. Total and partial mass balances (in solid and gaseous phase) and energy balance equations for the main components and streams can be represented as follows:

Mass balance in the solid phase:

$$mSd^{in} = mSd^{out} + mWd^{evap} \tag{7.1}$$

where mSd^{in}, mSd^{out} and mWd^{evap} represent the inlet and outlet sludge mass and the evaporated water mass respectively, which are expressed in kg. For these calculations, a reduction on the sludge moisture content from 50% to 3% was considered.

Mass balance in the gaseous phase:

$$fmWd^{out} = fmWd^{in(air)} + fmWd^{evap} \tag{7.2}$$

$$fmAd^{out} = fmAd^{in} + fmWd^{evap} \tag{7.3}$$

where $fmWd^{out}$, $fmWd^{in(air)}$ and $fmWd^{evap}$ are the outlet, inlet (with the air flow) and evaporated water mass flow respectively. Moreover, $fmAd^{out}$ and $fmAd^{in}$ are the outlet and inlet mass flows of air in this stage. All these variables are expressed in kg/s. For the balance, a 65% of humidity of the inlet flow of air was considered as it was the average humidity percent of the air at regular weather conditions in Cuba (Weather data archive of Villa Clara province, 2011).

Energy balance:

This analysis was carried out assuming a tray drying efficiency (η_d) of 85% and a drying time of 4 h, as selected from the drying regimen data (Table 7.1).

$$Q_{gd(sludge)} = \eta_d \cdot Q_{cd(air)} \tag{7.4}$$

$$Q_{gd(sludge)} = mSd^{in} \cdot CpSd \cdot (T_{2d} - T_{1d}) + mWd^{evap} \cdot \lambda_{H2O} \tag{7.5}$$

where $Q_{gd(sludge)}$ and $Q_{cd(air)}$ represent the flux of heat delivered by the sludge and the heat liberated by the air in kJ/s. From equation (7.5), CpSd and λ_{H2O} are the heat capacity of the sludge (kJ/g·K) and the latent heat of water (kJ/kg) respectively at 80 °C and 1 atm. T_{2d} and T_{1d} correspond to the outlet and inlet temperatures of the sludge (80 °C) and (25 °C) respectively.

7.2.4.2. Mass and energy balance of thermal treatment system

The mass and energy balances equations (steady-state) at bench scale were developed taking into account the mercury reaction scheme reported in Chapter 6. The main equations of mass and energy balances are represented as follows:

7.2.4.2.1. Mass and energy balance of the laboratory furnace

Mass balance:

Partial mass balance of Mercury (mMlf):

$$mMlf^{out} = mMlf^{in} + mMlf^{gen} \tag{7.6}$$

$$mMlf^{gen} = (nMClf \cdot \frac{n_{estM}}{n_{estMC}} + nMSlf \cdot \frac{n_{estM}}{n_{estMS}} + nMSulf \cdot \frac{n_{estM}}{n_{estMSu}}) \cdot MM_{Hg} \tag{7.7}$$

where $mMlf^{out}$, $mMlf^{in}$, $mMlf^{gen}$ and MM_{Hg} are the outlet, inlet and generated mass of mercury (g) and its molecular weight (g/mol) respectively. Moreover, nMClf, nMSlf and nMSulf correspond to the moles of $HgCl_2$, HgS and $HgSO_4$ respectively while n_{estM}, n_{estMC}, n_{estMS} and n_{estMSu} represent the stoichiometric moles of Hg, $HgCl_2$, HgS and $HgSO_4$ in that order.

Partial mass balance of Oxygen (mOlf):

$$mOlf^{out} = (nOlf^{in} - nOlf^{cons}) \cdot MM_{O2} \tag{7.8}$$

where $mOlf^{out}$ and MM_{O2} represent the outlet mass of oxygen (g) and its molecular weight (g/mol) respectively. For calculations, the inlet moles of oxygen ($nOlf^{in}$) were determined considering the oxygen that comes from the air plus the oxygen generated by the reaction R_4. The moles of oxygen consumed ($nOlf^{cons}$) were obtained taking into account the mercury reaction R_1 (Table 6.1/Chapter 6).

Partial mass balance of Nitrogen (mNlf):

$$mNlf^{out} = mNlf^{in} = (\frac{V_{lf} \cdot \rho_{air}}{MM_{air}}) \cdot MM_{N2} \tag{7.9}$$

where $mNlf^{out}$, $mNlf^{in}$ and MM_{N2} represent the outlet and inlet mass of nitrogen (g) and its molecular weight (g/mol). The moles of nitrogen were determined as a fraction of the moles of air that goes in to the laboratory furnace. The V_{lf}, ρ_{air} and MM_{air} variables correspond to the volume of the laboratory furnace (m^3), the density of air (kg/m^3) and the molecular weight of air (g/mol).

Partial mass balance of Sulphur Dioxide (mSDlf):

$$mSDlf^{out} = mSDlf^{gen} = (nMSlf \cdot \frac{n_{estSD}}{n_{estMS}} + nMSulf \cdot \frac{n_{estSD}}{n_{estMSu}}) \cdot MM_{SO2} \tag{7.10}$$

where $mSDlf^{out}$, $mSDlf^{gen}$ and MM_{SO2} represent the outlet and generated mass of sulphur dioxide (g) and its molecular weight (g/mol) respectively. The stoichiometric moles of sulphur dioxide (n_{estSD}) were obtained from reactions R_1 and R_4 (Table 6.1/Chapter 6).

Partial mass balance of Chlorine (mClf):

$$mClf^{out} = mClf^{gen} = (nMClf \cdot \frac{n_{estC}}{n_{estMC}}) \cdot MM_{Cl2} \tag{7.11}$$

where $mClf^{out}$, $mClf^{gen}$ and MM_{Cl2} correspond to outlet and generated mass of chlorine (g) and its molecular weight (g/mol) respectively. The stoichiometric moles of chlorine (n_{estC}) were obtained from reaction R_6 (Table 6.1/Chapter 6).

Partial mass balance of Water (mWlf):

$$mWlf^{out} = mWlf^{in(air)} + mWlf^{in(sludge)} \tag{7.12}$$

where $mWlf^{out}$, $mWlf^{in(air)}$ and $mWlf^{in(sludge)}$ are the outlet mass of H_2O, the inlet mass of water that comes with the humidity of the air and the inlet mass of water that goes in to the process by the moisture content of the sludge sample respectively (expressed in grams).

Energy balance:

The heat flow was calculated taking into account the heat of the mercury reactions, (Table 6.1/Chapter 6) the heat transferred by the sludge mass and heat of gases. In these determinations, a retorting time (t_{lf}) of 3 h was considered. To determine the heat released by the mercury reactions (Q_{Rlf}) which is expressed in kJ/s, the following expression was used:

$$Q_{R(lf)} = \frac{(n_{MClf} \cdot \Delta H_{R(MC)} + n_{MSlf} \cdot \Delta H_{R(MS)} + n_{Mlf} \cdot \Delta H_{R(M)} + n_{MSulf} \cdot \Delta H_{R(MSu)})}{t_{lf}} \tag{7.13}$$

where $\Delta H_{R(MC)}$, $\Delta H_{R(MS)}$, $\Delta H_{R(M)}$, $\Delta H_{R(MSu)}$ represent the heat of reaction of $HgCl_2$, HgS, Hg and $HgSO_4$, respectively. These values were obtained from the thermodynamic data (Chapter 6) and are expressed in kcal/mol.

$$Q_{sludge(lf)} = \frac{mSlf \cdot CpS \cdot \Delta T}{t_{lf}} \tag{7.14}$$

where $Q_{sludge(lf)}$ corresponds to the heat liberated by the sludge sample (kJ/s) and ΔT represents the difference of working temperature in the laboratory furnace (425 °C).

$$Q_{gases(lf)} = \frac{(\sum m_K \cdot Cp_K) \cdot \Delta T}{t_{lf}} \tag{7.15}$$

where $Q_{gases(lf)}$ is the heat contained in the gasses of the thermal decomposition process (kJ/s); m_k and Cp_k represent the mass (g) and heat capacity (kJ/g·K) of the gaseous compounds (k) respectively which correspond to Hg, Cl_2, SO_2, O_2, N_2 and H_2O.

7.2.4.2.2. Mass and energy balance of the electric resistance furnace

A scaled-up factor (S_f) of 5150 was used to design the electric resistance furnace at pilot-scale, considering the sludge mass input to the pilot plant furnace (386 kg) and the sludge mass input to the laboratory furnace (75 g). This scale up factor was included in the solution of the mass and energy balances at pilot scale. The main equations of mass and energy balance are represented as follows:

Mass balance:

$$mSerf^{out} = mSerf^{in} - mMerf^{evap} - mWerf^{evap} - mIGerf^{out} \tag{7.16}$$

where $mSerf^{in}$ and $mSerf^{out}$ are the inlet and outlet mass of sludge (kg) processed in the electric resistance furnace (pilot-scale). For these calculations, the outlet mass of evaporated mercury ($mMerf^{evap}$ expressed in kg) was determined affecting the mercury mass obtained at bench scale by the scaled-up factor. Moreover, the mass of evaporated water ($mWerf^{evap}$ expressed in kg) obtained during this stage was determined considering the water content in the sludge as well as the humidity of the air. The mass of incondensable gases ($mIGerf^{out}$) was determined using the following equation:

$$mIGerf^{out} = mOerf^{out} + mNerf^{out} + mSDerf^{out} + mCerf^{out} \tag{7.17}$$

where $mOerf^{out}$ and $mNerf^{out}$ represent the outlet mass (kg) of O_2 and N_2 respectively and were determined as the mass obtained from the process at bench-scale affected by the volumetric ratio between the Electric Resistance Furnace (V_{ERF}) and the Laboratory Furnace (V_{LF}). Moreover, $mSDerf^{out}$ and $mCerf^{out}$ are the outlet mass of SO_2 and Cl_2 gases (kg) generated by the thermal process and were calculated affecting the mass obtained at bench-scale by the scaled-up factor (S_f).

Energy balance:

This analysis was carried out considering electric resistance furnace efficiency (η_{ERF}) of 85%. The different heats involved in the process were calculated using the scaled-up factor (S_f).

$$Q_{g(ERF)} = (Q_{R(LF)} + Q_{sludge(LF)} + Q_{gases(LF)}) \cdot S_f \tag{7.18}$$

where $Q_{g(ERF)}$ represents the heat delivered (kJ/s) in the electric resistance furnace and $Q_{R(LF)}$, $Q_{sludge(LF)}$ and $Q_{gases(LF)}$ were explained in the previous section.

7.2.4.3. Mass and energy balance of mercury recovery system

In this stage, mass and energy balances were carried in the *heat exchanger* to find out the outlet air temperature that is required to supply in the drying equipment. Furthermore, mass and energy balances in the *sedimentation tank* were assessed to determine the unknown composition of the outlet streams.

Energy balance of the heat exchanger:

Considering heat exchanger efficiency (η_{HE}) of 85% and employing Equation (7.4), the outlet air temperature was calculated following these equations:

$$\begin{aligned} Q_{c(HE)} &= fmIGhe \cdot CpIGhe \cdot (T_{g(in)} - T_{g(out)}) + fmMhe\, Cp^{v}Mhe \cdot (T_{g(in)} - T_c) + \\ & fmWhe\, Cp^{v}Whe \cdot (T_{g(in)} - T_b) + fmMhe\, \lambda_{Hg} + fmWhe\, \lambda_{H2O} + \\ & fmMhe\, Cp^{L}Mhe \cdot (T_c - T_{g(out)}) + fmWhe\, Cp^{L}Whe \cdot (T_b - T_{g(out)}) \end{aligned} \tag{7.19}$$

where $Q_{c(HE)}$, fmIGhe, fmMhe, fmWhe are the heat liberated (kJ/s) and the mass flow of Hg and H_2O (kg/s) that were obtained in the electric resistance furnace. Moreover, the variables T_w, T_f, T_c and T_e represent the working temperature of the furnace, the outlet sludge temperature, the mercury condensation temperature and the boiling temperature of the water, respectively. The Cp^v and Cp^L represent the heat capacity of the metallic mercury (Mhe) and the water (Whe) in vapour and liquid phase respectively expressed in kJ/kg·°C. The λ_{Hg} and λ_{H2O} variables correspond to latent heat of Hg and H_2O expressed in kJ/°C.

$$Q_{g(HE)} = fmAhe\, Cp_m Ahe \cdot (T_{2he} - T_R) \tag{7.20}$$

where $Q_{g(HE)}$, fmAhe, CpAhe represent the heat delivered (kJ/s), mass flow of air (kg/s) and the heat capacity of air (kJ/kg·°C) respectively. T_{2he} and T_R are the outlet air temperature and the reference temperature (°C).

7.2.4.4. Mass and energy balance of co-products recovery system

In this stage, mass and energy balances were focussed on the water recovery system in order to determine the capacity required in the *storage tank.*

Mass balance:

Mass balance of water (mWstort):

$$mWstort^{in} = mWstort^{accum} = mWst^{overflow} + mWd^{evap} \quad (7.21)$$

where $mWstort^{in}$ and $mWstort^{accum}$ represent the inlet and accumulated water mass (kg) in the storage tank while $mWst^{overflow}$ and mWd^{evap} correspond to the overflow water mass (kg) that comes from the sedimentation tank and the evaporated water mass (kg) that comes from the drying stage.

7.2.5. Design and selection of the equipments at pilot scale

As it was previously explained, the furnace was the only equipment of the process that was designed at pilot scale by scaling-up employing the laboratory data obtained from the ceramic muffle furnace. The other equipments involved at pilot-scale thermal treatment process were selected and designed considering the mass and energy balances (mentioned above) and the equipment design equations reported in the literature.

7.2.5.1. Mercury sludge pre-treatment system

The excavator machine was selected from a JBC catalogue (ECOI 25, 2012) for an extraction capacity of 1 m^3 of sludge/h and a maximum excavation depth of 3.5 m. In order to contain and feed the mercurial sludge excavated into the trays a feed hopper with 1 m^3 of capacity was designed (ECOI 25, 2012).

A conveyor belt was the equipment selected to transport the mercurial sludge until the drying equipment. This type was preferred as it can carry on solid materials of different nature (size, bulk density, humidity) horizontally or at an appreciable angle, in the most efficient and economic manner (Towler and Sinnot, 2008). The main design parameter for the equipment was the motor power consumption which was calculated using the data and equation reported in Table 5.5 (Couper et al., 2010).

For the drying operation a tray drying equipment was selected. This device is recommended for filtering cake material such as the mercurial sludge and it has a high efficiency for reducing the sample moisture content (Couper et al., 2010). The design of this equipment was done using the procedure reported by Perry and Green (1999).

The size reduction equipment selected was the rod mill due to its operating range (from 20 mm to 2 mm) fulfill with the process requirements (Walas, 1990). The main design parameter for the

rod mill was the motor power consumption which was calculated using equation 12.6 (Couper et al., 2010).

7.2.5.2. Thermal treatment system

An electric resistance furnace was selected regardless its high energy consumption to avoid a pollution inside the furnace. It has been reported by Trinks et al. (2004) that combustion furnaces are not recommended for treating toxic materials. The design of the electric resistance furnace was carried out using the design considerations reported by Trinks et al. (2004).

7.2.5.3. Mercury recovery system

A double pipe heat exchanger was selected as it is the simplest and economical model, used for cooling or heating (Towler and Sinnot, 2008). Design equation 12.1 reported by Towler and Sinnot (2008) was employed to determine the heat transferred per unit time. The main design parameters were calculated following the methodology reported by Perry and Green (2007).

The sedimentation tank was designed as a common decantation tank (cylinder form with a conic bottom). It can be assumed that the sedimentation of metallic mercury will be very adequate because of its insolubility (Perry and Green, 2007) and high density ($\rho Hg = 13550$ kg/m^3) (Perry and Green, 2007).

7.2.5.4. Co-products recovery system

A water recovery system with a common design of storage tank (cylinder form) was developed for 2 m^3 of capacity in order to reuse the overflow released from the sedimentation stage. For the treated sludge recovery system a retention hopper was designed for the same capacity (1 m^3) of the feed hopper mentioned above.

7.2.6. Techno-economic and environmental 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 or to reach the TCLP permissible limit. The economic assessment was done for both technical alternatives using the factorial method of cost estimation developed by Lang (1948) and reported by Towler and Sinnot (2008) and Peters et al. (2003) 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 sludge) treatment plant of the electrochemical factory “ELQUIM”. The environmental analysis was

developed considering the environmental impact assessment of proposed technology using the Eco-indicator 99 (H) V2.04/ Europe EI 99 H/H method (Ecoinvent, 2007; SimaPro, 2007). A comparative environmental analysis between both technological alternatives and the current treatment that has been employed by the chlor-alkali Cuban plant was also performed.

7.3. Results and Discussion

7.3.1. Bench-scale thermal treatment process

For the drying stage, the average temperature of 80 °C was established and a drying time of 4 h was established from the drying test analysis and drying regimen curve (Table 7.1). The input variables and design parameters of the mercury removal stage (laboratory muffle furnace) have been previously reported (Chapter 6/Table 6.3). The operating conditions of this stage were established considering the mercury reaction scheme previously developed (Chapter 6). It was shown that the same kinetic reaction scheme is applicable at 350 °C and at 450 °C during the whole retorting period (3 h).

A high variability (30%) was observed in total mercury content at different depths in the disposal niche. Total mercury average values of 1747, 1377 and 1223 mg/kg were obtained at 20, 40 and 60 cm of depth. All thermal treatment analyses have been performed using a composite sample (1320 mg/kg of total Hg content), such a variability of 24.5% respect to the maximum content of mercury (sample taken from 20 cm of depth) was observed. According to this and the explained above (section 7.2.1.1), the most suitable temperature of mercury removal was 450 °C in order to guarantee the TCLP permissible limit and to acquire a better mercury removal percent.

7.3.2. Operating conditions of the proposed thermal treatment plant

According to Directive 2008/1/EC (2008), all chlor-alkali plants that still use mercury cell must change this technology for best available techniques (membrane cell) or must close down before 2020. It has been reported by workers of the chlor-alkali Cuban plant that currently a total amount of 7668 tons of mercurial sludge are buried in 52 niches. The proposed pilot plant was designed to treat 3 tons of sludge/d, and thus could process all buried mercurial sludge in less than 8 years. The main operating characteristics of the plant are:

- ✓ The thermal treatment plant will works 4 batch/d, treating 750 kg of mercurial sludge/batch.
- ✓ The thermal treatment plant will operates 320 d/y keeping 45 d/y for the plant's maintenance and other eventualities.
- ✓ The thermal treatment plant will needs 3 workers/batch.

7.3.3. 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 (Table 7.2). From the mass and energy balance, 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 (Figure 6.2/Chapter 6). 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.

Table 7.2. Definition of the inlet and outlet streams of the pilot-scale thermal treatment process [a]

Nomenclature	Symbols	Values	Units
	Tray Drying (D)		
Sludge inlet mass	mSd^{in}	750	kg
Sludge outlet mass	mSd^{out}	386.25	kg
Water evaporated mass	mWd^{evap}	363.75	kg
Water inlet mass flow (by the air)	$fmWd^{in(air)}$	0.007	kg/s
Water evaporated mass flow	$fmWd^{evap}$	0.025	kg/s
Water outlet mass flow	$fmWd^{out}$	0.033	kg/s
Water inlet mass (by the sludge)	$mWd^{in(sludge)}$	375	kg
Water outlet mass (by the sludge)	$mWd^{out(sludge)}$	11.25	kg
Air outlet mass flow	$fmAd^{out}$	0.599	kg/s
Air intlet mass flow	$fmAd^{in}$	0.574	kg/s
Sludge heat capacity	CpSd	1.867	kJ/kg °C
Outlet temperature	T_{2d}	80	°C
Inlet temperature	T_{1d}	25	°C
Equipment efficiency	η_d	85	%
Heat liberated (by the air)	$Q_{cd(air)}$	69.5	kJ/s
Heat delivered (by the sludge)	$Q_{gd(sludge)}$	59	kJ/s

Table 7.2. Cont.

Nomenclature	Symbols	Values	Units
Laboratory Furnace (LF)			
Mercury inlet mass	$mMlf^{in}$	$1.23 \cdot 10^{-4}$	g
Mercury generated mass	$mMlf^{gen}$	$3.84 \cdot 10^{-3}$	g
Mercury outlet mass	$mMlf^{out}$	$3.96 \cdot 10^{-3}$	g
Mercury chloride inlet moles	nMClf	$9.91 \cdot 10^{-6}$	mol
Mercury sulphide inlet moles	nMSlf	$8.47 \cdot 10^{-6}$	mol
Mercury sulphate inlet moles	nMSulf	$3.75 \cdot 10^{-7}$	mol
Oxygen inlet moles	nOlf	3.12	mol
Oxygen outlet mass	$mOlf^{out}$	99.75	g
Nitrogen outlet mass	$mNlf^{out}$	23.2	g
Chlorine outlet mass	$mClf^{out}$	$7 \cdot 10^{-4}$	g
Sulphur dioxide outlet mass	$mSDlf^{out}$	$5.7 \cdot 10^{-4}$	g
Sludge outlet mass	$mSlf^{out}$	2.997	g
Water inlet mass (by the air)	$mWlf^{in(air)}$	0.15	g
Water outlet mass	$mWlf^{out}$	0.153	g
Heat of reaction (Hg)	$\Delta H_{R(M)}$	14	kcal/mol
Heat of reaction (HgS)	$\Delta H_{R(MS)}$	-39.02	kcal/mol
Heat of reaction ($HgSO_4$)	$\Delta H_{R(MSu)}$	122	kcal/mol
Heat of reaction ($HgCl_2$)	$\Delta H_{R(MC)}$	76.4	kcal/mol
Volume	V_{lf}	$9.8 \cdot 10^{-3}$	m^3
Total operating time	t_{lf}	180	min
Temperature difference	ΔT	425	°C
Heat liberated (by the reactions)	$Q_{R(LF)}$	$1.84 \cdot 10^{-5}$	kJ/s
Heat liberated (by the sludge)	$Q_{sludge(LF)}$	$1.3 \cdot 10^{-4}$	kJ/s
Heat liberated (by the gases)	$Q_{gases(LF)}$	$5.16 \cdot 10^{-3}$	kJ/s
Electric Resistance Furnace (ERF)			
Sludge outlet mass	$mSerf^{out}$	374	kg
Mercury outlet evaporated mass	$mMerf^{evap}$	0.48^{b}	kg
Water outlet evaporated mass	$mWerf^{evap}$	12	kg
Oxygen outlet mass	$mOerf^{out}$	436	kg
Nitrogen outlet mass	$mNerf^{out}$	101	kg
Chlorine outlet mass	$mCerf^{out}$	0.091	kg
Sulphur dioxide outlet mass	$mSDerf^{out}$	0.073	kg
Heat liberated (by the reactions)	$Q_{R(ERF)}$	2.38	kJ/s

Table 7.2. Cont.

Nomenclature	Symbols	Values	Units
Heat liberated (by the sludge)	$Q_{sludge(ERF)}$	16.72	kJ/s
Heat liberated (by the gases)	$Q_{gases(ERF)}$	664.5	kJ/s
Equipment efficiency	η_{ERF}	85	%
Volume	V_{ERF}	43	m^3
Double Pipe Heat Exchanger (HE)			
Water mass flow	fmWhe	$1 \cdot 10^{-3}$	kg/s
Incondensable gases mass flow	fmIGhe	0.05	kg/s
Mercury mass flow	fmMhe	$4.61 \cdot 10^{-5}$ [b]	kg/s
Air mass flow	fmAhe	0.574	kg/s
Boiling temperature of mercury	$T_{b(Hg)}$	357	°C
Boiling temperature of water	$T_{b(H2O)}$	100	°C
Gases inlet temperature	$T_{g(in)}$	450	°C
Gases outlet temperature	$T_{g(out)}$	40	°C
Air outlet temperature	T_{2he}	118	°C
Air inlet temperature	T_{1he}	25	°C
Equipment efficiency	η_{HE}	85	%
Heat liberated (by the gases)	$Q_{c(HE)}$	25.3	kJ/s
Heat delivered (by the air)	$Q_{g(HE)}$	29.7	kJ/s
Sedimentation Tank (ST)			
Water overflow mass	$mWst^{overflow}$	12	kg
Water Storage Tank (StorT)			
Water accumulated mass	$mWstort^{accum}$	482	kg
Water inlet mass	$mWstort^{in}$	470	kg

Note: [a] Values obtained per batch of treatment. [b] Values of Hg recovery reported are from alternative 2.

7.3.4. Design and selection of the overall process equipment

An approximate design of the most important equipment of the thermal process (tray dryer, electric resistance furnace, double pipe heat exchanger and sedimentation tank) was done, taking into account the mass and energy requirements and the design equations mentioned above (section 7.2.5). On the other hand, a selection of the other equipments (excavator, feed hopper, conveyor belt, rod mill, storage tank, exhaust gas, axial fan and centrifuge pump) was carried out considering the mass and energy balances and the flux requirements of the process. In Table 7.3 the main design parameters as well as operating conditions of all equipments at pilot-scale are shown.

Table 7.3. Design parameters and operating conditions of the pilot-scale thermal treatment plant.

Equipments	Design parameters	Operating conditions	Power consumption (kWh/d)	Construction material
Rod mill	Dimensions: 1 m of length x 0.67 m of diameter	works 2 h/d	84.5	Carbon steel
Axial fan	Δp=0.11 psi and 0.574 kg/s of air requirement	works 12 h/d	1.67	Carbon steel
Air blower	Δp=$4.92 \cdot 10^{-4}$ psi and 0.54 kg/s of air requirement	works 2 h/d	0.38	Carbon steel
Excavator	Max. load capacity 1.1 m^3 and max. excavation deep 4 m	works 0.5 h/d	-	Carbon steel
Tray drying	Dimensions: 1.1 x 1.1 x 1.65 m, 11trays, 15 cm free space between trays and 10 cm between the trays and the equipment whole.	Average temperature (80 °C), pressure (1 atm); works 16 h/d, inlet air (mass flow of 0.574 kg/s at 118 °C)	-	Carbon steel recover with mineral wool
Feed hopper	Dimensions: 1 m^3 of capacity	feed 2.2 m^3/d	-	Carbon steel
Conveyor belt	15 m of length x 1 m of width	works 2 h/d	0.22	Carbon steel
Centrifuge pump	Three-phase motor 220/440 V, 60 Hz and nominal power of 0.011 kW	works 3.3 h/d	0.036	Carbon steel
Retention hopper	Dimensions: 1 m^3 of capacity	feed 2.2 m^3/d	-	Carbon steel
Sedimentation tank	Dimensions: 0.1 m^3 of capacity (1.7 m of heigh x 0.2 m diameter)	Max. temp inside 36 °C and pressure 1 atm; works 12 h/d	-	Carbon steel
Exhaust gas-drying	Δp=0.32 psi and 0.599 kg/s of air requirement	works 16 h/d	5.57	
Exhaust gas-furnace	Δp=0.05 psi and 0.051 kg/s of air requirement	works 12 h/d	1.12	
Double pipe heat exchanger	16 m^2 of heat exchange area	works 12 h/d	-	Carbon steel
Electric resistance furnace	Dimensions: 5 x 3 x 3 m, 75 resistance rags, which have 7 m of hot line and will be disposal in zigzag position to cover more area.	Temperature (450 °C) and Pressure (1 atm), works 12 h/d as thermal process, 30 min to cool the equipment and 15 min to load and download.	1072	Refractory steel with a thickness of mineral wool as isolate material

7.3.5. Detailed description of the thermal treatment process at pilot scale

The proposed thermal treatment plant to treat the mercurial sludge generated by chlor-alkali Cuban plant at pilot scale is depicted in 3D in Figure 7.3. The plant was designed for a production capacity of 3 ton/d, a detailed description of the process per batch of treatment was done.

The process starts with the excavation of 1 m^3 of the sludge material from the niche which is deposited in a feed hopper of that capacity. One operator is in charge of distributing 750 kg of sludge in 11 trays that are introduced later in the drying equipment by means of the conveyor belt.

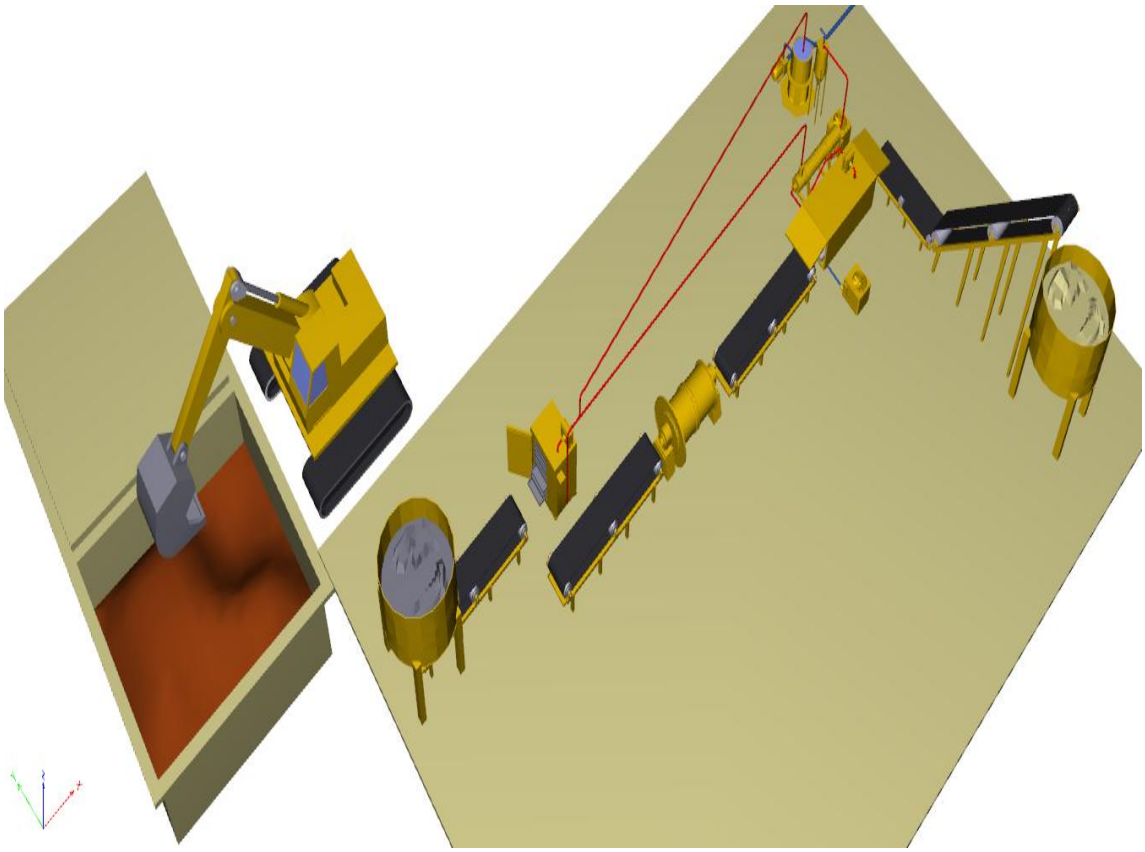


Figure 7.3. Representation in 3D of the proposed thermal treatment plant (superior panoramic view).

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 sludge sample from 50% to 3%. Following, the total mass of dry sludge (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 sludge 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 (Chapter 6). It is worth to explain that from thermal analyses at laboratory scale (Chapter 6), 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 to recover energy from the hot gases (450 °C) that leave the thermal desorption 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 desorption 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 down pipe. 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 desorption 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 sludge (374 kg/batch) is stored in a retention hopper for its next packaging. According to the chemical composition of the sludge obtained after the thermal treatment and the Cuban standard for the construction material (NC: 251/2005), 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.

7.3.6. Economic assessment of the thermal treatment technology

The economic assessment was addressed to determine static economic indicators such as Total Capital Investment (TCI), Total Production Cost (TPC) and Annual Gross Profit (AGP). The evaluation of the thermal treatment technology involved two different operating alternatives of the thermal treatment system (electric resistance furnace):

- ***Alternative 1***: Thermal treatment system working at conditions suited to achieve a maximum Hg removal (Temp = 450 °C and time = 3 h)

- ***Alternative 2***: Thermal treatment system working at conditions that allow treating the waste up to a point that it meets TCLP leaching criteria (Temp = 450 °C and time = 1 h)

Table 7.4. Equipment investment costs of the Thermal treatment plant [a]

Equipments	Investment Costs (US$)	Reference
Rod mill	4 600	(ECOI 25, 2012)
Axial fan	11 669	(Matches, 2007)
Air blower	9 586	(Matches, 2007)
Tray drying	14 715	(Matches, 2007)
Feed hopper	1 924	(ECOI 25, 2012)
Storage tank	9 989	(Towler and Sinnot, 2008)
Conveyor belt	46 203	(Towler and Sinnot, 2008)
Centrifuge pump	4 821	(Towler and Sinnot, 2008)
Retention hopper	1 924	(ECOI 25, 2012)
Sedimentation tank	6 113	(Matches, 2007)
Exhaust gas-drying	10 419	(Matches, 2007)
Exhaust gas-furnace	2 084	(Matches, 2007)
Double pipe heat exchanger	23 200	(Matches, 2007)
Electric resistance furnace	171 431	(Matches, 2007)

Note: [a] The excavator was not included on the equipment investment cost as was rented for working hours

The updated equipment investment costs (CEIndexJUNE/2012=729.9) (Chemical engineering, June, 2012) of the thermal treatment plant (Table 7.4) as well as the estimation of the TCI by percentage of delivered equipment method (Table 7.5) have been outlined. High value of Total Capital Investment (US$ 1 417 080) are mainly attributed to equipment investment cost (US$ 318 678) where the electric resistance furnace represents 54% of the total equipment investment cost.

Table 7.5. Estimation of the Total Capital Investment of the Thermal treatment plant.

Parameters	Fraction of delivered equipment[a]	Calculated values (US$)
	Direct Costs	
Purchased equipment, E'	-	318 678
Delivery, fraction of E'	0.10	31 868
Subtotal: delivered equipment	-	350 545
Purchased equipment installation	0.39	136 713
Instrumentation and Controls(installed)	0.26	91 142
Piping (installed)	0.31	108 669
Electrical systems (installed)	0.10	35 055
Buildings (including services)	0.20	70 109

Table 7.5. Cont.

Parameters	Fraction of delivered equipment[a]	Calculated values (US$)
Yard improvements	0.12	42 065
Service facilities (installed)	0.55	192 800
Total direct costs	1.93	1 027 098
	Indirect Costs	
Engineering and supervision	0.25	87 636
Construction expenses	0.34	119 185
Legal expenses	0.04	14 022
Contractor's fee	0.19	66 604
Contingency	0.10	35 055
Total indirect costs	0.92	322 502
Fixed capital investment (FCI)	-	1 349 600
Working capital (WC)	0.19	67 480
Total capital investment (TCI)		1 417 080

Note: [a] Fractions of delivered equipment were taken from Towler and Sinnot (2008)

The annual TPC without depreciation was determined for both treatment alternatives (Table 7.6). Significant differences of the TPC were observed between alternative 1 (US$ 352 459) and alternative 2 (US$ 293 416) mainly due to the increase in power consumption. The first alternative involves a three times higher consumption of electricity (electric resistance furnace) than the second one.

Table 7.6. Estimation of the Annual Total Production Cost (without depreciation) at 100% capacity of the thermal treatment plant for the Alternatives 1 and 2.

Parameters	Factor	Alternative 1 Cost (US$/y)	Alternative 2 Cost (US$/y)
Operating labour (OL)	*	51 840	51 840
Operating supervision (OS)	0.1 of OL	5 184	5 184
Utilities	**	170 150	113 469
Maintenance and repairs (MR)	0.02 of FCI	26 992	26 992
Operating supplies	0.1 of MR	2 699	2 699
Laboratory charges	0.05 of OL	2 592	2 592
Variable Cost		259 457	202 776
Taxes (property)	0.01 of FCI	13 496	13 496
Insurance	0.004 of FCI	5 398	5 398

Table 7.6. Cont.

Parameters	**Factor**	**Alternative 1 Cost (US$/y)**	**Alternative 2 Cost (US$/y)**
Rent	0.004 of FCI	5 398	5 398
Fixed Charges		24 293	24 293
Plant Overhead		42 008	42 008
Manufacturing cost		325 758	269 077
Administration	0.15 of OL, OS and MR	12 602	12 602
Distribution and selling	0.02 of CTP	7 049	5 868
Research and Development	0.02 of CTP	7 049	5 868
General Expense		26 701	24 339
Total Production Cost		352 459	293 416

* Operating labour cost (OL) was determined considering 3 operators/batch, working 4 batch/d and 1.8 US$/h of operator rate.
** Utilities cost was determined considering air cost (0.9 US$/100m^3), electricity cost (0.11 US$/kWh) and water cost (0.53 US$/m^3).

From a techno-economical point of view, the alternative 2 represents a more feasible technology considering several criteria:

- The difference of mercury removal efficiency (97.8%) for this alternative is not representative with the mercury removal efficiency obtained for the first one (97.96%). Although, for this alternative a higher leachability of mercury (0.14 mg/l) compared with the first one (0.02 mg/l) was observed (Figure 6.2/Chapter 6), it was preferred as fulfil with the TCLP permissible limit (0.2 mg/l) at lower technological costs.
- A cost-benefit assessment for both alternatives clearly indicates that the alternative 2 should be preferred due to around 98% of mercury is recovered at less total production cost by means of less electricity consumption (56 681 US$/y).

Although alternative 2 represents more suitable operating conditions for the proposed technology, it does not report by its own any profit (-US$ 420 655). This can be mainly attributed to the high cost of Total Capital Investment (US$ 1 417 080) and the reduced project life of the proposed technology (8 years).

The current analysis was carried out under the assumption that further production using the chlor-alkali process stops. Therefore, the economic assessment of the proposed technology aims at cleaning up all mercury waste that currently is stored on the site. Nevertheless, the possibility to integrate such a sludge treatment in a continued use of the process constitutes another real option to assess and implement the proposed technology. In the following section an integrated economic

assessment of the proposed mercurial sludge treatment plant with the chlor-alkali Cuban plant have been developed.

7.3.6.1. Integrated economic assessment (Mercurial sludge treatment plant and chlor-alkali Cuban plant "ELQUIM")

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 2011 by the ELQUIM plant are shown in Table 7.7 (data reported by personnel of the plant).

Table 7.7. Capital spending and annual sales reported by the ELQUIM plant in 2011.

Products	Annual sales (US$/2011)
Caustic soda	2 353 910
Bottled Soda	213 914
Liquid chlorine	2 654 946
Chloride acid	430 799
Descaling	117 854
pH-D	118 527
Sodium hypochlorite	1 811 049
Superior bleach	2 856 593
Clorin P	188 537
Hydrogen	8 163
Total annual sales (US$/2011)	10 754 292

Items	Direct costs (US$/2011)	Items	Indirect costs (US$/2011)
Electrolysis	6 284 007	Cells maintenance	208 547
Bottled Soda	102 167	Laboratory	96 083
Liquid chlorine	496 977	UEB Management	193 518
Acid	51 241	Auxiliary services	89 802
pH-D	69 267	Plant general services	372 726
Hypochlorite	182 946	Cl_2 cylinder maintenance	1 815
Clorin P	115 966	Electrolysis	331 276
Hydrogen	429	Liquid chlorine	301 166
Cl_2 cylinder maintenance	194 048	Hydrochloric acid	3 945
Capital reparation	633 451	Hypochlorite	531 417
Total Capital spending (US$/2011)			10 191 526

Considering the proposed thermal treatment technology as a mercurial sludge treatment plant of the chlor-alkali Cuban plant, static and dynamic economic indicators were evaluated for both alternatives (Table 7.8). 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 7.8. 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)	10 517 284	10 460 603
Annual depreciation (US$/y)**	168 700	168 700
Annual Gross Profit - AGP (US$)	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	12156
Internal Rate of Return - IRR (%)	10	15

* Considering the economic data reported by the ELQUIM plant.
** Considering an annual depreciation factor of 0.125 (8 years of project's health life).

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 1a higher payback period was required (5 y). It is necessary to remark that for these profitability measures the time values of money (inflation) was not included. The profiles of the Net Present Value (NPV) obtained for both integrated alternatives are shown in Figure 7.4. An Internal Rate of Return (IRR) of 15% was acquired from the integrated alternative 2 while for the first integrated alternative only 10% was attained. A residual treatment plant project that reaches an IRR superior of 10% can be considered profitable (Ulrich and Vasudevan, 2004).

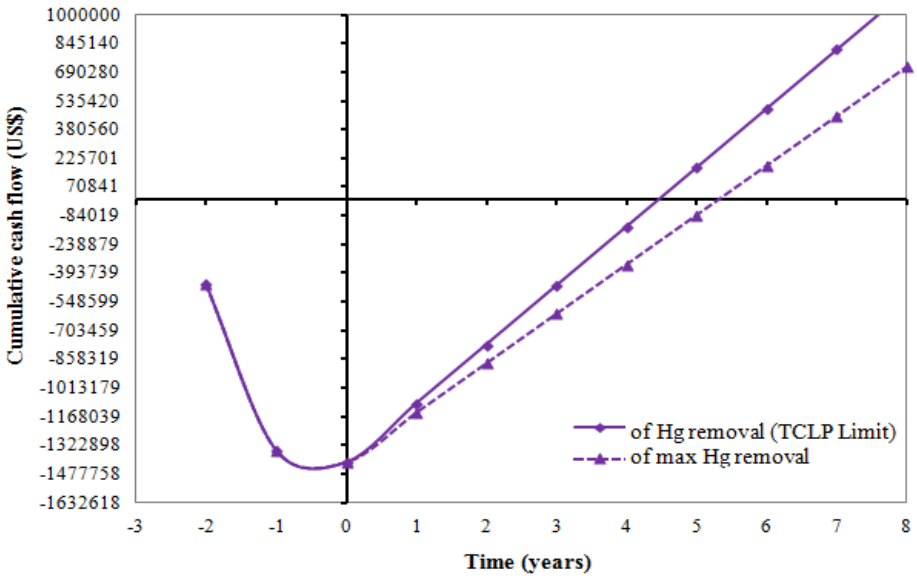


Figure 7.4. Comparison of Net Present Value profiles during the health life of the project for both integrated alternatives

From this integrated economic assessment it is clearly demonstrated that the integrated alternative 2 represents the most suitable alternative to treat the mercurial sludge 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 sludge that are currently buried in niches can be solved. The alternative 2 leads to higher residual Hg levels in the treated sludge (29 mg/kg of sludge) compared to levels that naturally occur in soils (< 0.4 mg/kg) (Kabata-Pendias and Pendias, 1984). 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 sludge as a “pozzolanic material” need to be done.

7.3.7. Environmental impact assessment by Life Cycle Analysis (LCA)

In order to evaluate the environmental impact of the proposed thermal treatment technology a comparative analysis using LCA methodology considering two comparative scenarios was done. In Scenario 1 a comparison between both operating conditions (alternative 1 and alternative 2, detailed above) of the proposed technology was assessed while in Scenario 2 a comparison between the proposed alternative 2 (more suitable option) and the current treatment (existing) applied by the

chlor-alkali Cuban plant have been evaluated. The existing treatment applied by the Cuban plant which includes stabilization of the mercury waste and disposal in concrete niches was earlier detailed (Chapter 1).

- **Scenario 1:** Compare two operating conditions (alternative 1 and alternative 2) of the proposed thermal treatment technology.

Figure 7.5 shows the general description of this scenario in which the main difference between alternative 1 and 2 is the electricity consumption and the amount of Hg recovery. For the comparative environmental analysis of this scenario the functional unit employed was 1 day of work which implicates 3 t of mercurial sludge (reference flow) that will be treated.

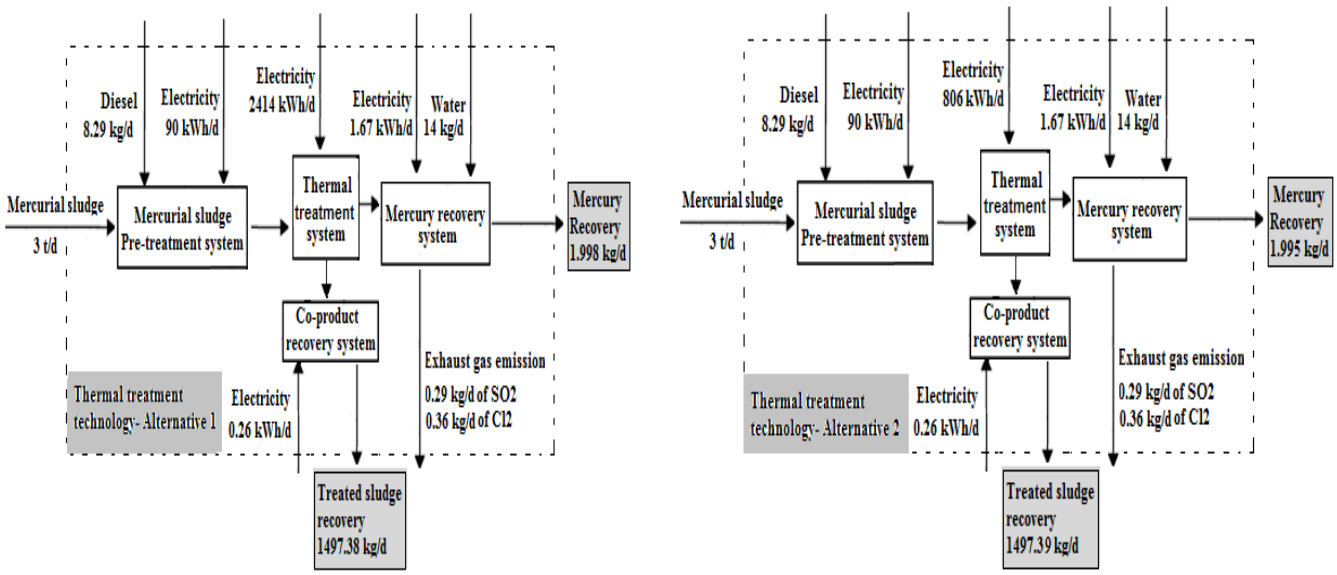
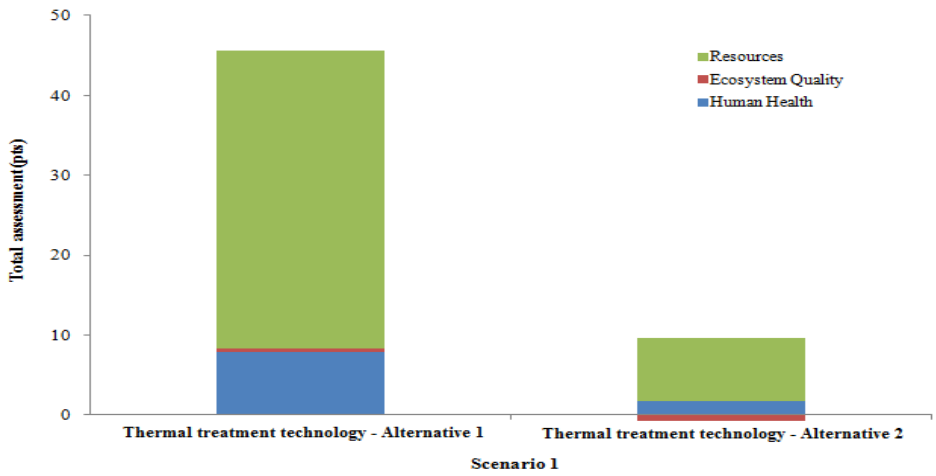


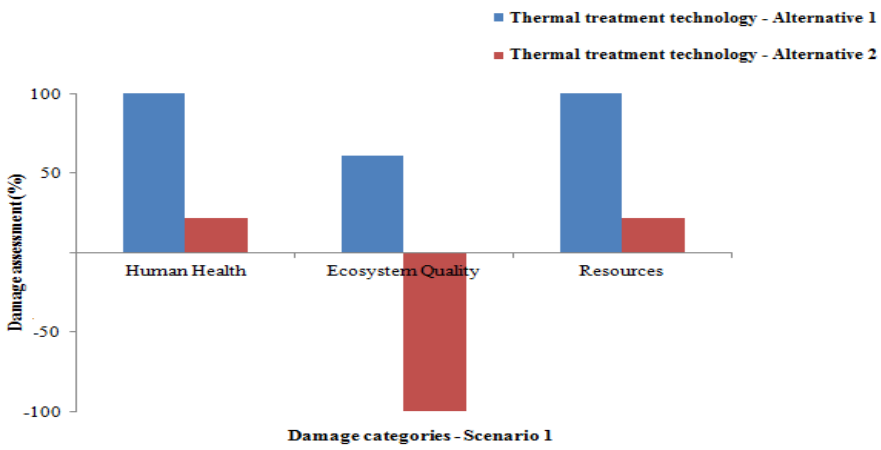
Figure 7.5. General description of the Scenario 1

Figure 7.6a represents a comparative analysis of the environmental impact assessment between alternatives 1 and 2 based on a unique punctuation. The unique punctuation is a manner to express by points, the environmental impact assessment of a scenario considering both damage and impact categories. From a global comparison of both alternatives it appears that alternative 2 impacts 80% less than alternative 1 in to the environment.

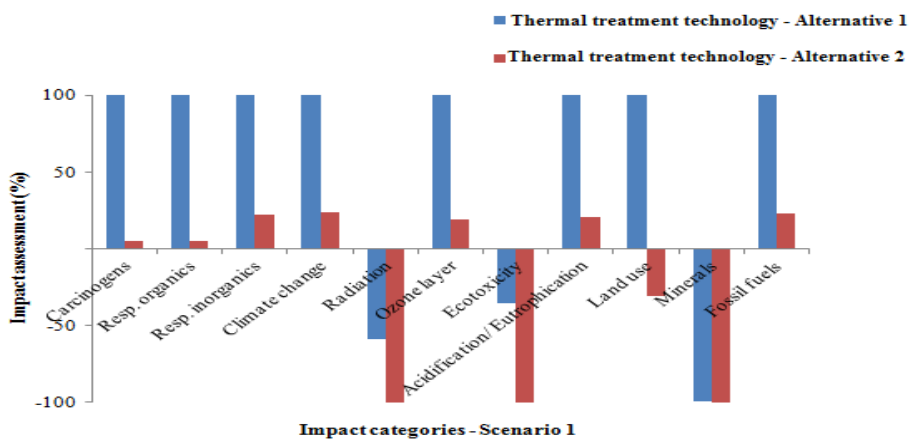
From a specific evaluation by means of damage category (Figure 7.6b) it was found that for both alternatives the most impacted damage category was the resources. Nevertheless, the alternative 2 contributes less in to environmental damage than alternative 1 where a significant damage reduction by concept of Human health (78%), Ecosystem Quality (-161%) and Resources (78%) was observed. This phenomenon is mainly due to a considerable reduction on the electricity consumption (three times less) for the second alternative.



[a] Expressed in a unique punctuation



[b] Expressed in damage categories



[c] Expressed in impact categories.

Figure 7.6. Comparative analysis by environmental impact assessment of the Scenario 1 [(a,b,c)]

The present scenario was also evaluated considering the environmental effect of both alternatives by means of impact categories (Figure 7.6c). It was clearly demonstrated that the alternative 2 has a fewer effect in all impact categories.

The negative values observed for the impact categories of radiation, minerals and ecotoxicity represent a positive effect to the environment. In this sense, this can be linked with the high efficiency of mercury recovery which avoid the ecotoxicity problems by Hg pollution and less extraction of the mineral (Hg) for its commercial use. Finally, the environmental impact assessment of the scenario 1 allowed us to select the alternative 2 as the best of the two studies alternative's, from environmental point of view.

- **Scenario 2:** Compare the current mercurial sludge treatment that is carried out by the chlor-alkali Cuban plant (existing scenario) and the alternative 2 of thermal treatment technology (future scenario)

Figure 7.7 shows the general description of this scenario establishing the system boundaries. A comparison between the current mercurial sludge treatment developed by the ELQUIM factory and the selected thermal treatment technology was done. For the comparative environmental analysis of this scenario the same functional unit and reference flow (employed in scenario 1) were used.

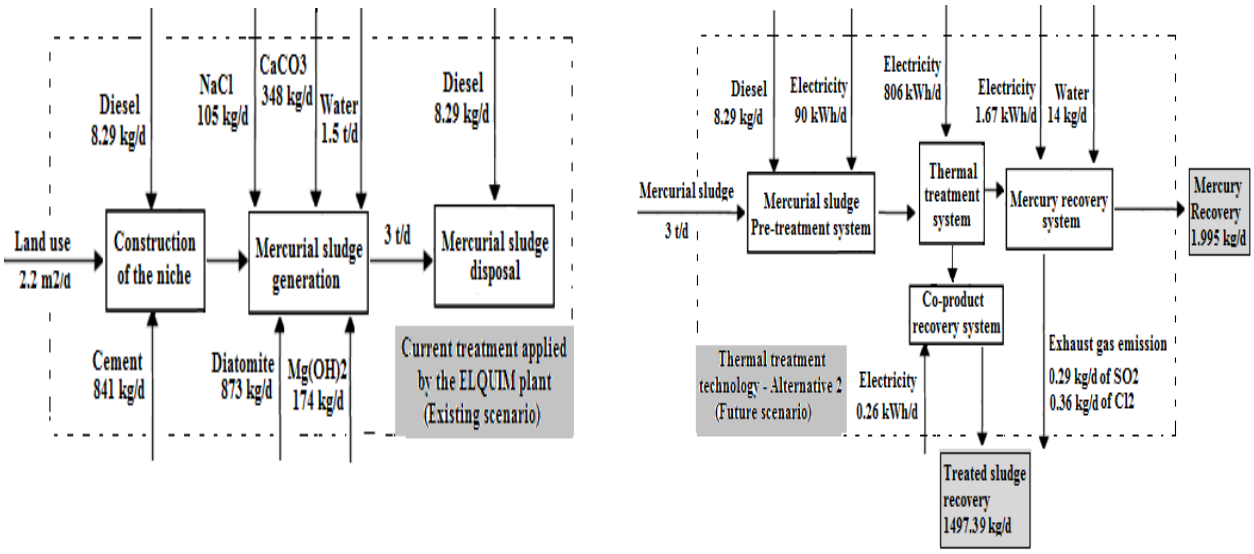
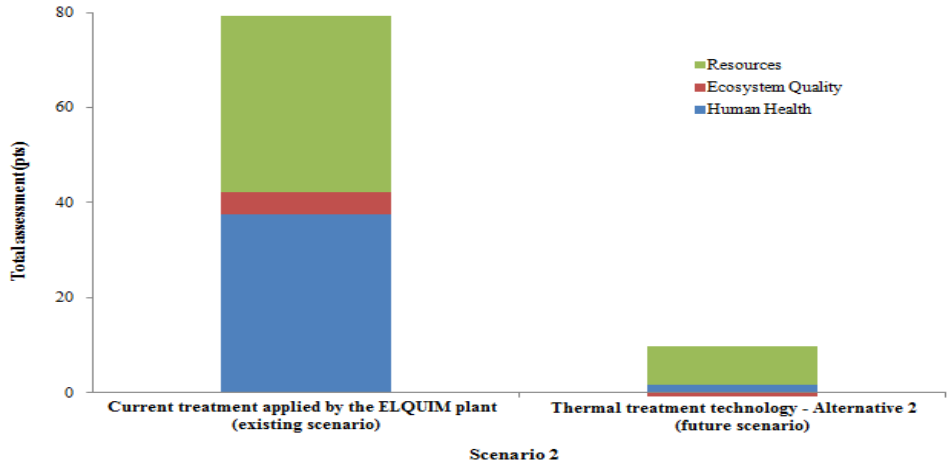
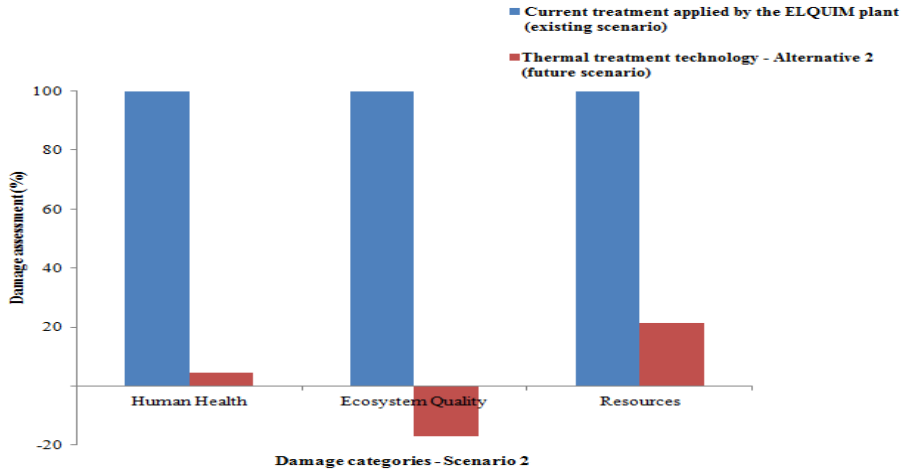


Figure 7.7. General description of the Scenario 2.

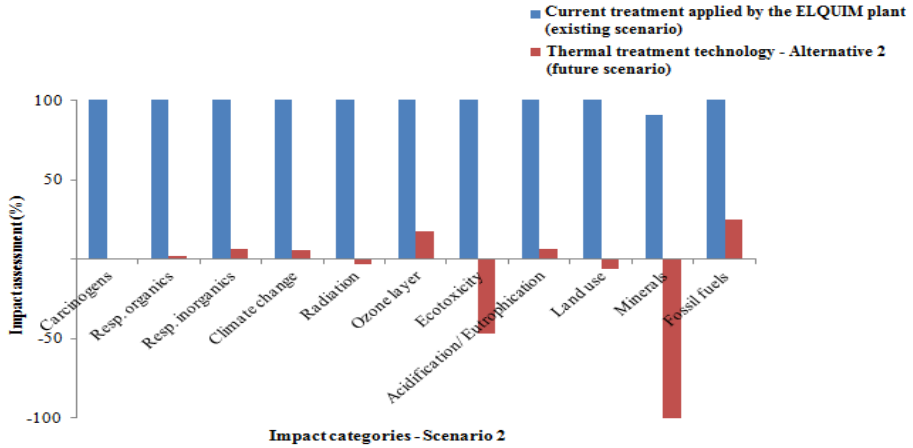
The environmental impact assessment between the existing scenario and the future scenario based on a unique punctuation is represented in Figure 7.8a. A comparative analysis demonstrated that the future scenario impacts 89% less than the existing scenario in to the environment. The current treatment employed by the ELQUIM factory (existing scenario) impacts in the same way in the human health and resources damage category.



[a] Expressed in a unique punctuation



[b] Expressed in damage categories



[c] Expressed in impact categories.

Figure 7.8. Comparative analysis by environmental impact assessment of the Scenario 2 [(a,b,c)]

This phenomenon is associated with the high amount of chemical products that are used to stabilize the mercury solution that comes from the chlor-alkali production process as well as the high amount of cement needed to build the niches for the further mercurial sludge disposal. Although in the existing scenario the mercurial sludge is dispose in niches, this buried sludge represents a potential contamination risk, which can cause an extreme damage to the human health, resources and ecosystem quality. On the other hand, for the proposed thermal treatment technology (future scenario) the resources represent the most impacted category (89.5%) (Figure 7.8b).

A comparative analysis of the behaviour of the existing and future scenario based on their effects on the impact categories was also evaluated (Figure 7.8c). The existing scenario has a significant and negative effect on fossil fuel, respiratory inorganics, carcinogens and climate change impact categories. This is linked with the high consumption of chemical products, cement and diesel. In the future scenario the main impacted category is the fossil fuel (24.6%). This is associated with the fossil fuel consumption required to supply the amount of electricity needed in the thermal treatment process. However, the use of green energy could achieve a substantial reduction on this impact category. Nevertheless, the future scenario has a lower effect in all impact categories than the existing scenario. The negative values observed for the impact categories of minerals, ecotoxicity, land use and radiation, represents a positive effect to the environment. This effect is associated with the high efficiency of mercury recovery avoiding ecotoxicity problems by Hg pollution which represents less extraction of the mineral (Hg) for its commercial use and no land use is required during the technological process.

For this environmental assessment it has been assumed that the Cuban company keeps processing the sludge in the same way, where the stabilisation procedure aims to optimize towards low leachability. Future studies should focus on possibilities to adapt the current stabilisation procedure in order to optimize the subsequent recovery of mercury.

General highlights from the environmental impact assessment:

- Significant environmental benefits across all impact indicators (impact and damage categories) arise from applying the thermal treatment technology (alternative 2). This behaviour is expected as the technological alternative 2 (future scenario) constitute the most suitable approach for mercury recovering and recycling.
- The negative numbers in Figures 7.7 (Scenario 1) and 7.9 (Scenario 2) indicate that there are overall environmental savings. These reductions in overall impact and damage categories are dominated by the environmental benefits that arise from the reuse of mercury and arid material, which can substitute for primary resources.

- The potential changes in environmental impacts that may arise from the mercury levels reduction have been assessed. Specifically in scenario 2, the current treatment applied by the Chlor-alkali Cuban factory (existing scenario) did not contribute in any measure to mercury level reduction as it is based on stabilizing and disposing the mercury contaminated waste in niches. On the other hand, the alternative 2 (future scenario) gives a reduction of -100% of minerals and -47% of terrestrial ecotoxicity impacts which result from a direct reduction of mercury emissions from landfill disposal as the mercury contaminated waste is treated and the mercury is recovered. These negative numbers reflect the environmental benefits of the avoided mercury emissions.

Finally, the future scenario (alternative 2 of the thermal treatment technology) represents an attractive treatment alternative from techno-economic and environmental point of view for Cuban conditions.

7.4. Conclusions

In the present Chapter, a pilot-scale thermal treatment technology to treat high mercury containing wastes from chlor-alkali plants has been designed. According to the international legislations and the Cuban government dispositions, the project has been developed to process all amount of mercurial sludge that is currently confined in niches in less than 8 years. A pilot plant with a treatment capacity of 960 ton of sludge/y, able to recovery 639 kg of metallic mercury/y and 479 ton/y of treated sludge (“arid” that can be sold) was designed. The scale-up methods as well as the mercury reaction scheme (developed in Chapter 6) were employed to design the electric resistance furnace at pilot scale. The design and selection of the other equipments of the pilot process was done considering the equipment design equations and process requirements.

A 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). Nevertheless, this alternative by its own does not represent a profitable option because this technology is focussed on treating contaminated waste in order to avoid environmental hazards rather than to generate a commercial product.

An integrated economic assessment of the alternative 2 with the Chlor-alkali Cuban production plant was done. This alternative represented an attractive option due to an annual gross profit of US$ 166 450, a return on investment of 10.6 %/y, a net present value of US$ 12 157 and an internal rate of return of 15%. This integration represents a decrease in profit of US$ 396 316 (70%) for the Chlor-alkali Cuban plant by comparing with the current scenario of the plant but it allows pay the total capital investment of the proposed technology in 4.2 years.

A comparative analysis of the environmental impact assessment for the alternative 2 (future scenario) and the current treatment applied by the chlor-alkali Cuban plant (existing scenario) was done. The future scenario represents the most suitable alternative from environmental point of view.

For Cuban conditions, the implementation of the proposed thermal treatment technology (alternative 2) although stand for a project of significant costs, represents considerable benefits for the environment and human health. These findings could be important for decision makers in the chlor-alkali industry sector to develop strategies for risk reduction of mercury emissions and to develop environmental policies.

GENERAL DISCUSSION, CONCLUSIONS AND FUTURE PERSPECTIVES

8.1. General discussion

This PhD project dealt with the thermal treatment technology as alternative to decontaminate high mercury containing wastes from chlor-alkali plants. The most important findings from the small-scale experiments, simulation and pilot-scale technological design are discussed in the following sections.

8.1.1. Mobility, availability and leaching behaviour of mercury in wastes generated by the chlor-alkali plant.

In Chapter 3 while performing the DIN leaching test, mercury concentrations in all fractions of Sample 2 by far exceeded the permissible limit of 0.02 mg/l according to the Council Directive 91/689/EEC. Although Sample 1 showed a much slower release of Hg, the concentrations in all fractions were still hundredfold above the permissible limit. The concentrations of Hg in the fractions of the DIN test differed greatly, by more than a factor of ten, between both tested samples. The cumulative leaching of Hg over the entire leaching test amounted to less than 0.1% for Sample 1, but was in the order of 7.0% for Sample 2, which exhibited a lower total Hg content but a much more intensive leaching. As Sample 1 was one year older, the more limited release of Hg from that sample, despite its higher total Hg content, might be attributed to an ageing effect. However, it might also reveal a significant variability in the quality of stabilization applied to the sludge. Regular sampling and testing of the produced sludge would be required to ascertain the variability in the production.

The stabilization of the mercurial sludge currently applied by the chlor-alkali Cuban factory using Na_2S is aimed to convert mercury into insoluble HgS. Nevertheless, the high concentrations of Hg observed in the DIN test fractions indicate the presence of more soluble mercury forms. $HgCl_2$ has a practical solubility in water of 70 g/l. High mercury concentrations in the leachate of contaminated soils have been mainly attributed to the presence of $HgCl_2$ (Bollen et al., 2008). In addition, oxidation of mercury sulphides during the leaching process may contribute to an enhanced mercury mobility (Barnett et al., 2001; Holley et al. 2007).

The fractionation results from Chapter 4 indicated that Hg associated with the F4 fraction (residual), which is the least available Hg form based on its potential of solubilisation (mainly HgS), represented 42.7% of the total mercury content. Nevertheless, this value does not guarantee the necessary encapsulation of this metal in the sludge matrix. The most mobile fractions (F1 + F2) corresponded with the highest percentages of Hg content (52.2 ± 1.5% of total Hg) indicating an elevated risk for Hg mobilisation by the presence of water-soluble and exchangeable mercury compounds such as $HgCl_2$, $HgSO_4$ and HgO. Although the mercury content present in fraction F3

(organic) only accounts for 0.9 ± 0.1% of the total Hg content obtained in the analysed sample, it still represents a significant amount (21.2 mg/kg) and therefore an environmental concern.

For a second time, the findings demonstrate that the current treatment with sulphide applied by the Cuban electrochemical plant is inadequate for immobilizing and encapsulating mercury compounds to an extent that leaching of the mercury would not anymore impose a significant hazard for the environment under the current disposal conditions. Taking into account that thermal treatment is the recommended method by USEPA (2008) to treat high mercury content wastes (> 260 mg/kg), it was selected as the most suitable alternative to remediate this sludge.

Next to the treatment selection, bench-scale thermal experiments at different temperatures and exposition times would further corroborate the potential of thermal treatment to decontaminate this mercury waste.

8.1.2. Potential of thermal treatment to decontaminate high mercury contaminated wastes.

Mercury removal efficiencies increased with temperature and with treatment time. Temperature was the most important factor in order to achieve quantitative removal of the Hg. for temperatures higher than 300°C, more than 90% removal of Hg was achieved in less than 15 minutes.

The waste with the higher total mercury content (waste B), was the one with the least Hg leaching. The higher buffering capacity which is reflected in a higher pH after the extraction (TCLP test) was responsible for the differences observed on the Hg leaching behaviour of the analyzed samples. Theoretically, $Hg(OH)_2$ solubility is expected to decrease by a factor of 100 for each unit increase in pH (Lindsay, 1979). As such, a higher pH value of only 0.25 units (waste B) represented a significant influence into the leaching behaviour. A decreased Hg leachability in the residue to below the TCLP reference value at temperatures above 350 °C was observed, demonstrating that technically, the thermal treatment allows decreasing total mercury contents, and consequently also achieves to reduce leachability to values below the threshold value.

Considering the high mercury removal efficiency, close to 100%, obtained in the present survey, the potential of the thermal treatment for this kind of sludge have been proven. Next to this thermal experiment, the kinetic survey of the mercurial sludge considering the fractionation findings (Chapter 4) and thermodynamic studies would further elucidate the mercury removal mechanism from mercury wastes using thermal treatment.

8.1.3. Mechanism and kinetics of mercury removal from mercury contaminated wastes during thermal treatment.

To depict the thermal decomposition of the mercurial sludge sample, a scheme of six reactions was proposed (Table 6.1). Thermal decomposition reactions in the solid phase were considered the

fast process influenced by the temperature, but limited by the diffusion and particle size of the sludge sample (L'vov, 2001; 2008).

Reactions R_1 and R_4 were found to be exothermic while the other reactions were endothermic. On the other hand, for all reactions, except for R_2, the direct reaction was favoured as the equilibrium constant was higher than for reverse one. The difference on the thermodynamic behaviour found for R_2 was expected as the inverse reaction (formation of HgO) is favoured, corresponding with findings of L´vov (1999).

Once the reaction scheme was created and a bench-scale kinetic survey was performed at different exposure times for three retorting temperatures (250, 350 and 450 °C) the kinetic parameters (α_f, k_j and n_r) were experimentally obtained at each retorting temperature (Table 6.6). The accuracy of fit was evaluated comparing the modelled conversion profile with the experimental data. A different behaviour was observed from comparing the conversion profiles at 250 °C and 350-450 °C (Figure 6.4). This variation was presumably attributed to the difference in the controlling reaction mechanism that takes place at low and high temperature (Peralta, 1993). Moreover, it is worth mentioning that at 250 °C the phase change of the mercury has not been reached yet.

Our results confirmed that not a single mechanism was ruling the process. The D_1-diffusion (one-dimensional diffusion according to Table 6.2) could be considered the controlling mechanism of the process at high retention times while at low thermal decomposition times (< 15 min) the diffusion mechanism (D_1) as well as the third order reaction mechanism (F_3) could be controlling the process. Note that this behaviour was observed at low (250 °C) and high (450 °C) temperatures as indicated by a good fit of the thermal decomposition data over the whole range of conversions (Figure 6.5). As a first in-depth to the knowledge of this type of systems (polydisperse and multicomponent), the diffusion mechanism (D_1) can be considered the overall controlling mechanism as an increase of the temperature smooths the progress of the chemical reactions involved.

The thermal decomposition of the mercurial sludge showed changes in the diffusive phase that controls the reaction mechanism. Specifically, at the beginning, the external diffusion of the gas (O_2) through the sludge particle was the controlling mechanism. Nevertheless, as the thickness of the product layer (ashes) increased with time the diffusion of products through the ashes to the gaseous phase became the controlling reaction mechanism.

In the present work we also paid attention to mass and energy balances as well as the design of equipments considering technical, economical and environmental criteria in order to propose a pilot-scale thermal treatment plant to treat mercury contaminated wastes.

8.1.4. Technological proposal of a thermal treatment plant to treat mercury contaminated wastes generated from chlor-alkali plants, Cuba as study case.

A pilot-scale thermal treatment technology to treat high mercury containing wastes generated by the chlor-alkali Cuban plant was designed. The proposed pilot plant with 960 ton of sludge/y of processing capacity would be able to recover 639 kg of metallic Hg/y and 479 ton/y of treated sludge ("arid") that can be valorized as construction material.

The proposed technology represents an attractive alternative to remediate high mercury contaminated wastes generated by chlor-alkali plants, mainly in developing countries. In order to count with a more efficient, economically viable and environmentally compatible technology we would like to make the following suggestions:

- ✓ To design a technology that focuses on working at optimal operating conditions not only the time and temperature should be considered as key factors but also, the mercury removal mechanism should be established in the process.
- ✓ To design a technology that focuses on minimizing the effluent streams of the process through evaluation of its further reuse in the same process (the water as a utility) or in another process (the recovered mercury as a raw material).
- ✓ To design a technology that allocates the energetic integration of the process, reducing energy losses.

For developing countries an attractive alternative would be the integration of the proposed plant (thermal treatment technology) with the existing chlor-alkali production plant. Considering the technological proposal as a mercury waste treatment plant instead of an independent production plant implies the reduction of the costs effects and transforms the mercury cell chlor-alkali plants into a less aggressive technology to the environment.

8.2. Conclusions

1. The mercury contaminated wastes from chlor-alkali Cuban plant are characterized as "toxic" (TCLP test), "hazardous" (German DIN 38414-S4 test) and "high mercury wastes" (LDR, USEPA), corroborating that the current treatment applied by the Cuban factory (stabilisation and disposal) is not effective to adequately immobilize mercury into the solid matrix.
2. Mercury fractionation analysis demonstrated the presence of other mercury compounds besides HgS. It is suggested that $HgCl_2$, $HgSO_4$ and HgO are present in the mercury contaminated waste as high mercury concentration in the mobile fraction (water-soluble and exchangeable mercury compounds) were observed.
3. Thermal treatment technology stands for a suitable option to decontaminate mercury solid wastes generated by the chlor-alkali Cuban plant. Small-scale experiments demonstrated that this technology is very effective to remove the Hg (close to 100%) and also for reducing the leachability of the residual mercury waste below the threshold value (0.2 mg/l).
4. This study contributed to increasing our understanding of the behaviour and removal mechanism of mercury by thermal treatment. For the first time, a kinetic reaction mechanism was proposed for the thermal treatment of this type of system (polydisperse and multi-component system).
5. The pilot-scale thermal treatment technology developed to treat high mercury contaminated wastes represents the first in-depth survey that proposes a technological design which includes the kinetic reaction mechanism that takes place during the thermal decomposition of mercury contaminated waste. Moreover, the economical integration of the proposed thermal treatment technology with chlor-alkali production plants constitutes an attractive option to implement, mainly in developing countries. In addition, the environmental impact assessment of the proposed technology based on Life Cycle Analysis (LCA) stands for the starting point to qualitatively assess this kind of process.
6. For Cuban conditions, the implementation of the proposed thermal treatment technology, although implying considerable costs, represents significant benefits for the environment and human health.

8.3. Future Perspectives

1. Although insights into the reactions of mercury in coal combustion processes have increased considerably, an integrated mercury removal model comprising the complex web of chemical-physics characteristics and mercury compounds present in mercury contaminated wastes by thermal removal processes is yet to be developed. Modelling efforts should be performed to integrate the current knowledge.
2. There is a vital need for more advanced methods for speciation of mercury in highly contaminated solid wastes from chlor-alkali plants, as many research studies have focussed on fractionation analysis. However, with the aim of further elucidating the removal mechanism of mercury in this complex matrix (mercurial sludge) more specific speciation methods should be achieved to further corroborate the present findings.
3. Many research reports on thermal decomposition of solid compounds have been published so far. Nevertheless, there is a lack of studies with the focus on mercury compounds (mainly HgO). In this sense, more investigations should be addressed expanding the current knowledge of the thermal decomposition behaviour on this specific topic.
4. There is an urgent need for more research about the thermal decomposition process of polydisperse and multicomponent systems as the current knowledge have been only focussed on developing thermal decomposition mechanisms of mono-component and homogeneous solid matrices. Sufficient attention should be given in this sense as the majority of the solid systems on the nature are polydisperse and multicomponent.
5. In line with the continuing debate on the role of mercury removal mechanism that depict the behaviour of mercury compounds in contaminated wastes from chlor-alkali plants by thermal treatment, direct effect on the mercury removal kinetic behaviour comes from obtaining a well experimental data set (measuring all streams of the process at solid and gaseous phase with emphasis on mercury species quantification). Eventually, the development of more specialized analytical instruments to measure gas phase compounds during thermal treatment analysis, require more attention as it will contribute to a better understanding of mercury removal mechanism as well as to an improved design of thermal treatment technologies at pilot or full scale.
6. Even though the number of studies on environmental impact assessment by Life Cycle Analysis (LCA) (qualitative analysis) and Externalities Cost (quantitative analysis) have increased considerable over the last decade to assess the sustainability of a product or process, a lack of knowledge on mercury removal process was found. In line with the present study, more attention should be given to these fields that provide helpful tools in decision making in the chlor-alkali

industry sector to develop strategies reducing the risk of mercury emissions and developing environmental policies.

7. Finally, more research is needed on possible end-uses of mercury wastes obtained after thermal treatment, especially their potential use as “arid” or “puzollanic material” in construction. This could trigger their application, especially in developing countries.

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CURRICULUM VITAE

Personal Information

Last name:	Busto Yera
First name:	Yailen
Date of birth:	4 May 1983
Place of birth:	Havana, Cuba
Address:	Camajuani Road km $2^{1/2}$, Nº 124, Santa Clara, Villa Clara, Cuba
Tel:	+53 42 281738
Email:	BustoYera.Yailen@UGent.be
Nationality	Cuban

Education

2001-2006	**Chemical Engineer**
	Las Villas University, Faculty of Chemical Engineering
	(with Great Distinction)
2009 - 2012	**PhD in Applied Biological Sciences**
	Ghent University, Faculty of Bioscience Engineering
	Promoters: Prof.dr.ir. Filip Tack (Belgium), Prof. dr. Xiomara Cabrera (Cuba) and Prof. dr. Luis M. Peralta (Cuba)

Teaching and tutoring experience

2009 - 2010	Automatic Fundaments
2010 - 2011	Computation
2011 - 2012	Numerical Methods
2008	Tutor of thesis.
	Title: Study of technological alternatives to treat mercurial sludge generated by the Chlor-alkali plant "ELQUIM".

Scientific Contributions
Publications

- **Busto, Y.**, Cabrera, X., Peralta, L. M. 2010. Tratamiento Térmico: posible alternativa de recuperación de mercurio presente en lodos generados en la producción de cloro-sosa. *Revista Tecnología Química* **XXX** (2): 67-73. ISSN paper: 0041-8420. (English version: Thermal treatment: a possible alternative for mercury removal from sludge generated by the chlor-alkali production. Journal of Chemical Technology).
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