Doctoral thesis

Processing of mercury-contaminated industrial wastes, particularly from former chlorine-alkali electrolysis facilities and acetaldehyde sites in soil washing plants

(Die Aufbereitung quecksilberkontaminierter Industrieabfälle unter besonderer Berücksichtigung ehemaliger Chloralkalielektrolyse- und Acetaldehydstandorte in Bodenwaschanlagen)

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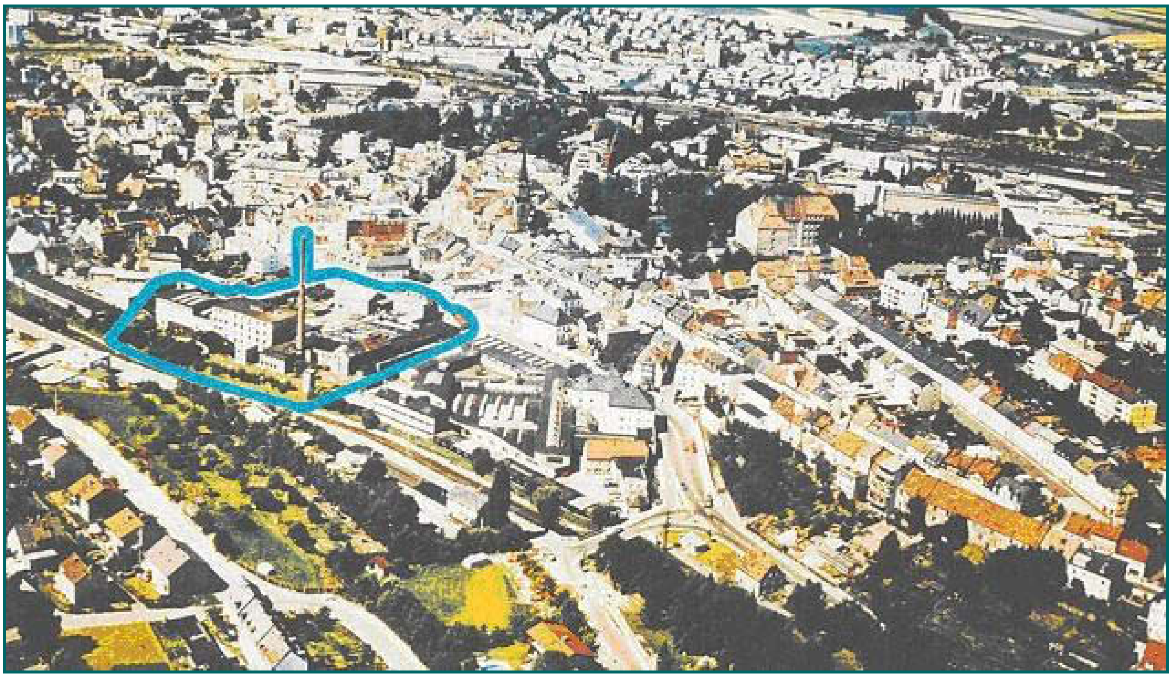
Abu Dhabi, June 2011



The Chemical Factory Marktredwitz was the first large-scale mercury remediation project worldwide (photo: Harbauer)

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To

my dear wife Robinah for her tolerance and patience

and

to

baby Caelyn Gerda – welcome to the world!

ACKNOWLEDGEMENTS

This doctoral thesis would not have been possible without the support of many people. The author wishes to express his gratitude to his supervisor, Professor Dr. Helmut FLACHBERGER, holder of the Chair of Mineral Processing who was abundantly helpful and offered invaluable assistance, support and continual guidance but also excellent cooperation during the associated industrial project study.

My appreciation is extended to Professor Dr. Karl LORBER, co-reviewing member of the thesis supervisory team, for a couple of fruitful discussions and for giving the permission to perform necessary tests under specific HSE and PPE conditions in his laboratory associated to the Institute for Sustainable Waste Management and Technology.

I am also deeply indebted to my wife, Robinah, for her support and her patience all the way through when I worked on many weekends and during all my recent leaves on this thesis.

The candidate wishes also to express his special gratitude to his passed away mother Gerda Waltraut Ingeborg, nee VOLLMER by supporting and encouraging him all the way with the intention of becoming an engineer, but also to his supervisor, when the author was an apprentice in crafts, Mr. Matthias GEIER, an excellent craftsman and one of the most well-read persons he ever met, but also to two very special professors during his basic engineering education at the technical college in Graz (Höhere Technische Lehranstalt) Arch. Prof. Dipl.-Ing. Hermann WORSCHITZ and to the current head master, Prof. Dipl.-Ing. Reinhold NEUMANN.

The author also wants to express his gratitude to his earlier academic teacher Prof. Dr.rer.nat. Wolfgang SIMONIS (the ‘father of the free jet flotation’), no longer with us, and formerly holder of the Chair of Mineral Processing and Beneficiation of the Technical University of Berlin and to Dr. Lutz ROLF, formerly assistant professor of the same department for the most creative time as an engineer in his life.

Besides this I am also obliged to some of my former colleagues and co-workers in various mercury and soil/waste treatment projects performed in the past twenty years in various countries and in particular to my co-authors in diverse publications in particular to Dipl.-Berging. Andreas J. SCHMIDT and Dr.-Ing. Frank STAPELFELDT but also to my current employer TAKREER giving me the opportunity to write this thesis in parallel to my normal duties as a Department Manager of the BeAAT waste treatment facilities in the Ruwais Refinery Division/United Arab Emirates.

Special thanks also to all the laboratory staff of the Chair of Mineral Processing in Leoben and of the Institute for Sustainable Waste Management and Technology, but especially to the lab technicians of the BeAAT plant laboratory in Ruwais/United Arab Emirates supporting me in completing the required chemical analysis for this thesis, but also to my secretary Khurram Maqsood, who helped me to format the entire document during the final phase of this work and to my friend and colleague Nayaz Sohale Sayed, Sr. Environmental Engineer for his review and advice.

Last but not least the candidate wants to say ‘thank you’ to his dear colleague Dipl.-Ing. Andreas SCHMID, he became a friend during the course of this thesis, for all his constructive and helpful assistance.

The author would also like to convey thanks to the Administration Department of the Montanuniversität Leoben for their always helpful and competent support and their uncomplicated approach which is remarkable enough to be mentioned here.

It is my dearest wish to thank honestly the ‘Republic of Austria’ for their well-established school system, giving everybody a fair chance to learn and get access to higher education.

ABSTRACT

The PARCOM-decision 90/3 from 14 June 1990 recommends that all chlorine-alkali electrolysis facilities in Western Europe using the amalgam process shall be phased out for reasons of environmental protection at the latest by 2010. For the treatment of the demolition material from decommissioned chlorine plants in particular soil and rubble soil washing should be considered as a treatment option as an alternative to underground mine or mono dump disposal.

Physical-chemical soil washing plants have proven to be suitable for the treatment of contaminated soils during the last 25 years. The first soil washing plants were based on the principle that soil was liberated by mechanical energy input and the contaminant-soil separation took place by applying subsequent combinations of classifying and separation processes.

Because of the concentration of contaminants in the fine particle fraction, flotation becomes a significant separation process in the particle-size-fraction below 500 µm. In the past the successful application of soil flotation was mostly related to the treatment of organic contaminants such as Petrol Hydrocarbons (PHC) and Polycyclic Aromatic Hydrocarbons (PAH).

Previous investigations regarding the flotation of heavy-metal contaminated soils were performed with material from a former steel works and rolling mills inner city site in Berlin. A recovery of maximum 75 % lead and 44 % zinc was obtained for a one step flotation. The recovery of the cleaned soil amounted to 92 %[1]. Preliminary tests performed with mercury-contaminated soil in a range of 1,000 mg/kg have shown that a removal of mercury from the soil under the given laboratory conditions in a particle size range of 25-500 µm is possible. The best results were received with KAX as a collecting agent at a pH of 8.

In order to provide the best treatment for different soils from various chlorine-alkali electrolysis plants and acetaldehyde factories a categorization based on various samples selected from former and currently ongoing mercury remediation cases worldwide could be made, showing that the silt and clay fraction in very cohesive soils from chlorine-alkali plants have a much lower mercury content than sandy soils up to a concentration of fine in a range of 20 mass-%. Next to the positive effect of attrition for the enrichment of mercury in the fin particle range the importance of the removal of other with mercury closely linked soil components in chlorine-alkali soils such as carbon (mostly as graphite from the electrodes) was highlighted in this thesis.

Owing to the different solubility of various mercuric sulphide species in aqueous systems such as in particular the sulfur mercuric ion HgS_2^{2-} a flotation method was developed using organic sulphidisation agents and xanthates in the same process.

Performing tests rows with different mercury concentrations have proven that this process is applicable for solid high mercury wastes up to 1,000 mg/kg up to a particle size range of 500 µm and is capable to be implemented in existing or newly designed soil washing plants. All TCLP-tests performed with treated soil in laboratory scale were passing the leaching criteria for $Hg < 0.2$ mg/l. In the dry substance the target value “Zuordnungswert 2 (Z2)” of the German LAGA: $Hg \leq 10$ mg/kg DW could be reached.

The thesis includes also experience made with other treatment options than soil washing such as in particular stabilization/solidification and thermal desorption.

Keywords: Mercury, soil washing, solubility of mercury sulfide species, physical/chemical separation and froth flotation

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[1] STAPELFELDT F. AND RICHTER R.: Flotation von kontaminierten Böden und artverwandten mineralischen Abfällen in Bodenwaschanlagen (Flotation of contaminated soils and similar mineral waste materials in soil washing plants, Altlastenspektrum (04/2002), pp.: 188 - 192

KURZFASSUNG

Die „PARCOM-Entscheidung 90/3“ vom 14. Juni 1990 empfiehlt, dass alle nach dem Amalgamverfahren arbeitenden Chloralkalielektrolyseanlagen der 176 Mitgliedstaaten aus Gründen des Umweltschutzes bis spätestens 2010 stillzulegen oder umzurüsten. Aufgrund der umfangreich vorgenommenen weltweiten Stilllegungen und des damit einhergehenden Rückbaus zahlreicher Chloralkalielektrolysen und Acetaldehydfabriken sind zuverlässige und kostengünstige Aufbereitungstechnologien zur Behandlung der quecksilberkontaminierten Abfälle aus dem Rückbau derartiger Anlagen von großer Bedeutung. Anwendbare technische Verfahren für die Behandlung quecksilberkontaminierter, mineralischer Abfälle sind insbesondere die Bodenwäsche und die Vakuumdestillation als Alternative zu einer etwaigen Untertagedeponierung oder einer Einlagerung in Monodeponien.

Physikalisch-chemische Aufbereitungsanlagen (Bodenwaschanlagen) haben sich in Deutschland, Österreich und in der Schweiz in den letzten zwanzig Jahren bei der Reinigung kontaminierter Böden und anderer mineralischer Abfälle bewährt. Das Behandlungsprinzip basierte lediglich auf dem Aufschluß des Bodens durch den Eintrag mechanischer Energie. Die Abtrennung der Schadstoffe erfolgte vorwiegend durch Kombinationen von Klassier- und Sortierprozessen. Durch die Aufkonzentration der Kontaminanten im Feinkornbereich, erlangt die Flotation Bedeutung als Separationsprozeß im Partikelgrößenbereich bis 500 µm. Bisher wurde die Flotation in der Bodenwäsche lediglich bei der Behandlung organisch kontaminierter Böden, insbesondere bei polycyclischen aromatischen Kohlenwasserstoffen (PAK) erfolgreich eingesetzt[1].

Im Rahmen von Vorarbeiten zu dieser Dissertation wurden u.a. entsprechende Untersuchungen mit einem hochgradig blei- und zinkbelasteten Bodenaushubmaterial von einem innerstädtischen Walzwerksgelände aus Berlin durchgeführt. Dabei wurde nach entsprechender Vorbehandlung ein Bleiausbringen von 75 % und ein Zinkausbringen von 44 % durch Flotation erzielt. Das Ausbringen an gereinigtem Boden betrug 92 %[i]. Anhand von Vorversuchen mit quecksilberkontaminiertem Boden konnte gezeigt werden, dass im Korngrößenbereich von 25-500 µm eine Abreinigung durch Flotation von 1000 mg/kg auf die Zielwerte der LAGA (Z2: Hg ≤ 10mg/kg) möglich ist.

Anhand von Bodenproben, die an verschiedenen Chloralkalielektrolyse- und Acetaldehydstandorten weltweit entnommen wurden, konnte eine Kategorisierung hinsichtlich des korngrößenbezogenen Quecksilbergehaltes im Feststoff und des Auslaugungsverhaltens vorgenommen werden. Es wurde u.a. festgestellt, dass bei ton- und schluffreichen Böden der Quecksilbergehalt in dieser Fraktion vergleichsweise geringer ist, als in sandigen Bodentypen mit einem Feinkorngehalt bis ca. 20 Massen-%. Auf den positiven Effekt durch Attrition zur Anreicherung von Quecksilber in der Feinfraktion bei sandigen Böden und auf die Bedeutung der notwendigen Abtrennung der meist hoch quecksilberbelasteten kohlestämmigen Fraktion aus Chloralkalielektrolyseböden (zumeist Anodenkohle) wurde hingewiesen.

Auf der Kenntnis des unterschiedlichen Löslichkeitsverhaltens einzelner Quecksilbersulfidspezies in aquatischen Systemen bei variierendem pH-Wert wurde ein Flotationsverfahren auf der Basis organischer Sulfidisierungsreagenzien und Kaliumamylxanthat (KAX) als Sammler entwickelt, wobei dem Komplex HgS_2^{2-} eine besondere Bedeutung zukommt. Es konnte gezeigt werden, dass das Verfahren im Kontaminationsbereich von etwa 1000 mg/kg Quecksilber durchaus zuverlässige Reinigungsergebnisse erbringen kann. Als Zielwert für eine Verwertung des gereinigten Bodens wurde der Zuordnungswert 2 (Z2) der LAGA: Hg ≤ 10 mg/kg herangezogen. Sämtliche Ergebnisse der Eluierversuche nach dem TCLP-test lagen eindeutig unterhalb der Toxizitätsgrenze von Hg < 0,2 mg/l.

Schlüsselworte: Quecksilber, Bodenwäsche, Löslichkeit von Quecksilbersulfiden, physikalisch/chemische Trennung, Schaumflotation

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[i] STAPELFELDT F. UND RICHTER R.: Flotation von kontaminierten Böden und artverwandten mineralischen Abfällen in Bodenwaschanlagen (Flotation of contaminated soils and similar mineral waste materials in soil washing plants, Altlastenspektrum (04/2002), pp.: 188 - 192

PUBLICATIONS AND CONFERENCE CONTRIBUTIONS ASSOCIATED WITH THIS THESIS

Richter R. B., Stapelfeldt F, Flachberger, H and Araujo, M. D.
Physikalisch-chemische und biologische Verfahren zur Behandlung quecksilberkontaminierter mineralischer Abfälle (physico-chemical and biological processes for the treatment of mercury contaminated wastes), Altlastenspektrum (03/2008), Seite 101 bis 115

Richter R.B. and Stapelfeldt F.
Sanierung quecksilberkontaminierter Altlasten und Anwendung von Dekontaminationsverfahren (Remediation of mercury-contaminated former industrial facilities and application of treatment processes), lecture given during DepoTech 2008 (environmental exhibition) in Leoben/Austria (12 up to 14 November 2008), published in DepoTech 2008 conference transcript, pp. 109 to 114.

Richter R.B.
Treatment and decontamination of highly mercury-contaminated industrial wastes, speech held during Austrian Mining Day (Österreichischer Bergbautag) in Leoben/ Austria (26 and 27 May 2009), published in conference transcript, pp. 25 and 26.

Richter R.B.
Strategy for remediation of industrial sites highly contaminated with mercury and dioxins, speech held on 2009 Jade Mountain Forum on Sustainable Environment at National Cheng Kung University Tainan/Taiwan on 3 June 2009, published in conference transcript.

Richter R.B. and Schmidt A.J.
Mercury recovery from solid hazardous wastes by thermal desorption, presentation given during DepoTech 2010 (environmental exhibition) in Leoben/ Austria (3 up to 5 November 2010), published in DepoTech 2010 conference transcript.

Richter R.B. and Flachberger, H.
Physical/chemical treatment of mercury-contaminated wastes from former Chlorine-Alkali-Electrolysis Plants – Application of flotation technologies in soil washing plants, Presentation for the XXV International Mineral Processing Congress in Brisbane, Australia, September 2010, published conference transcript, pp. 3881 to 3895.

Richter R.B. and Flachberger, H.
Soil washing and thermal desorption: Reliable techniques for remediating materials contaminated with mercury, BHM (Berg- und Hüttenmännische Monatshefte), 155 Jg. (2010), Heft 12, pp. 1-7.

“The determining factor in a successful life is not what you know, but how you use it; is not your technical training, but your strength of character and your social vision, which will direct your energies into channels that are wise for you and helpful to your fellow men….”

Earle Wesley Frost

AFFIDAVIT

I hereby declare in lieu of oath, that I have prepared this thesis independently and that I also have performed the associated research myself, by exclusive reliance on the literature and tools indicated therein.

This thesis has not been submitted to any other examination authority in its current or an altered form.

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Acronym	Description
A	**Area; [m^2]**
ABW	**Abbruch-, Boden- und Wasserreinigungsgesellschaft m.b.H., formerly PORR Umwelttechnik, is operating a soil washing plant in Vienna**
ADNOC	**Abu Dhabi National Oil Company**
AEG	**Allgemeine Elektrizitäts-Gesellschaft (General Electricity Company)**
Agfa	**Aktiengesellschaft für Anilinfabrikation**
AIAG	**Allgemeine Industrie Aktien-Gesellschaft (Switzerland)**
aka. (a.k.a.)	**as known as**
ALSAG	**Altlastensanierungsgesetz: Federal law (7 June 1989) with regard to the Act on the Clean-Up of Contaminated Sites for the Republic of Austria recorded and documented under the terms of the Contaminated Sites Atlas Act (Altlastenatlas)**
APC	**Air pollution control**
ARAR	**Applicable or relevant and appropriate requirements**
ARM	**Absolute Residual Mean**
ASAW	**Ammonia Soda Ash Waste**
ASTM	**American Society for Testing and Materials**
BAT	**Best Available Technology**
BeAAT	**Central Environment Facilities in Ruwais, Emirate of Abu Dhabi/UAE, hazardous waste treatment and recycling facility of TAKREER/ADNOC**
BD	**Bedrock**
($BDET^{2-}$)	**1,3-benzenediamidoethanethiol dianion**
BDAT	**Best demonstrated available technology**

bgs	**below ground surface**
BL	**Berlin list; Berliner Liste (1996)**
BNL	**Brookhaven National Laboratory**
BUNA	**Buna works named after butadiene and sodium (Natrium), established in Schkopau, Marl, Hüls and Monowitz**
BvS	**Bundesanstalt für vereinigungsbedingte Sonderaufgaben (Federal Agency for Reunification Operations)**
[C]	**Coulomb; SI Unit for electric charge; [C] = [A·s], Ampere seconds**
CAP	**Chlor alkali plant (synonym for chlorine-alkali electrolysis plant)**
CAS	**Chemical Abstracts Service**
c_C	**Metal or contaminant concentration in the concentrate (effluent)**
c_{eq}	**Equilibrium concentration of an ionic compound in an aqueous solution**
c_F	**Metal or contaminant concentration in the feed**
CERCLA	**Comprehensive Environmental Response, Compensation, and Liability Act**
CFE	**Chemische Fabrik Elektron**
CFG	**Chemische Fabrik Griesheim**
CFM	**Chemische Fabrik Marktredwitz (Chemical Factory Marktredwitz)**
CGR	**Centra voor grondreiniging (soil treatment center) see also GRC**
CIS	**Chemical Immobilization and Solidification**
CKB	**Chemisches Kombinat Bitterfeld**
CKD	**Cement kiln dust**
[cm]	**centimeter**
[cm/sec]	**centimeters per second**
c_{max}	**Maximum possible metal or contaminant concentration in the concentrate (see SI Selectivity Index)**
COC	**Contaminant of Concern**
CP	**Chlorine Plant**
CPDC	**China Petrochemical Development Corporation**
CUB	**Coal Utilization By-product**
DAF	**Dissolved air flotation (type of a flotation machine without agitation)**
DDT	**Dichlorodiphenyltrichloroethane**
DEF	**Delayed Ettringite Formation**
DEV S4	**Originally part of "Deutsches Einheitsverfahren zur Untersuchung von Schlamm und Sedimenten" (German Leaching Procedure after DIN 38414-S4; DEV S4)**
DNAPL	**Dense, non aqueous phase liquid**
DM	**Deutsche Mark (Former currency of the Federal Republic of Germany)**
DM	**Dry Matter (see DW)**
DRP	**Deutsches Reichs-Patent (German Reich Patent)**
DTCB	**Dithiocarbamate**
DW	**Dry Weight considering analysis results in [mg/kg DW]**
E_A	**Electrical potential as per Lippmann Equation; [V]**
EBCT	**Empty Bed Contact Time (Residence time for adsorption on char coal etc.)**
EDL	**Electrical Double Layer**
ER	**Environmental Restoration; a commonly used term is: ER Technologies**
EWC	**European Waste Code**
F_A	**Force of adhesion; [N]**
FCAP	**Former Chlorine-alkali electrolysis Plant**
FCPS	**Former Chlorine Plant Site**
FDA	**Food and Drug Administration**
Flask	**Trade Unit for mercury in iron bottles: 1 Flask is containing approx. 34.5 kg**
FNM	**Fond národního majetku České republiky (Fond of the National Property of**

	the Czech Republic)
GRC	**Grondreiniging Centra**
HCB	**High Concentrated Brine**
HELP	**Hydraulic Evaluation of Landfill Performance**
Hg	**Mercury**
HHRA	**Human Health Risk Assessment**
HHW	**Household Hazardous Waste, also referred to as domestic hazardous waste**
HI	**Hazard Index**
HMI	**Human Machine Interface**
HSAB	**Hard and soft acids and bases theory as introduced by Perkins**
HSWA	**Hazardous and Solid Waste Amendments (associated to LDR)**
HMW	**High mercury waste**
ICI	**Imperial Chemical Industries Ltd, founded in the UK in 1926 from a group of four chemical companies: Brunner, Mond & Co., Nobel Industries, United Alkali and British Dyestuffs Corporation**
ICIANZ	**Imperial Chemical Industries of Australia and New Zealand Ltd**
ID	**Inside Diameter**
IDW	**Investigation Derived Wastes**
IG Farben AG	**Interessengemeinschaft Farben (German Dye Industry Syndicate), founded in 1925, was the world's largest group of consolidated companies in the chemical industry and owned a number of chemical factories including chlorine-alkali electrolysis plants such as in Buna Schkopau and in Bitterfeld**
IMERC	**Incineration of wastes containing organics and mercury**
k	**Hydraulic conductivity as per Darcy's law; [m/s]**
κ	**Mineral content; [g/l] or [t/m^3]**
K_{sp}	**Solubility product; [mol^3/l^3]**
KAX	**Potassium Amyl Xanthate (nomenclature as introduced by Taggert)**
KEtX	**Potassium Ethyl Xanthate (nomenclature as introduced by Taggert)**
[l/min]	**liters per minute**
LDR	**Land disposal restriction**
$\log K_{sp}$	**Decimal logarithm of the solubility product**
m	**Number of molecules of an ionic compound in aqueous solution (see also n)**
[m]	**metres**
m_s	**mass of solids (marked with a dot indicated mass flow of solids)**
MAK	**Maximale Arbeitsplatzkonzentration (see OEL)**
MCL	**Maximum Contaminant Level**
[mg/kg]	**milligrams per kilogram (parts per million)**
[mg/m^3]	**milligrams per cubic meter**
MODFLOW	**Modular three-dimensional finite-difference groundwater flow model**
MODPATH	**particle-tracking postprocessor program for MODFLOW**
MSC-E	**Meteorological Synthesizing Centre-East, located in Moscow/Russia, was established as an international centre for monitoring and evaluation of long-range transmission of air pollutants in Europe (EMEP)**
[mS/cm]	**milli-Siemens per centimeter (technical Unit for conductivity)**
MS/MSD	**Matrix Spike/Matrix Spike Duplicate**
MSL	**Mean Sea Level**
MSW	**Municipal Solid Waste**
MUT	**Miljøvern Umwelt-Technik**
MW	**Monitoring Well**
MWH	**Montgomery Watson Harza**
n	**Number of molecules of an ionic compound in aqueous solution (see also m)**
N_2	**Nitrogen**
NFHR	**North Fork Holston River**
NFHRM	**North Fork Holston River Mile**

[ng/L]	**nanograms per liter (parts per trillion)**
NIOSH	**National Institute of Occupational Safety and Health**
NOAA	**National Oceanographic and Atmospheric Administration**
NPL	**National Priorities List**
[ns]	**nanosecond (one billionth of a second)**
OD	**Outside Diameter**
OEL	**Occupational Exposure Level (corresponds to Austrian/German MAK)**
OU	**Operable Unit**
ÖGPs	**Ökologische Großprojekte were managed and financed as ecological superfund projects by the BvS (German Federal Agency for Reunification Operations)**
OSPARCOM	**Oslo and Paris Commission (Environmental Regulations for the European Community)**
PAH	**Polycyclic Aromatic Hydrocarbons**
PAK	**Polyzyklische Aromatische Kohlenwasserstoffe**
PCDD/F	**Polychlorinated Dibenzodioxins/-furans, simply referred to as dioxins/furans**
PEL	**Permissible Exposure Limit (see also OEL, TWA and MAK)**
PID	**Piping and Instrumentation Diagram**
PFD	**Process Flow Diagram**
PG	**Packing groups (for dangerous waste)**
pH	**Negative logarithm of hydrogen-ion activity**
PHC	**Petroleum Hydrocarbon**
PPE	**Personal Protection Equipment**
PRAP	**Proposed Remedial Action Plan**
PSD	**Particle Size Distribution aka Grain Size Distribution**
PVC	**Polyvinyl Chloride**
Q	**Flow Volume**
QA/QC	**Quality Assurance/Quality Control**
q_A	**Specific electric charge density per area** $[C/m^2]$
RA	**Risk Assessment**
RAP	**Remedial Action Plan**
R_C	**Recovery of the contaminant; [%]**
Re	**Reynolds number; [-]**
R_M	**Recovery of the contaminant; [%]**
RCRA	**Resource Conservation and Recovery Act**
RI/FS	**Remedial Investigation/Feasibility Study**
RIWHF	**Ruwais Industrial Waste Handling Facility of TAKREER/ Abu Dhabi**
RL	**Reporting Limit**
RM	**Residual Mean**
R_M	**Mass recovery in the concentrate; [%]**
RMERC	**Retorting or roasting in thermal processing Units volatizing mercury and condensing the volatized mercury for recovery as per 40 CFR part 268.42**
ROD	**Record of Decision**
RQD	**Rock Quality Designation**
R_S	**Mass recovery of the decontaminated soil; [%]**
RSD	**Residual Standard Deviation**
S	**Solubility of ionic compounds in water; [mol/l] or [g/l]**
SAP	**Sampling and Analysis Plan**
SDMC (SDDC)	**Sodium** Dimethyl **Dithiocarbamate**
SKET	**Schwermaschinenbau-Kombinat Ernst Thälmann (Vendor of froth flotation equipment)**
SPT	**Standard Penetration Test**

SI	**Selectivity Index for separation processes as introduced by Douglas**
SR	**State Route**
S/S	**Solidification/Stabilization**
SWCB	**State Water Control Board**
T	**Temperature; [^{o}C]**
T	**Tension force; [N]**
TAIC	**Taiwan Alkali Industrial Corporation**
TBG	**Tiefbauberufsgenossenschaft: Heavy earthwork and construction accident prevention and insurance association**
TCLP	**Toxicity Characteristic Leaching Procedure**
TDS	**Total Dissolved Solids**
TVA	**Tennessee Valley Authority**
	Time Weighted Average related to PEL, normally based on an 8 hour work shift adequate to German/Austrian MAK
UAE	**United Arab Emirates**
USACE	**United States Army Corps of Engineers**
USCS	**Unified Soil Classification System**
USEPA or US EPA	**United States Environmental Protection Agency**
USGS	**United States Geological Survey**
$\dot{V}$	**Pulp volume flow**
VDEQ	**Virginia Department of Environmental Quality**
W	**Surface energy; [J]**
WWTP	**Waste Water Treatment Plant**
γ	**Surface tension (interfacial tension) of the Lippmann equation; [kg/s^2]**
ε	**Enrichment factor; [%]**
θ	**Contact angle; [^{o}]**
σ	**Surface tension; [J/m^2] = [N/m]; [mN/m] = [dyn/cm]**
[µg/day]	**micrograms per day**
[µg/l]	**micrograms per liter (parts per billion)**
[µS/cm]	**micro-Siemens per centimeter**
Z2	**Zuordnungswert 2: Hg ≤ 10 mg/kg DW according to German LAGA; different lists exist for soil and construction rubble**

1 INTRODUCTION

Chlorine-alkali electrolysis is one of the most important large-scale processes of the chemical industry worldwide. In chlorine-alkali plants important chemicals such as chlorine, caustic soda (caustic potash) and hydrogen are obtained by electrolytic decomposition of aqueous sodium or potassium chloride solutions and in some cases also from high concentrated sea water brine also often referred to as HCB.

Figure 1-1: Chlorine-alkali electrolysis plant in the Middle East (Site remediation supervised by the author in 2004/05)

Experience gained with the mercury cell process over more than eighty years has shown considerable environmental damages affecting in particular the surrounding soil and the building structure of the chlor-alkali electrolysis plants due to uncontrolled release of mercury in consequence of emergency shut-downs and damages, but also as a result of war destruction and lack of appropriate maintenance such as in Buna Schkopau and Bitterfeld

In particular on locations of former synthetic rubber (SR) production 'acetaldehyde factories' are often associated to chlorine-alkali electrolysis plants. In acetaldehyde factories, mercury(II) sulfate as a catalyst was used for the direct hydration of acetylene to acetaldehyde (Kucherov reaction), an important mean product of the 'four-step-process' for the production of butadiene and synthetic rubber.

Beginning in 1935 vinyl chloride was first produced in Germany in Bitterfeld and in the nearby Wolfen on the basis of the patent of Fritz Klatte (1880-1934) and the I.G. Farben patent 671889[1], where hydrogen chloride was attached to ethyne (acetylene) by using mercuric chloride as a catalyst and making the symbiosis of chlorine alkali electrolysis plants to acetaldehyde factories more logical.

A very special remediation case and most probably unique in this world is the former 'Chemical Factory Marktredwitz' in Upper Franconia. Since mercury-containing products were manufactured for almost 200 years the soil contamination showed a similar pattern than those of abandoned acetaldehyde factories.

1.1 THE ORIGIN OF THE CHLORINE INDUSTRY IN AUSTRIA AND GERMANY

In 1894 the first chlorine-alkali electrolysis plants were established in Germany near the Prussian City of Bitterfeld by "Elektrochemische Werke" (Electro-chemical works) as a subsidiary company of AEG under the leadership of Walther Rathenau[ii] and by 'Chemische Fabrik Elektron'[iii], but only short time later also in Aussig an der Elbe (Ústí nad Labem) in Bohemia (today Czech Republic) by the 'Österreichischer Verein für chemische and metallurgische Produktion Aussig/ Elbe[iv].

The 'Aussiger Verein' was founded in 1856 and worked very closely together with Solvay & Cie. in Belgium, founded 1863[2]. Since 1888 the AEG had established in cooperation with the 'Schweizer Metallurgische Gesellschaft' the 'Aluminium-Industrie AG (AIAG)' in Neuhausen am Rheinfall in Switzerland, later known as 'Alusuisse' supporting with their knowledge about electrolysis also AEG in Bitterfeld[3].

The first chlorine factory using mercury cells was built in England in 1895 as the largest in Europe by the 'Castner-Kellner Alkali Co. in Runcorn/ Cheshire' (today's INEOS chlor) based on an US patent granted for the 'rocking cell' in 1892 to the US-American Inventor Hamilton Castner (1858–1899)[4] and a similar patent, held by one of the most important captains of the Austro-Hungarian industry, Carl August Kellner (1851–1905)[5] in association with Solvay. In 1920 Caster-Kellner was taken over by Brunner, Mond & Co.[6] and later became Imperial Chemical Industries (ICI). Kellner who was holder of more than 80 patents also founded in 1889 with E. Partington in England the 'Kellner-Partington Paper Pulp Co. Ltd.' and launched branches in various European states such as also in his home country Austria, where he built a paper mill in Hallein[v] and established a chlorine facility in Jajce (today Bosnia). The first chlorine plant in Hallein, associated to the 'Halleiner Salinen', using the mercury cell process was started much later, in the twenties of the last century, by the 'Solvay Werke Betriebsgesellschaft Ges.m.b.H.'

After 1935 the chemical industry in Austria and Germany was more or less under the control of the largest merger of the chemical industry in Europe the 'IG-Farben AG'. Having access to the almost unlimited mercury deposits of their close collaborators in Spain and Italy, all existing chlorine plants were changed during this time to much more efficient mercury cell amalgam process, using a rotating cathode of metallic mercury, for the electrolysis of pure brine. The 'IG Farben' established also four new factories for the production of synthetic rubber, starting in Schkopau (near Halle) in 1936, including large scale mercury cell chlorine plants and acetaldehyde factories.

During World War II, German Engineers supported the construction of chlorine plants for their Japanese allies such as in Anshun/Taiwan. Mercury was transported from Germany to Japan during World War II in large vessels and from 1944 onwards under utmost secrecy via Norway in submarines of the German Navy. The wreck of the German submarine U-864 with its toxic cargo of 1,857 flasks of mercury was just recently discovered in the Norwegian coastal waters[7]. The author and novelist LEHNHOFF wrote in 1982 the famous roman "Quicksilver" based on the true story of the submarine boat U-859.

After WWII, plants of the defeated 'German Reich' were dismantled by the victorious nations and transferred to places in their home countries such as the acetaldehyde factory Buna Monowitz, which was shifted by the Soviet army to the city of Temirtau in today's Central Kazakhstan, where the close-by Nura River in our days is

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[ii] Dr. Walther Rathenau (1867–1922), the son of the AEG founder Emil Rathenau and later German Minister of Reconstruction and Foreign Affairs was also the first Managing Director of "Elektrochemische Werke GmbH" in Bitterfeld, where a type an electrolysis cell, the 'Rathenau cell' was named after him.

[iii] 'Chemische Fabrik Elektron' was part of 'Chemische Fabrik Griesheim'

[iv] Society for chemical and metallurgical production in Aussig/ Elbe (Aussiger Verein)

[v] The paper factory in Hallein (M-real Hallein AG) was just recently partially closed in April 2009.

heavily contaminated with mercury over a length of several hundred kilometres which currently is affecting the natural reserve of the Zhaur Swamp, the Samarkand and Intumak Drinking Water Reservoirs but also the Lake Tengiz[8].

1.2 NECESSITY FOR RELIABLE MERCURY WASTE TREATMENT TECHNOLOGIES

The PARCOM Decision 90/3 from 14 June 1990 recommends that existing mercury cell chlorine-alkali electrolysis plants of the contracting parties to the Paris Convention[vi] shall be phased out completely by 2010 for the prevention of marine pollution from land-based sources[9]. Since conversion to mercury-free technology is not all the time possible the plants using the amalgam process are going to be de-commissioned and demolished, which is linked to a necessary site remediation technology. The PARCOM Decision is accepted so far, but in fact there is currently no sufficient and economical treatment technology available, which is able to handle large amounts of contaminated soil, rubble or other mercury-contaminated mineral wastes from dismantling and demolishing of such plants.

In the past only a few middle size mercury remediation projects were able to undergo a “state of the art” engineered treatment such as the remediation of the Chemical Factory Marktredwitz (CFM) between August 1993 and June 1996 and the Old Lonza Works in Waldshut-Tiengen (Alusuisse) in 1998[10], where the waste was treated in plants using basically thermal treatment technologies, which is expensive. The treatment price in Marktredwitz for example was in a range of 600 DM/metric ton, which was calculated on the amortization of the plant investment and a throughput of 70,000 metric tons.

Almost all the demolition debris from the eight former East German chlorine plants and an acetaldehyde facility were dismantled between 1998 and 2003 during the course of the large-scale Buna and Bitterfeld ecological superfund projects (Ökologische Großprojekte - ÖGPs) in the Central German ‘chemistry triangle’ ended up in underground mine disposals and in local hazardous landfills. Compared to an entire investment of 9.3 billion DM (Deutsche Mark) made by the German Federal Government in Buna Schkopau, disposal deems not to be an appropriate solution. On the other hand it was found difficult to provide adequate and safe treatment capacities in sufficient number and quality.

For the treatment of the demolition waste from chlorine plants and acetaldehyde factories in particular soil and rubble soil washing could be considered as a treatment option. Since the currently existing few soil washing plants in Austria, Germany, Switzerland and the United States of America as far as they are designed for the treatment of high-level hazardous solid wastes are multi-purpose treatment plants, there is a restriction for the treatment of mercury waste, containing more than 500 mg/kg mercury. Even plants allowed by permitting authorities to accept mercury wastes with a concentration in a range of 1,000 mg/kg mercury, complain about accumulation of beaded mercury in all low points of process equipment causing unsafe conditions during all phases of operation and maintenance.

Thermal, biological and physical-chemical processes are generally used for the treatment of contaminated soils. In Germany about 40 % of these materials are treated by physical-chemical soil washing plants[11]. Soil washing processes work by detaching contaminants from the soil particles and surrounding them in the finer particle fractions with an adjusted input of mechanical energy. The contaminants are subsequently concentrated in the light and/or heavy product of the gravel and sand fractions as well as in the silt fraction. These highly contaminated fractions are separated by a sequence of classification and separation processes. The separation processes are generally based on density separation. Problems arise in particular with the selective material separation in the fine particle fraction. Flotation could provide a solution for these problems.

[vi] Currently 173 states signed as contracting parties the Paris Convention

1.3 OBJECTIVE AND SCOPE OF THIS THESIS

This dissertation examines and compares the status of waste treatment technologies for remediation of soils and solid wastes, contaminated with mercury in particular from chlorine alkali electrolysis plants and acetaldehyde factories, but also gives an overview of recently performed or ongoing mercury remediation cases that have been undertaken by the involvement of the author worldwide from 1990 onwards till today.

Laboratory and bench scale tests have been performed in various laboratories in particular in the 'Bench scale laboratory' of the soil washing plant Berlin Gradestrasse, the laboratory of the Department of the Technical University Berlin, the BeAAT laboratory in Ruwais, United Arab Emirates but also in the laboratories of the 'Institute for Sustainable Waste Management and Technology' and at the 'Chair of Mineral Processing' of the University of Leoben.

The target of this thesis is to improve existing soil washing technologies in particular by using flotation and density separation processes. This thesis also reviews the various technology types and pilot/full-scale field applications of treatment technologies applicable to wastes highly contaminated with mercury. The physical separation technologies, the chemical extraction processes and the integrated processes that combine both physical and chemical methods are discussed separately. Other treatment technologies such as thermal desorption and solidification but also the proper disposal of mercury waste is subject of this Doctoral Thesis which is in order to create a helpful guideline for an industrial application based on practical experience made and on case studies in bench and industrial scale so that they would be helpful for other practical users.

2 ENVIRONMENTAL ASPECTS OF MERCURY

Mercury has been utilized by mankind for thousands of years and is most probably one of the best-documented but if not the best-known of all noxious substances. As a priority pollutant[12] it can be mobilized in the environment to form extremely toxic organic compounds, supported by global atmospheric transport and accumulation in the food chain. It is emitted to atmosphere both from natural sources and from sources associated with human activity. Major natural sources are volcanic discharge into the atmosphere (volcanic ash with sulfur dioxide emissions, generating sulfate aerosols)[13,14], steam blast eruptions (aka phreatic eruptions), large scale forest/wild land fires[15] and emissions from the oceans.

Owing to industrialization and more effective production methods at the beginning of the 20th century, the environment had to deal with a considerable increase in pollutants in particular mercury, since it has been and is still used in many large-scale industrial processes (Table 1). Ice cores collected from the Upper Fremont Glacier in Wyoming/USA contain a high-resolution record of total atmospheric mercury deposition covering a period of almost 300 years[16] showing the effects of both natural and anthropogenic (industrial) sources. Clearly the beginning of the industrialization age in the USA and the increased industrial use of mercury after 1880 but also the influence of volcanic eruptions and military conflicts are indicated in the ice core diagram.

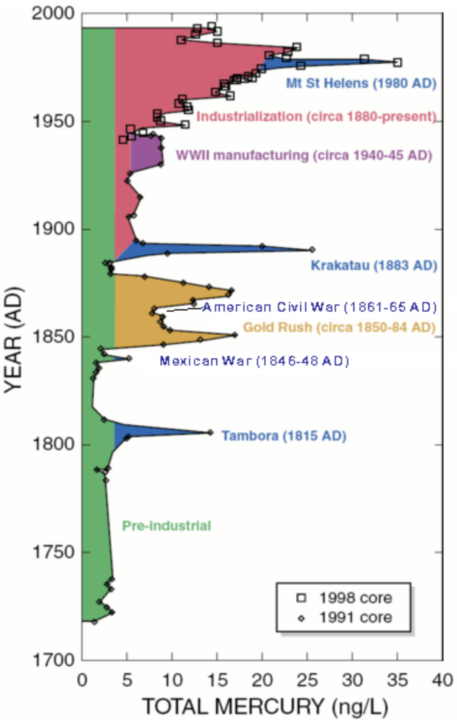

Figure 2-1: Profile of historic concentrations of mercury in the Upper Fremont Glacier (after Schuster et al, 2002[16])

2.1 USE OF MERCURY IN HUMAN HISTORY AND EARLY MINING ACTIVITIES

The oldest sample of metallic mercury, preserved in a small glass bottle, dates to the 18th or 19th Egyptian Dynasty (1500 BC) and was found in a tomb of Sheikh Abd-el-Qurna (Thebes)[17]. The Babylonians called it 'nebu uru', tracing back to the old Egyptian word for precious metal[vii], and associating it with the planet mercury.

The mineral 'red cinnabar (HgS)' later understood as α-cinnabar, crystallizing in the trigonal system, had already been mined in the Roman Empire, where it was confusingly called 'minium', same as red lead, and it had been the primary ore of mercury all over the centuries[18]. It was used since antiquity as a natural red pigment later called vermilion verifiable at the frescos in Pompeii[viii], but also used for poly-chrome mural and ceiling paintings in the 'European Renaissance' and another time in the 'Neo-Renaissance Style' of the second half of the 19th Century[19].

Next to the already mentioned red α-cinnabar, in the Hg-S binary two other mercury sulfide species are known: metacinnabar (β-cinnabar), a black or grayish variety, crystallizing in the tetrahedral zinc blende (sphalerite) structure and the very rarely occurring black/red γ-cinnabar (hypercinnabar), crystallizing in the hexagonal wurzite structure[ix, 20]

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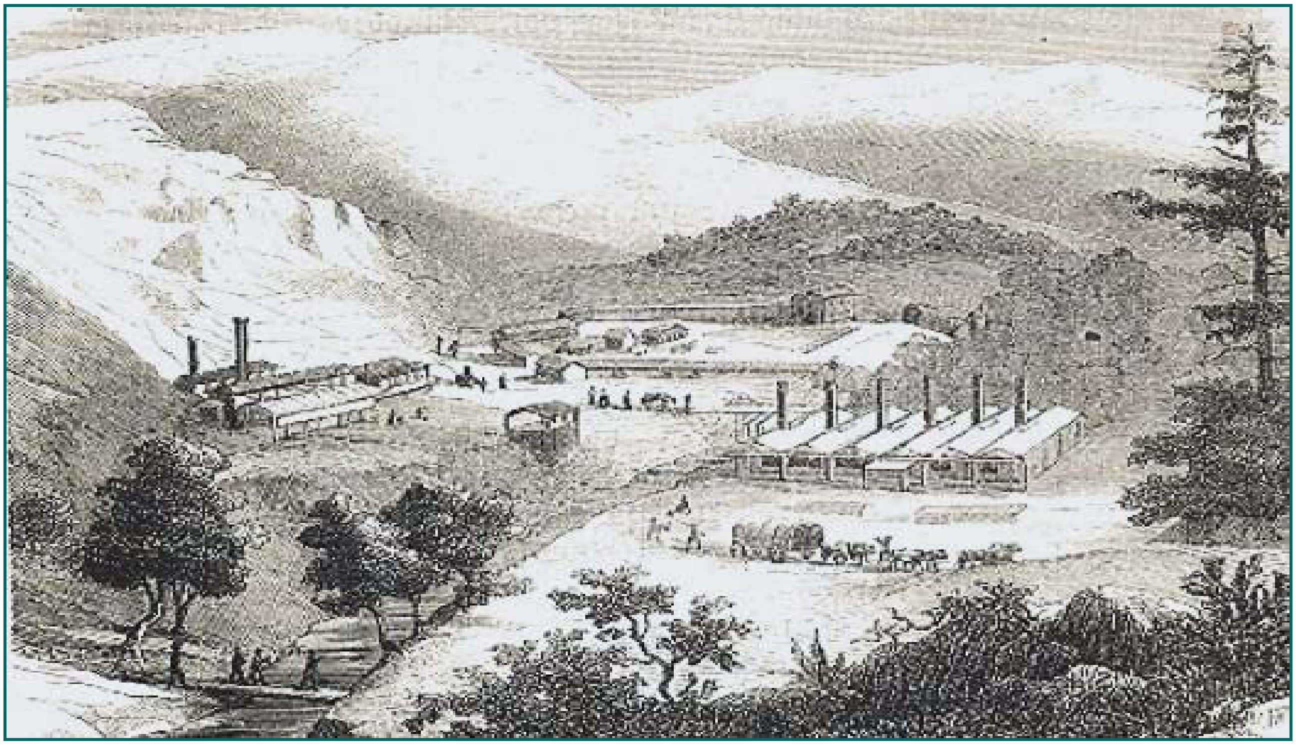

Figure 2-2: Ore beneficiation facilities of the 'New Almaden Quicksilver Mine' in Santa Clara County California, approx. 1875 (woodcut by Mary Hallock Foote; author's collection)

The most important type of natural mercury deposits is called 'Almadén type' (cinnabar and metacinnabar)

[vii]  nb, nebu: precious metal/gold

[viii] Famous frescos using cinnabar are particularly in the 'Casa dei Vettii' and in the so-called 'Villa of Mysteries'

[ix] Found for the first time at Mount Diablo Mine/California and described by R. W. Potter and H. L. Barnes in 1978

and was mined in Spain in Almadén[x]/Sierra Morena, in Almeria/Andalusia and in Brañalamosa/Asturias[21], but also in today's Italy such as in Montamietta (Monte Amiate/Tuscany) and in Vallalta/Venetia some of the oldest mercury mining areas in the world are located in today's Turkey near Konya, Karaburun and Ödemiş, where cinnabar already was mined in the pre-bronze age about 8000 years ago. In the early 20th century modern Turkey started again mining activities in the old mercury mining areas and after introduction of the rotary furnace the output increased and reached 1974 about 5% of the world production[22]. Environmental impacts on ground water and sediments from Karaburun district were reported just recently[23].

Cinnabar was also extracted from mines in Idrija (Krain) close to Ljubljana (in today's Slovenia), in Avalaberg, Beograd (Serbia) and starting in the early 19th century also from the Californian Quicksilver Mines in New Almaden (San Francisco Bay Area) but also in New Idria (San Benito County). Here the cinnabar as the principal mercury-bearing mineral is typically associated either to chalkstone or to trachyte but also it was found related to pyrite, quartz, calcite, chalcedony and even to bituminous material[24].

Some mercury ore deposits in Nevada are closely related to blanket opalite bodies, where the cinnabar and sometimes corderoite, a mercury chloride (bromide) sulfide is associated to opalized tuff. Since the ore is located nearby the surface it is mined mostly in open pits such as in the B and B mine in Esmeralda County (fig. 2-3)[25] and in particular the McDermitt open pit mercury mine in the opalite district of Humboldt County, which was the largest North American mercury producer during operations from 1975-1989.

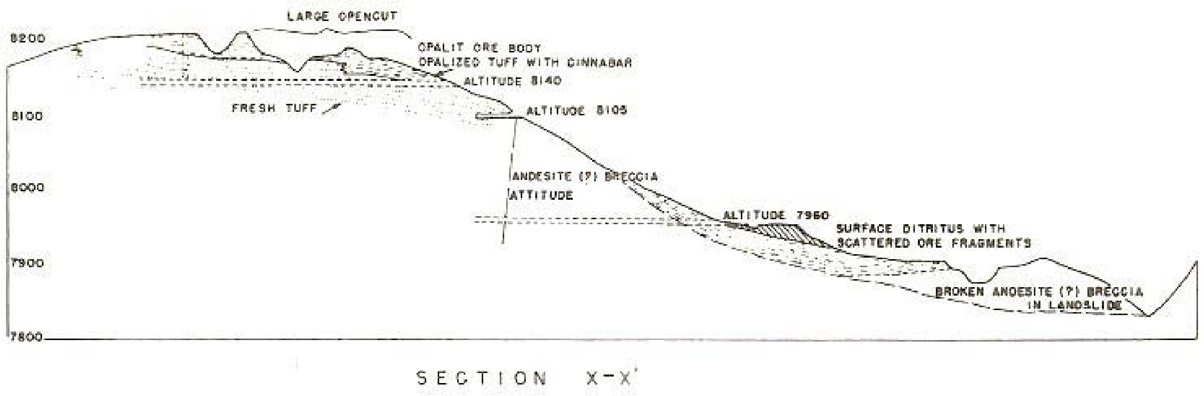

Figure 2-3: Cross section of the B and B mine in Esmeralda County/Nevada (blanket opalite type, Benson 1950[25])

Related to the McDermitt mining area even the very rare mercury mineral 'corderoite' was described for the first time as $Hg_3S_2Cl_2$ by FOORD in 1973[26] for occurrence in the 'Cordero Mine' as the McDermitt Mine was formerly called. Further remarkable quicksilver deposits in Nevada are located in the 'Pilot Mountains' close to the Californian border, distributed around Cinnabar Mountain, Mineral County, occurring either in limestone, or in conglomerate and sandstone but also in silicified tuff[27].

Rich limestone (limestone/clay) mercury deposits are also known from the 'Chisos Mine', 'Mariposa Mine' and others in the Terlingua mercury district, located in the southern part of 'Trans-Pecos'/Texas. In the years from 1899 to 1970 more than 150,000 flasks were produced from this mining district[28].

In the Huancavélica mine in central Peru the mercury ore is very fine dispersed in carbonatic sandstone. In the silver mining districts of Chili (La Rosilla Mine) and in British Columbia/Canada (Kwanika and Vital

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[x] المنجم al maden; Arabic: 'the mine'

Creek) mercury is found as Arquerite (Ag,Hg), which is a very rare variety of a mercurial silver amalgam[xi].

In Germany mercury mining was performed in the Black Forest (Sulzburg), in the Hunsrück region (Schmittenstollen) and in the northern and western Palatinate (Moschellandsberg, Niedermoschel and in Mörsfeld). Here mercury was sometimes found in fissures as another amalgam from silver and mercury, called Moschellandsbergite (Ag_2Hg_3) but also amalgams with copper from this location are known[xii]. In the Mörsfeld mining area, mercury deposits are linked to Paleozoic vulcanite along the Saar-Nahe-Depression. The main mining activities were performed here in the second half of the 18th century and came finally to an end due to fall in price of mercury in 1860. Between 1936 and 1942 the mining residues were reprocessed and about 250 metric tons of mercury recuperated from the tailings. Environmental impacts from the abandoned mercury mines in this area were reported already 20 years ago[29].

In the Austrian hereditary lands metal mining was started already 5,000 years ago. The Schwarzleo valley mining district in Mitterpinzgau/Salzburg and the neighboring Tyrolean Pillersee are the oldest known mining regions in Austria. In Leogang, Vogelhalte and Nöckelberg various metals such as silver, lead, copper, nickel and in particular mercury ores were mined since the 15th century. The mining activities were finally disrupted at the end of the 19th century. Merely magnesia was mined at Inschlagalpe in the years between 1936 up to 1970.

The first large scale industrial application for mercury was closely related to the processing of low-grade silver ores in the Spanish Americas in the 16th century, using the ‘patio amalgamation process’ whilst the recovery of the normally richer European silver ores (associated mostly with galenite) was performed by lead cupellation[30], which is in the main source of micro-structural embrittlement of archeological silver artifacts[31]. During the period from 1570 up to 1920, before the silver prices collapsed, North and South America established hegemony on the silver market causing considerable losses of mercury of almost 200,000 metric tons dispersed in the Spanish Americas and more than 60,000 metric tons in the United States[32].

The already mentioned New Idria Mine and the New Almaden Mine supplied most of the mercury required for the California Gold Rush (1850-1884). In the ‘Californian Almaden Mining District’ large scale industrial mining activities started accordingly in 1845. The production by the end of the year 1936, when the mines were closed, had reached 1,039,996 flasks (approx. 36,000 metric tons) only interrupted between 1858 and 1861 by litigation[33]. The world’s annual mercury production at the end of the 19th Century was in a range of 3,600 metric tons. In the year 1891 Spain produced 1,556 mt, followed by the United States with 893 mt. With 517 mt Austria was the third-largest mercury producing nation of its time followed by Italy and Russia[34], were Mercury was mined in Nikitowka.

Due to the decreased need of mercury in the Western World all former quicksilver mining activities in Europe and USA are stopped in our days. The last quicksilver mine in the US was Nevada’s above already mentioned McDermitt Mine in Humboldt County, which was abandoned in 1992. In Europe, the already mentioned Idrija mine in Slovenia was finally shut down in 1995[35] after more than 500 years of mining activity, were between 100,000 and 150,000 metric tons of quicksilver were produced[36, 37].

In today’s China mercury mining is still ongoing. In particular the five large mines Wanshan, Wuchuan, Lanmuchang, Tongren and Danzhai make currently the Guizhou province one of the most important active mercury mining areas in the world[38].

[xi] First described by the Belarusian mineralogist and mining engineer Ignacy Domeyko in 1841. Another member of the silver amalgam group is ‘Eugenite’ (Ag_9Hg_2), named after **o.Univ.-Prof. Eugen F. Stumpfl** (1931-2004), one of the leading ore deposit mineralogists of his time, who was holder of the chair of mineralogy at the Mining University of Leoben from 1976 to 1997.

[xii] In particular the trigonal copper amalgam Belendorffite (Cu_7Hg_9) was found in the Moschellandsberg Mining District, but not the cubically crystallizing variety Kolymite (Cu_7Hg_6).

2.1.1 Anthropogenic sources of mercury and recent industrial applications

Anthropogenic/industrial sources emitting the largest amounts of mercury to the atmosphere are:

Table 2-1: Industrial and commercial processes generating/emitting mercury

Process/application	Generated products/ sources of emission	Further description
Coal-fired power stations	Energy from stationary combustion of fossil fuel in particular coal generate mercury	Main source of atmospheric mercury pollution world wide[39]
Artisanal gold mining	Mercury is used for recovering gold in hydraulic mining from alluvial placer gold but also from crushed gold bearing lode ores	Small-scale gold mining is the second-largest source of mercury pollution in the world
Metallurgical processes/ non-ferrous metal smelters	Primary and secondary production of copper, zinc, aluminum and lead	Metallurgical processes refining slag and metal wastes
Cement manufacturing plants, especially when accepting fly ash from coal-fired power stations[40]	Production of different grades and types of Portland cement, blended with slag, fly ash or other pozzolanic components. Dry process kiln systems emitting considerable amounts of Hg	Pyro-processing such as calcination and sintering in order to form 'clinker'
Municipal and hazardous waste incineration plants	Thermal destruction of municipal and industrial wastes, containing traces of mercury	Oxidized mercury Hg^{2+} can be captured in scrubbers as calomel
Waste disposal in landfills[41], and in underground mines	Leachate water and emissions from volatile contaminants such as mercury.	'High mercury wastes' require pre-treatment before disposal in landfills
Incineration of cheap heavy fraction oil and PHC sludge as a fuel in large oversee marine vessels	Petroleum hydrocarbon sludge (PHC), generated as a waste in oil refineries such as from tank cleaning and others contain considerable amounts of Mercury	Using PHC sludge mixed with very cheap heavy fraction oil as a fuel for ship diesel engines is currently still a common practice
Chlorine-Alkali Electrolysis Plants using the mercury cell (amalgam) process	Chlorine gas from electrolysis of enriched brine (solutions of potash or sea water), caustic soda (NaOH), bleach lye (NaOCl) and hydrochloric acid (HCl) etc.	The mercury cell process a.k.a. Castner-Kellner process uses metallic mercury as a circulating bed electrode
Processing plants of the Oil and gas industry such as refineries	Crude oil will be processed and refined; typical products are gasoline, diesel fuel, kerosene and liquefied petroleum gas (LPG)	Mercury will be emitted, adsorbed on metal catalysts and is often concentrated in heavy PHC fractions
Mercury mining and facilities for extraction and processing of mercurial ore	Mercury occurs mainly as cinnabar (HgS), not very often as corderoite ($Hg_3S_2\{Cl,Br\}_2$) or livingstonite ($HgSb_2S_8$) and quite rarely it is found as metal or as amalgam from silver (or copper) and mercury	Mining activities and metallurgical upgrading/ore benefication, for example by roasting
Iron and steel manufacturing	Pig iron and steel production	Diverse

The total mercury emissions generated worldwide by current industrial processes are in a range of about 2,270 metric tons[42] per year. Combustion of fossil fuels in particular coal is believed to be the main source of anthropogenic mercury emissions to atmosphere.

Table 2-2: Industrial and commercial processes and equipments using mercury

Process/application	Generated products/ sources of emission	Further description
Chlorine-Alkali Electrolysis Plants using the mercury cell process	See table 2-1	See table 2-1
Acetaldehyde - or acetic acid factories	Acetaldehyde aka. ethanol (CH_3CHO), or acetic acid (CH_3COOH) from acetaldehyde	Via hydratization of ethyne (acetylene) $HC \equiv CH$ with mercuric sulfate or HgO as a catalyst in presence of sulfuric acid (H_2SO_4)
Production of chloroplasts	Vinyl chloride (VC: $CH_2 = CHCl$), a highly toxic gas used for generation of chloroplasts, such as PVC	By addition of hydrogen chloride to ethyne in the presence of a mercuric chloride/activated carbon catalyst: $HC \equiv CH + HCl \rightarrow CH_2 = CHCl$
Chemical factories, and manufacturers †.)	Manufacturing pharmaceuticals, fungicides, pesticides, seed protectants, impregnating agents, pigments and fur felt bodies for hats causing the mad hatters syndrome	Diverse (see foot note)
'Kyanising facilities' for wood preservation (J.H. Kyan, 1774 -1850)	Preservation for various types of wooden components such as railway sleepers, hop poles and construction timber	Steeping wood in a Hg(II)-chloride solution was used as a preservation method till to the 1970s
Private manufacturers †.)	Production of mirrors, sometimes in private houses	Mercury coating on glass surfaces by amalgamating polished tin foils
Production of percussion caps and blasting caps up to the early 20th century	Percussion caps/ blasting caps filled with Mercury fulminate $[Hg(CNO)_2]$[43] were used as a trigger/ detonator for explosives and primers for rifle and pistol ammunition	Mercury (II) fulminate is generated by reaction of Mercury nitrate with ethanol forming a grey powder, highly sensitive to shock and ignition.
Dental clinics	Dental wastes generated from removal of amalgam filling	Dental amalgams mostly used as alloys from copper and mercury
Rocket test areas	Mercury was used as a propellant in early electrostatic ion thrusters for rocket propulsion beginning in the 1960s in former Soviet Union, but also in the USA	Electrostatic ion thrusters, accelerating mercury plasma ions in an oscillating electric field by Lorentz force.
Natural gas pipelines	Transportation of natural gas	Broken mercury-filled manometers along natural gas pipelines caused considerable soil contaminations[44]
Mercury-containing batteries	Non-rechargeable mercuric oxide batteries, either as Zn/HgO or Cd/HgO cells	HgO is used as cathode, sometimes mixed with MnO_2; KOH or NaOH is used as an electrolyte
Mercury-containing lights	HID lamps and fluorescent light tubes, but also wiring devices and electrical switches	Mercury is used as an ionizing filling generated from sodium amalgam encapsulated in the glass tube
Mercury-filled electrical arc valve rectifiers	Specific type of electrical rectifier, widely used in the fifties and sixties in trams and electric locomotives but also in various industrial plants and in underground mines	Used for converting alternating into direct current for high voltage power transmission

†.)The Chemical Factory in Marktredwitz (Upper-Franconia) founded in 1788, manufactured mercury-containing products for almost 200 years. Mirror manufacturing was performed for centuries in many houses in the historic city of Fürth[45]. Felt for hats was produced mostly from rabbit fur using mercuric nitrate $Hg(NO_3)_2$ by carroting.

In particular coal combustion is contributing between 750[46] and 1,500 tons per year, followed by small-scale gold mining which amounts to considerable 10%. In fact the influence of mercury pollution to the atmosphere from other industrial processes (tab. 2-1) is higher than from processes using mercury (tab.2-2):

In the year 2000 chlorine-alkali electrolysis plants using the mercury cell (amalgam) process generated only 3% of the entire atmospheric mercury pollution worldwide[47]. In Europe the amount of emitted gaseous mercury emissions from CAPs was reduced from estimated 18 % in 1982[48] to 12 % in 1995[49].

Since many chlorine plants and acetaldehyde factories have been closed during this period of time, contaminated soil, rubble, but also other solid construction materials and river sediments are the main types of mercury-containing hazardous mineral wastes, currently generated.

2.1.2 SITUATION FOR OLD AND INHERITED INDUSTRIAL SITES IN AUSTRIA

All brownfield sites such as old waste deposits and former industrial and commercial sites in Austria referred to as ‘abandoned sites’ in accordance with the regulations of the Act on the Clean-Up of Contaminated Sites (Altlastensanierungsgesetz - ALSAG) are recorded and documented under the terms of the Contaminated Sites Atlas Act (Altlastenatlas - VO). Official directives for decommissioning abandoned sites are issued by the Austrian Ministry for Agriculture and Forestry.

The Austrian Environmental Protection Agency estimates the number of potentially contaminated sites in Austria in the range of approximately 80,000. By 1 January 2010, 57,970 suspected sites had been registered during the time since the Act on the Clean-Up of Contaminated Sites came into force in July 1989. This is a considerable increase compared to the year before. In fact more than 4,600 suspected sites have been newly recorded in 2009[50].

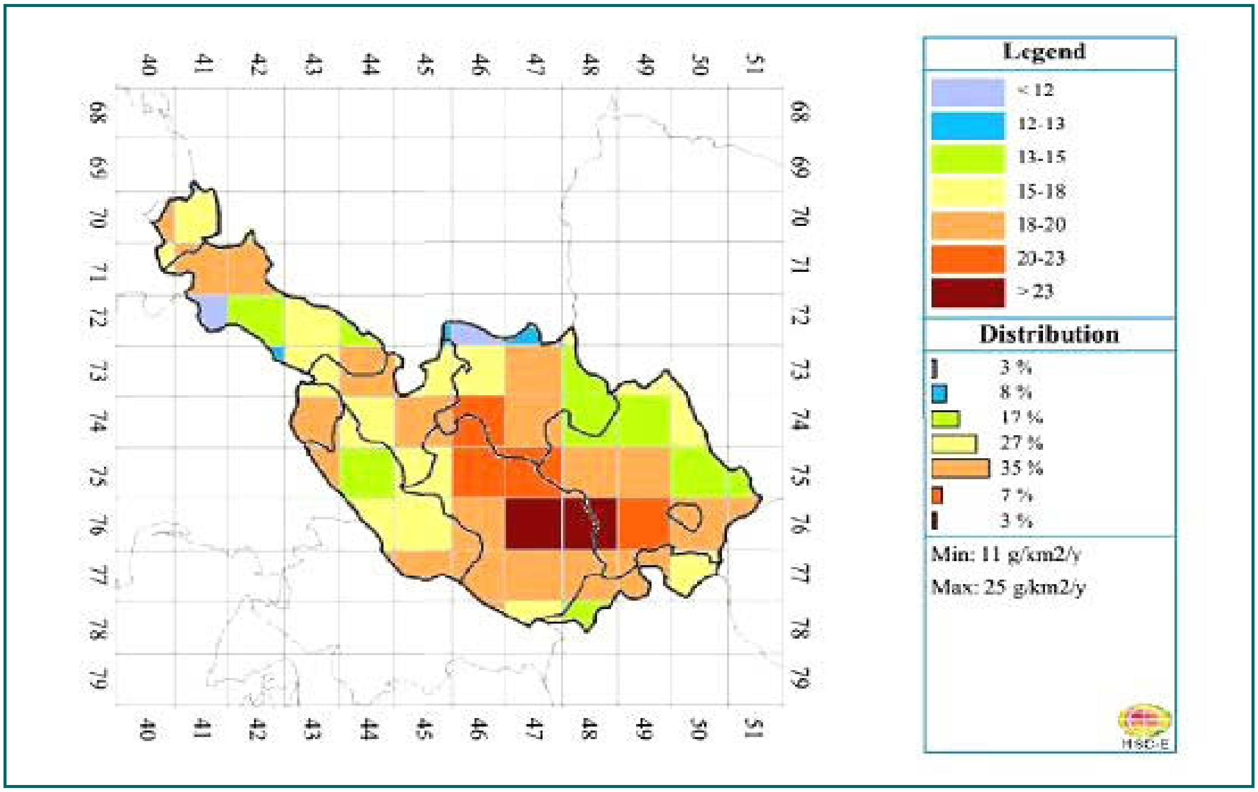

Figure 2-4: Mercury depositions to Austria from national and external sources in 2005 (Source: MSC-E)

Fig. 2-4 above shows the highest mercury emissions up to 25 gram, per square kilometer and year, in Styria. This is most probably related to metallurgical facilities and production of steel in this region. In Austria only one single chlorine plant is currently in operation, conducted by "Donau Chemie in Brückl", applying the mercury-free membrane process, with a capacity of around 70,000 m^3 Cl_2/year (see App.G-1).

2.2 CHARACTERIZATION OF MERCURY-CONTAMINATED WASTE AND ASSIGNMENT CRITERIA

Contaminants in soil from former industrial areas include most commonly Polycyclic Aromatic Hydrocarbons (PAH), Petroleum Hydrocarbons (PHC) and cyanides but also various heavy metals including mercury. In the USA 77% of the National Priority List Superfund sites (5×10^7 m^3 of soil), 72% of the contaminated sites of the 'Department of Defence' sites and 55% of the industrial sites from the Department of Energy are metal-contaminated[51].

2.2.1 Hg-containing wastes from closure and overhaul of industrial facilities

Owing to ongoing demolition activities in various international projects the major hazardous mercury wastes currently generated are:

- Contaminated soils, rubble and other contaminated solid construction materials sometimes also river sediments from remediation/demolition of former Chlorine plant sites, acetaldehyde factories or facilities from chemical manufacturers using mercury in their processes
- Contaminated liquids as well as solids and sludge generated by decommissioning, dismantling and decontamination activities of the former industrial facilities mentioned above
- Contaminated equipment such as metal waste from de-commissioning and dismantling of the former industrial facilities mentioned above.
- Residues from former mercury mining and their associated ore beneficiation facilities

Materials generated by remediation/demolition activities become wastes only if removed from their original location. Since in situ treatment methods for mercury contaminations are of restricted efficiency, controlled excavation/selective demolition is required as a first step for efficient treatment/decontamination. Other mercury-contaminated wastes generated from operation, maintenance or overhauls of industrial facilities are:

- Process residues such as Petroleum Hydrocarbon (PHC) sludge and solid catalysts from crude oil refineries and their associated facilities
- HID lamps and fluorescent light tubes, dental wastes, percussion and blasting caps filled with mercury fulminate etc.
- Filter dust, fly ash and slag from stationary combustion of fossil fuel, in particular coal and from municipal and hazardous industrial waste incineration plants.
- Wastes from overhaul, maintenance and operation of chlorine plants, described in greater detail below.

2.2.2 Mercury-containing wastes as per US EPA hazardous waste classification system

US EPA 40 CFR part 261 (Identification and listing of hazardous waste)[52] defines wastes to be hazardous either by being ignitable (I), reactive (R), corrosive (C), or toxic (T) and is widely used in various countries not only within the United States. The toxicity, as far as solid waste is concerned, it is characterized by using the 'Toxicity Characteristic Leaching Procedure – the so-called TCLP-test', mainly referred as test Method 1311 in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW–846. A solid waste that exhibits the characteristic of toxicity has the EPA Hazardous Waste Code Number specified in tab. 2-3, which corresponds to the toxic contaminant causing it to be hazardous.

Table 2-3: Maximum Concentration of metals for the Toxicity Characteristic Leaching Procedure

EPA HW No.[1]	Contamination/metal	CAS No.[2]	Regulatory Level [mg/l]
D004	Arsenic	7440–38–2	5.0
D005	Barium	7440–39–3	100.0
D006	Cadmium	7440–43–9	1.0
D007	Chromium	7440–47–3	5.0
D008	Lead	7439–92–1	5.0
D009	Mercury	7439–97–6	0.2
D010	Selenium	7782–49–2	1.0
D011	Silver	7440–22–4	5.0

[1]Hazardous waste code number; [2]Chemical abstracts service number

US EPA identifies only six mercury-containing waste types by hazardous waste code number such as from specific sources referring to the K-list or as discarded wastes as per P- and U-list.

Table 2-4: US EPA hazardous waste code numbers for hazardous mercury waste types

EPA hazardous waste code	CAS No.	Hazardous waste	Hazard code
K071	-	Brine purification muds from the mercury cell process in chlorine production, where separately pre-purified brine is not used	(T)
K106	-	Wastewater treatment sludge from the mercury cell process in chlorine production	(T)
K175	-	Wastewater treatment sludge from the production of vinyl chloride monomer using mercuric chloride as a catalyst in an acetylene-based process	(T)
P065	628–86–4	Mercury fulminate and fulminic acid, mercury(2+) salt	(R, T)
P092	62–38–4	Phenyl mercury acetate	(T)
U151	7439–97–6	Mercury; Mercury compounds not otherwise specified	(T)

In addition to the above numbered wastes in the US common mercury-containing wastes such as fluorescent light tubes/bulbs and mercury-containing devices are characterized as 'hazardous wastes', either as 'universal wastes' or 'Household Hazardous Waste (HHW)', also referred to as domestic hazardous waste. The disposal of HHW including mercury-containing wastes in Municipal Solid Waste (MSW) landfills is currently regulated on a state by state basis.

2.2.3 Assignment criteria for mercury contaminated wastes

Table 2-5: US Land Disposal Restrictions Regulations for Mercury-Containing Wastes (Source: US EPA)

Mercury Subcategory Description	LDR Treatment Requirements/ Concentration	Applicable Waste Codes	Federal Register Publication
High Mercury-Organic Subcategory (waste with a total Hg content ≥ 260 mg/kg), contains organics, and is not an incinerator residue	Incineration (IMERC); or Roasting/ Retorting (RMERC)	**D009** **P092**	55 FR 22569 (June 1, 1990)
Mercury fulminate waste regardless of total mercury content and is not an incinerator or RMERC residue.	IMERC	**P065**	55 FR 22569 (June 1, 1990)
Phenyl mercury acetate waste regardless of total mercury content and is not an incinerator or RMERC residue.	IMERC or RMERC	**P092**	55 FR 22569 (June 1, 1990)
High Mercury-Inorganic Subcategory (waste with a total Hg content ≥ 260 mg/kg),, and is inorganic, including residues from incineration, roasting and retorting.	RMERC	**D009** **K106** **U151**	55 FR 22569 (June 1, 1990)
Low Mercury Subcategory (waste with a total Hg content < 260 mg/kg) and that are residues from RMERC only.	0.20 mg/l TCLP	**D009** **K071** **K106** **P065** **P092** **U151**	55 FR 22569 (June 1, 1990) K071- 53 FR 31166 (August 17, 1988) D009 treatment standard revised 63 FR 28568 (May 26, 1998)
Low Mercury Subcategory (waste with a total Hg content < 260 mg/kg) and are not residues from RMERC.	0.025 mg/l TCLP	**D009** **K071** **K106** **P065** **P092**	55 FR 22569 (June 1, 1990) K071- 53 FR 31166 (August 17, 1988) D009 treatment standard revised 63 FR 28568 (May 26, 1998)
Elemental mercury contaminated with radioactive materials.	AMLGM	**D009** **U151**	55 FR 22569 (June 1, 1990)
Hydraulic oil contaminated with Mercury Radioactive Materials Subcategory.	IMERC	**D009**	55 FR 22569 (June 1, 1990)
High Mercury-Organic Subcategory (waste with a total Hg content ≥ 260 mg/kg), contains organics, and is not an incinerator residue	Incineration (IMERC); or Roasting/ Retorting (RMERC)	**D009** **P092**	55 FR 22569 (June 1, 1990)

In the United States of America handling and treatment of hazardous and nonhazardous waste is regulated by the U.S. Environmental Protection Agency (USEPA) under the Resource Conservation and Recovery Act (RCRA) from 1976 associated by Hazardous and Solid Waste Amendments (HSWA) in 1984. HSWA includes the Land Disposal Restrictions (LDR), which prohibit the land disposal of certain types of hazardous waste without prior treatment[53]. LDR consider mercury wastes as ‘high mercury wastes’ if they contain greater than 260 mg/kg total mercury.

2.2.4 Leaching tests and assignment criteria to landfills in Austria and Germany

Tab. 2-6 lists the assignment criteria in Germany according to LAGA (1997). The threshold value Z2 for disposal is 10 [mg/kg DM] and the threshold value of the leaching criteria for the landfill category III is 0.1 mg/l. The table clearly shows a low threshold values for mercury in comparison to the other heavy metals, this is due to the high toxicity.

Table 2-6: LAGA assignment criteria for inorganic contaminants in soil (LAGA, old 1997)

Parameter	**LAGA assignment criteria**										
	Inserting values for excavated soil								**Landfill eluate (leaching test) for soil [mg/l]**		
	solids for soil [mg/kg in dry matter]				**eluate (leaching test) for soil [µg/l]**						
	Z 0	**Z 1.1**	**Z 1.2**	**Z 2**	**Z 0**	**Z 1.1**	**Z 1.2**	**Z 2**	**Z 3**	**Z 4**	**Z 5**
Hg	0,3	1	3	10	0,2	0,2	1	2	0,005	0,02	0,1
Zn	120	300	500	1500	100	100	300	600	2	5	10
Pb	100	200	300	1000	20	40	100	200	0,2	1	2
Cr	50	100	200	600	15	30	75	150	0,05*	0,1*	0,5*
Cd	0,6	1	3	10	2	2	5	10	0,05	0,1	0,5
Cu	40	100	200	600	50	50	150	300	1	5	10

*chromium IV

For drinking water protection areas, the “Berliner Liste (1996)” (Berlin list; BL) is most commonly used in Germany. For water protection zones I and II A, referring to sand, gravel and marl the hazardous limit (Gefahrenwert) for mercury is postulated with Hg = 0.1 mg/kg.

One essential criterion for the disposability of untreated and treated wastes are thus the leaching tests where eluates (in Germany) are produced according to the DEV S4 and the pH_{stat}-procedure, the directive EW 98p or by means of the US-EPA testing method No. 1311, the so-called Toxicity Characteristic Leaching Procedure (TCLP-Test), which is applied in the meanwhile not only in the USA.

The threshold values for a subsequent disposal (TCLP-limits) as per EPA standard SW-846 (D-list) or in accordance with part 1 of appendix D of the technical instructions on waste, the values according to the landfill ordinance category III and the ordinance on environmentally compatible storage of waste from human settlement landfill category I and II, are listed in table 2-7.

Table 2-7: Threshold values for a subsequent disposal in landfills comparing different international guidelines

Parameter	TCLP-test threshold value (leachate) [mg/l]	Landfill category I corresponding to Z3 [mg/l]	Landfill category II Z4 [mg/l]	DEV S4-test; threshold value leachate Z5 and landfill category III [mg/l]	Landfill ordinance Austria; residual landfill [mg/l]
Arsenic	5.0	0.2	0.2	1.0 (2.5)	1.0
Cadmium	1.0	0.05	0.1	0.5 (0.5)	1.0
Total chromium	5.0	-	-	-	20.0
Chromium VI	-	0.05	0.1	0.5 (0.5)	1.0
Lead	5.0	0.2	1	2.0 (5)	10.0
Mercury	0.2	0.005	0.02	0.1 (0.2)	0.1 (20 [mg/kg]) (1)
Silver	5.0		-	-	1.0

(1) Total concentration of Hg in [mg/kg]; in case mercury is present as hardly soluble sulfured compound and has been solidified, disposal is allowed up to a maximum of 3,000 mg/kg in dry matter.

2.2.5 Mercury waste types as per European Waste Catalogue

Besides the above described mercury waste classification and assignment criteria, the member states of the European Community are obliged to the European Waste Catalogue (EWC).

Table 2-8: Mercury waste types as per European Waste Catalogue (EWC)

European Waste Code	Waste name	Source of Generation
05 07 01	Wastes containing mercury	Wastes from natural gas purification and transportation
06 04 04	Wastes containing mercury	Metal-containing wastes other than those mentioned in 06 03 (wastes from the MFSU of salts and their solutions and metallic oxides)
06 07 03	Barium sulfate sludge containing mercury	Wastes from the MFSU of halogens and halogen chemical processes
10 14 01	Waste from gas cleaning containing mercury	waste from crematoria
16 01 08	Components containing mercury	End-of-life vehicles from different means of transport (including off-road machinery) and wastes from dismantling of end-of-life vehicles and vehicle maintenance
16 06 03	Mercury-containing batteries	Mercury-containing batteries
17 09 01	Construction and demolition wastes containing mercury	Other construction and demolition wastes
20 01 21	Fluorescent tubes and other mercury-containing waste	Separately collected fractions, except 15 01 (packaging, including separately collected municipal packaging waste)

The six digital waste codes classify waste materials according to the source of generation. It is referred to in a number of European Union directives and Commission decisions regarding waste management.

All the mercury wastes as per EWC (tab. 2-8 above) are considered to be hazardous, without any exception.

This is different in the US EPA nomenclature where waste has to be proven to be hazardous, in particular being toxic, by performing the TCLP test.

The EWC code list is not linked to any recommendation for a preferable treatment such as per US Land Disposal Restrictions Regulations for Mercury-Containing Wastes (tab. 2-5). Otherwise are these waste codes commonly part of the permitted waste catalogue allowing a number of waste treatment plants to receive waste declared as per EWC accordingly. The selection of a specific waste code numbers sometimes is performed arbitrary. For all the mercury-containing wastes from the remediation of the former chlorine plants and the acetaldehyde factory in Saxony-Anhalt the permitting authority decided to use the waste code number for fluorescent tubes and other mercury-containing waste (20 01 21) instead of construction and demolition wastes containing mercury (17 09 01).

Hazardous soil and demolition waste types relevant for soil treatment facilities are in particular in group 17: 'Construction and demolition wastes (including excavated soil from contaminated sites)' and in group 19: 'Wastes from soil and groundwater remediation' as shown in tab. 2-9.

Table 2-9: Hazardous soil and demolition waste types as per European Waste Catalogue

European Waste Code	Waste name	Source of generation
17 01 06	Mixtures of, or separate fractions of concrete, bricks, tiles and ceramics containing dangerous substances	Concrete, bricks, tiles and ceramics
17 05 03	Soil and stones containing dangerous substances	Construction and demolition wastes such as soil (including excavated soil from contaminated sites), stones and dredging spoil
17 05 05	Dredging spoil containing dangerous substances	
19 13 01	Solid wastes from soil remediation containing dangerous substances	Wastes from soil and groundwater remediation
19 13 03	Sludge from soil remediation containing dangerous substances	

The correct classification of mercury-contaminated soil was in various mercury remediation projects subject of discussion. Whilst in Saxony-Anhalt the mercury-containing demolition wastes from Buna Schkopau and Bitterfeld were declared by the Ministry of the Environment as the responsible supervisory authority as 'Fluorescent tubes and other mercury-containing waste' under waste code number 20 01 21, it is often requested by other permitting authorities or by the client, in most cases for insurance purposes, to transport mercury-contaminated soil as a dangerous good as per UN classification system.

2.2.6 Mercury and its compounds under UN dangerous good regulations

For transport purposes hazardous wastes and various chemical substances but also mercury and mercury compounds are subject to the 'UN Recommendations on the transport of Dangerous Goods[54]'. Basically nine different 'dangerous good classes' and a variety of divisions are known, as shown in fig. 2-5 below:

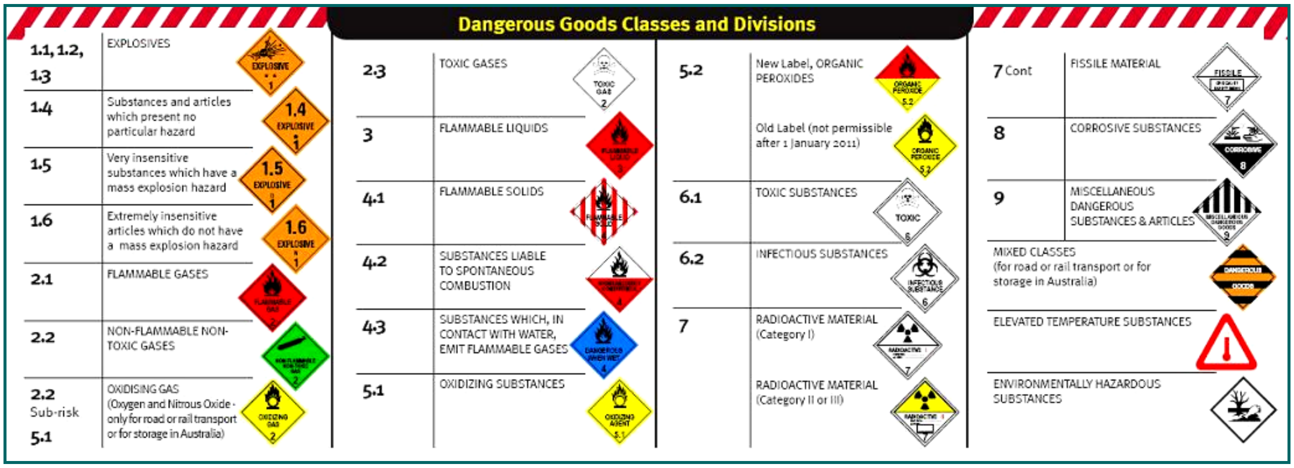

Figure 2-5: Dangerous good classes and divisions as per UN classification system (Source: www.deir.qld.gov.au)

Mercury compounds from UN 1623 (Mercuric arsenate) up to UN 1646 (Mercury thiocyanate) are rated as toxic and belong entirely to Class 6.1. Since Mercury reacts with other metals and elements by forming amalgams, elemental mercury is classified as corrosive and belongs under UN 2809 to group 8.

Since the UN coding system is related to transport, all dangerous goods are assigned to three possible packing groups such as for high danger (PG I), medium danger (PG II) and low danger (PG III).

In view of the fact that high mercury waste, transported under UN 2809 is handled as a corrosive substance, it only requires the lowest packing group III. Owing to this, some authorities request other UN numbers for such waste. Commonly for mercury-contaminated soil UN 3244 is used, which describes solids containing corrosive liquids. This code also belongs to group 8, but demands a higher packing group.

During the course of the remediation works performed along with the Chemical Factory Marktredwitz all the mercury-contaminated soil separated for a treatment in the Marktredwitz plant located outside of the town, was packed in 12 m^3 specially designed gas-tight transport containers, equipped with a hinged lid and char coal filters. The container was compatible to the Meiller truck lift system, which is entirely fulfilling the requirements for the transport of mercury as a dangerous good.

3 CHEMICAL AND PHYSICAL PROPERTIES OF MERCURY AND ITS COMPOUNDS

The properties of mercury and its compounds and the risk potential of mercury have already been discussed in a recently published article (RICHTER AND STAPELFELDT, 2008)[55].

3.1 MERCURY AS A CLASS B METAL

The element mercury belongs to the 2nd minor group (zinc group - II*b*) of the periodic system of elements. Seven naturally-occurring stable isotopes, such as ^{196}Hg, ^{198}Hg up to ^{202}Hg and ^{204}Hg exist.

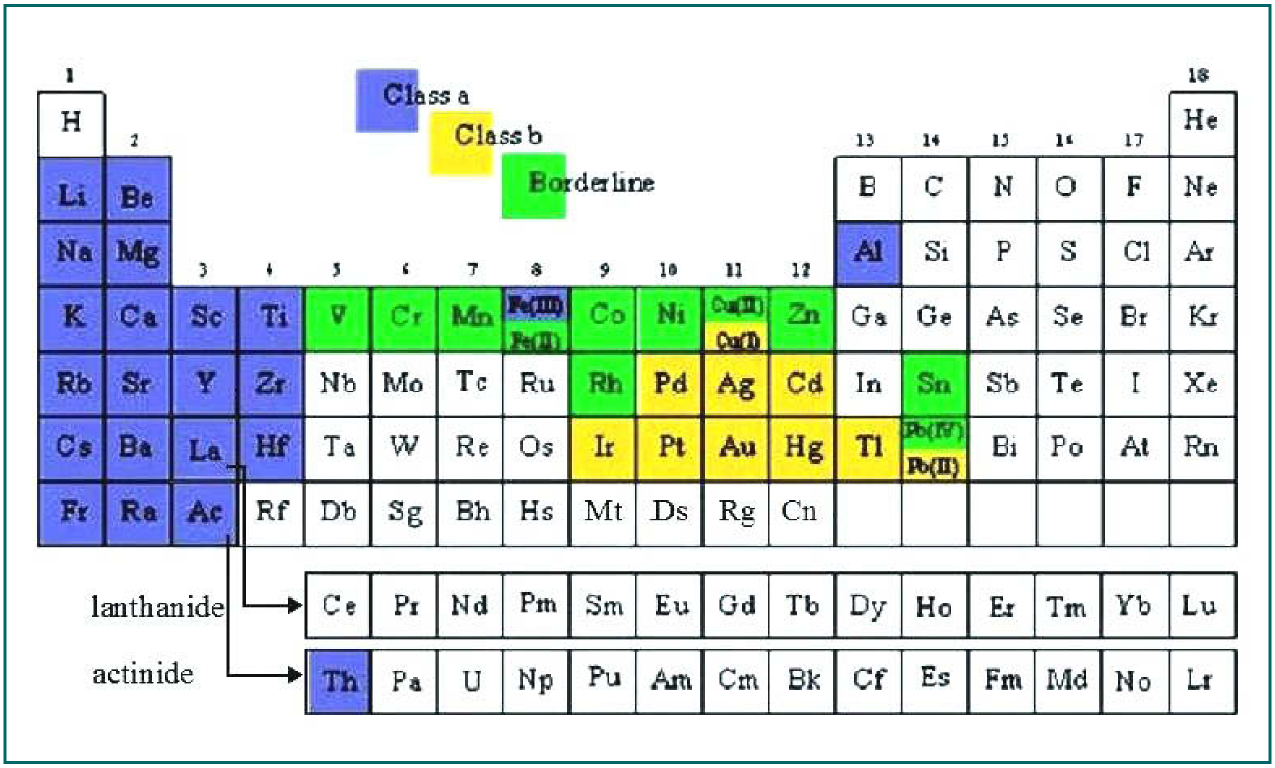

Figure 3-1: PSE classification of metals forming either strong (class a) or soft acids (class b); source: teachers.yale.edu

As per PEARSON'S acid base concept aka as 'hard and soft acids and bases theory' (HSAB theory)[56] certain hard acids react preferably with hard bases and soft bases react rather with soft bases. As far as hard and soft acids with regard to metals are concerned this model is in line with the classification of 'class a' and 'class b' metals.

Class b metals forming soft acids characterized by high polarizability, large radii and low surface charge. Soft acids formed from mercury are in particular[57]:

$$Hg^{2+}, CH_3Hg^+, Hg_2^{2+} \tag{3-1}$$

Forming very stable complexes with soft bases by pi-bonding (π-bonding) especially with the soft bases

$$S^{-2}, CN^{-}, I^{-}, P(CH_3)_3 \qquad (3\text{-}2)$$

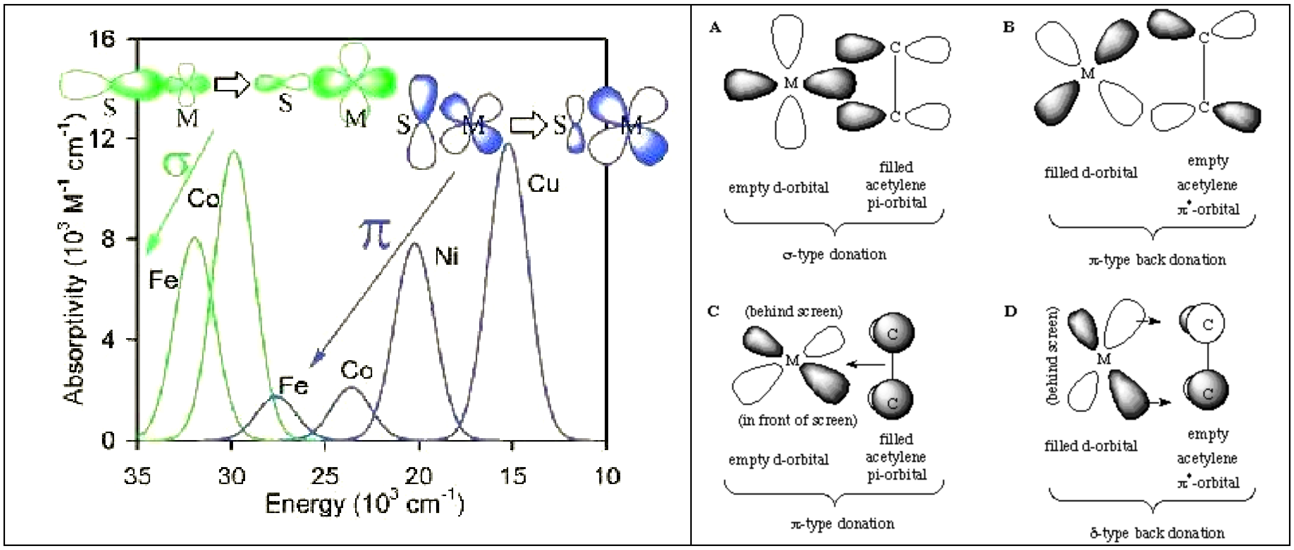

Figure 3-2: Covalent bonding to metals after S. I. Gorelskii (left) and bond principles (www.mathematik-forum.de)

Π-bonding and the π-effect are both basic principles in organometallic chemistry. Whilst π-bonding is a covalent chemical bond, metal-π interactions are non-covalent bonds, allowing electron-enriched organic complexes to bond to metals.

In the course of this thesis both phenomena are understood as vital for the mode of operation and effectiveness for the interaction between mercury and the applied sulphidisation and flotation collecting agents.

3.2 MERCURY AS PRESENT ON INDUSTRIAL SITES

At former industrial sites mercury may present itself in different shapes. These can be divided in three groups:

- elemental mercury
- inorganic mercury compounds
- organic mercury compounds

Apart from these compounds mercury forms alloys with most metals except for iron, so called amalgams. Metallic mercury and its compounds are suitable for a variety of uses. Besides elemental Hg they appear in the environment as inorganic mercuric compounds such as hydroxides ($Hg(OH)_2$), mercuric chlorides ($HgCl_2$) and sulfides.

Furthermore, organic mercury compounds can be encountered as RHgR' or more often as RHgX, (X is for example OH^-, Cl^-, etc.). It is assumed that mono methyl-Hg and phenyl-Hg-compounds make 90 % of all organically bound mercury in the soil. For the properties please refer to the table below:

Table 3-1: Chemical properties of some mercury compounds[58, 59]

Mercury compounds	Formula [-]	Density Mg/m^3	Melting point °C	Boiling point °C	Steam saturation at 20°C mg/m^3	Vapor pressure mm Hg at °C	Solubility in water g/100 ml
Elemental	Hg°	13.5	-38.84	356.95	13.6	$1.2*10^{-3}$ at 20°C	$3*10^{-6}$
Hg(II)-Sulfide	HgS	8.1	583.5	-	-	-	$1*10^{-6}$
Hg(II)-Chloride	$HgCl_2$	5.49	280.7	302.5	-	-	6.9
Dimethyl-Hg	$(CH_3)^2Hg$	3.07	-	96	-	58.6 at 23.7°C	-
Methyl-Hg-Chloride	$(CH_3)HgCl$	4.06	170	66		$4.7*10^{-3}$ at 20°C	5

In the environment chemical and microbiological conversions or a release of mercury compounds take place. Thus, the existence of inorganic or organic mercury compounds has to be anticipated even at sites with originally solely or predominantly metallic mercury contaminations.

In wide pH- and redox potential ranges the elemental form of mercury Hg^0 prevails. Depending on the redox potential and complexion agents the elemental mercury is oxidized to Hg^{2+} by exposure to air or oxygen-containing water. Particularly chloro complexes and sulfides are to be mentioned here.

Hg exhibits in soil a high affinity to solid organic components and enters strong bonds with dissolved and colloidally dissolved organic ligands. As depending on available sorption locations at OH and carboxyl groups the bonding capacity of organic substances is controlled by the pH-value. The bonding to organic substances is very stable and thus reduces the toxic effect. Bonds are mainly entered with humic acid, organic sulfur compounds and humic acids where oxygen is replaced by sulfur. Sulfur-containing soil components bind Hg to SH- and SS-groups[60].

In soils contaminated with mercury biological processes result in organic mercury compounds with alkyl or acryl groups like methyl mercury anion $[CH_3 Hg]^+$ and diphenyl mercury $Hg(C_6H_5)_2$. The proportion of methyl-Hg of the overall-Hg in sediments and soils is generally between 0.1 and 1.5 %. It has to be assumed that the concentration of methyl-Hg in soil is affected by the balance of methylation and demethylation[61].

3.3 HAZARDS AND TOXICITY OF MERCURY AND ITS COMPOUNDS

The displayed toxicity of mercury and its components is known and dreaded since the antiquities. Also the name hydrargyrum (gr., lat. liquid silver), known as Hg from the PSE hearkens back to Pedanius Dioscorides[xiii], who was an ancient Greek physician, pharmacologist and botanist and served as a surgeon in Emperor Nero's army. In his famous book 'De materia medica[xiv]' Dioscorides already described in more detail the symptoms of mercury poisoning.

Arabian physicians used ointments containing mercury to treat skin as well as parasitic, eczematous and leprous infections already in the 9th century. Zakarya Al-Quazwini (Arabic scholar *1203 to 1283)[62] describes the effects of mercury poisoning 300 years later very drastic as follows: *'Everyone who approaches mercury when fire caught it is benumbed and its vapor causes dire diseases such as tremors, paralysis, numbness,…, and withering of the brain'*

Nevertheless mercury and its compounds were used as a medicine for various diseases over many centuries such as against syphilis or phlebitis[63], but also as a laxative and home remedy against volvulus. Till in the 1960s

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[xiii] Πεδάνιος Διοσκορίδης; ca. 40-90 AD

[xiv] Περί ύλης ιατρικής

calomel was even used in teething powders for babies. The mercury poisoning symptoms caused by this medication were described by British medical practitioners as ‘pink disease’[64] and lead to serious childhood illnesses and to an ‘inexplicable high infant mortality rate’[65]. In our days the organic mercury compound ‘Thimerosal’[xv] (see fig. 3-2) is widely used as a preservation agent in Influenza and Hepatitis B vaccines. In the human body Thimerosal releases the ‘ethylmercury’ becomes effectively lethal to the neurons[66]. Even if banned in Europe and the US, the most probably largest negative input due to mercury –containing medication and cosmetics to the human mankind currently still occurs via skin lightening creams and soaps. Since mercury effectively is blocking the production of melanin (see fig. 3-2) in the skin and hair it is still widely used in Africa, Asia, the Middle East, but also in the US. - Just recently the Chicago Tribune reported about an investigation performed by the Food and Drug Administration (FDA) following a previously started initiative of the newspaper itself. Actually in 5 out of 50 creams purchased in Chicago shops, a higher mercury concentrations than 6,000 mg/kg of was found[67].

The chemist Alfred Stock[xvi], pupil of the Nobel Prize Winner Emil Fischer published already in the 1920s and 30s more than 50 papers on different aspects of mercury poisoning[68]. Elemental mercury, mercury salts, methyl mercury and other organic mercury compounds differ significantly regarding metabolism and toxicity. As a result of its high volatility at 20°C contact with mercury is mostly established via the airways. In the intestinal tract less than 0.01 % of elemental mercury (up to 80 % in the lungs), an average of 10 % of mercury salts and about 90 % of methyl mercury and other organic mercury compounds are absorbed. Mercury can be methylized abiotically and biotically by enzymes.

Mercury and its compounds destroy the red blood corpuscles and damage the central nervous system. It produces genetic changes and damages the immune system and the inner organs, especially the kidneys. Methyl mercury compounds have a negative effect on the cerebellum (minimata illness) and on foetal development.

The toxicity is highly increased by methylization reactions. In contrast to inorganic Hg compounds ‘methyl mercury’ quickly overcomes the blood-brain and placental barrier[69]. Destination organs are the synapses of the nerve tracts, where irreversible defects of the transmission mechanism occur due to the strong bonding to sulfuric atoms of proteins (enzymes)[70]. Chronic mercury poisoning can end up with the Korsakoff’s[xvii] syndrome, a neurological disorder due to the lack of thiamine (vitamin B1) in the brain, which was first discovered and described as a disease in consequence of persistent alcoholism[71].

[xv] ‘Thimerosal’ is the approved name by the US Pharmacopeia and in Europe commonly referred to as ‘Thiomersal’.

[xvi] Alfred Stock (1876-1946), one of the most important inorganic chemists at the beginning of the 20th century, had studied chemistry under Emil Fischer in Berlin, and followed him as Professor for Chemistry at the University of Breslau in 1909. In 1916 he became director of the Kaiser Wilhelm Institute for Chemistry in Berlin. After 1924 a severe mercury poisoning was diagnosed and after his recovery Stock became a strict opponent of the use of mercury in particular in dentistry.

[xvii] Sergei Sergeievich Korsakoff (1854-1900), Russian neuropsychiatrist and pupil of Theodor Meynert in Vienna

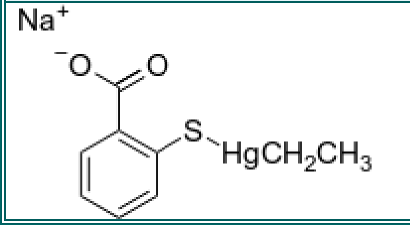
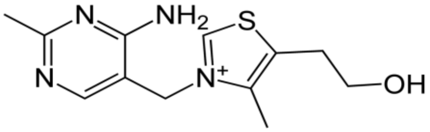
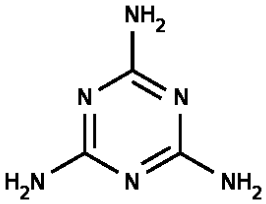
Thimerosal/Thiomersal	Thiamine (Vitamin B1)	Melamine
		

Figure 3-3: Structural formulas of Thimerosal, Thiamine and Melamine

Organic mercury compounds are classified as water hazard class 3 and are severely hazardous to waters affecting the food chain and in particular fish. Methyl mercury has a relatively long biological half-life in fish which is about 2 years and two to five times longer than that of inorganic mercury compounds. The half-life of methyl mercury in the human body is estimated to average 70 days (in some cases even up to 120 days)[72]. Mercury poisoning closely related to methyl mercury, accumulated in shellfish, became famous as Minamata disease, originally caused by methyl mercury-containing process water released in the Minimata bay from an acetaldehyde factory form Nippon Nitrogen Fertilizer Co. Ltd., but also known from a similar situation in another Japanese town named Niigata[73].

The largest exposure of metallic mercury to human beings and animals is generally via the respiratory tract, although mercury can also be absorbed through the skin. The occupational exposure limit (OEL) for gaseous, metallic mercury in Germany is indicated with 0.1 mg/m^3 and for dusts of organic Hg-compounds with 0.01 mg/m^3. Principle no. 9 (G 9) of the heavy earthwork and construction accident prevention and insurance association (Tiefbauberufsgenossenschaft – TBG) considers the mercury concentration in blood and urine merely as a sum parameter. A blood parameter ranging from 10 up to 50 µg/l is still considered to be uncritical. For work in the area of dismantling and dismounting of chlorine-alkali electrolysis facilities, where mainly elemental mercury occurs, principle 9 is sufficient. As a personal protection equipment (PPE) tight fitting full face respirators supported by fans with replaceable cartridge filters of the type ABEK2Hg/P3, protective gloves (gummed and with gauntlet), one-way protective clothing and rubber boots are mandatory for working in mercury-contaminated hazardous waste areas.

Blower supported respiratory helmets that don't fit tightly to the face in Germany are only allowed up to a concentration not exceeding more than five times the maximum allowed working place concentration (OEL value). The confirmation of the mask capability by passing the spirometric test according to principle 26 of the TBG is obligatory for everyone working in a contaminated area.

4. CHLORINE-ALKALI ELECTROLYSIS PLANTS, ACETADEHYDE AND CHEMICAL FACTORIES

Next to the mercury cell process other chlorine-alkali electrolysis methods are the elder (asbestos) diaphragm process, but also the membrane process, that was already developed about 40 years ago and that is currently used again as a state of the art technology by replacing existing mercury cell plants.

4.1 ALKALI ELECTROLYSIS TECHNOLOGY

In the Castner-Kellner mercury cell process the electrolysis of saturated brine is conducted at a rotating cathode of metallic mercury and at a titanium anode (formerly a graphite anode), followed by the alkali-amalgam decomposition and recovery of mercury within a closed circuit, as shown in fig. 4-1.

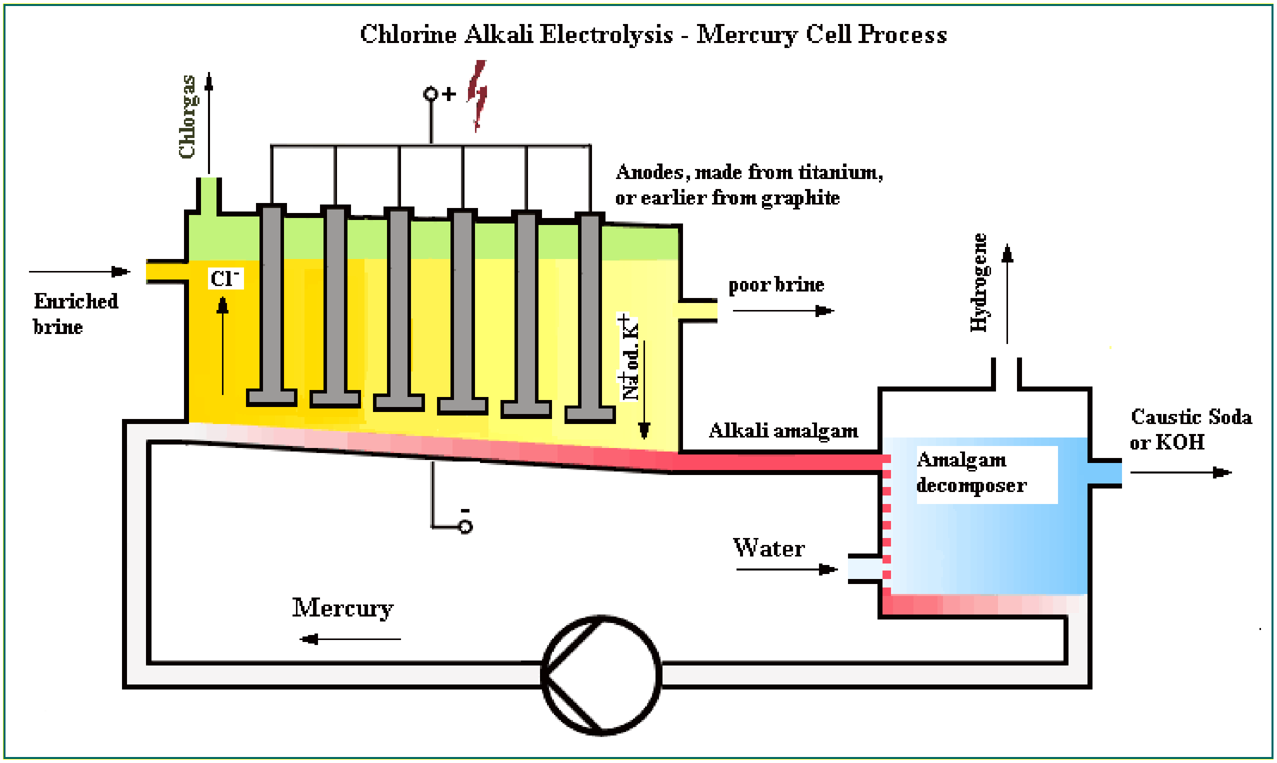


Figure 4-1: Amalgam process using metallic mercury as a rotating cathode in a closed circuit

Thereby the emission of mercury is constricted within normal controlled operations. In the process the following reactions take place. At the anode chlorine gas is generated:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{4-1}$$

The reaction at the mercury cathode is analogue for sodium and potassium (Sodium dissolved in mercury forming with mercury a sodium amalgam):

$$Na^+_{(aq)} + e^- + Hg \rightarrow Na/Hg \tag{4-2}$$

4.2 CHLORINE-ALKALI ELECTROLYSIS PLANTS IN WESTERN EUROPE

With a production capacity of 4,324 kilotons of chlorine per annum in 2005[74] Germany remains the largest chlorine producer in Western Europe (fig. 4-2).

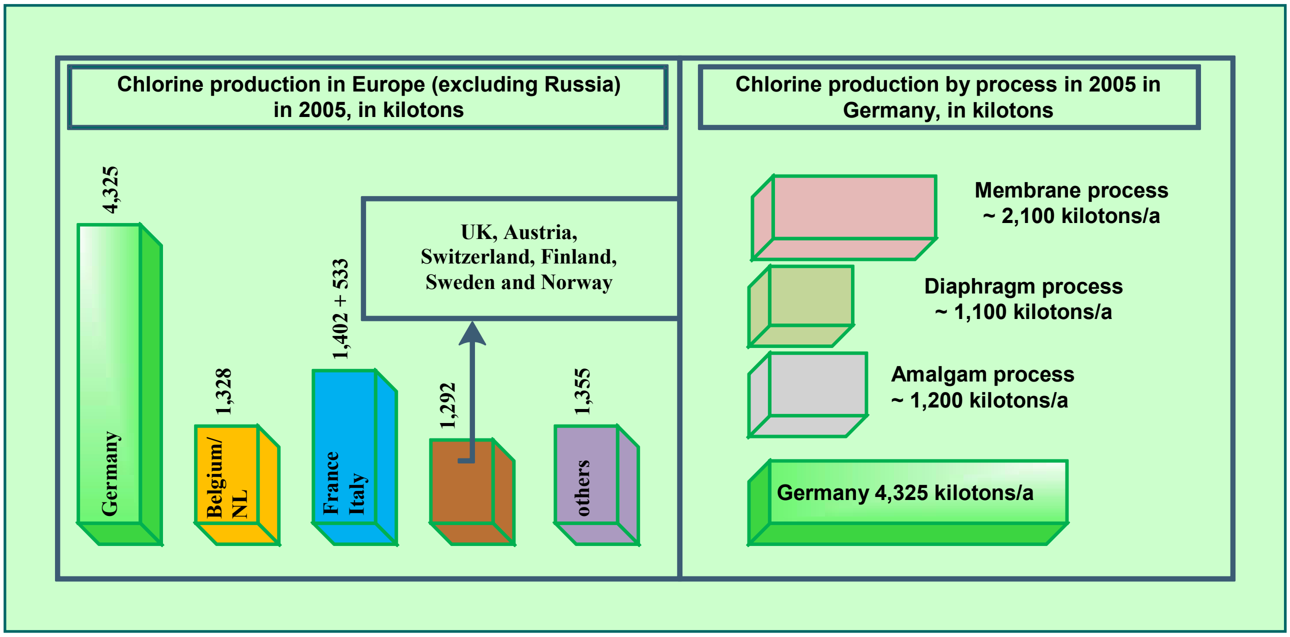


Figure 4-2: Chlorine production in Western Europe in 2005 in kilotons of chlorine per annum

In comparison with the above figures, the entire world chlorine production at about the same time was approximately 45,000 kilotons Cl_2/a. With about 1,200 kilotons Cl_2/a in 2005 Germany is also the largest user of the amalgam process in Europe. This equates to a reduction of about 500 kilotons Cl_2/a compared with the year 2000.

Nowadays the European Commission is attempting either to close facilities currently still using the amalgam process or to replace these facilities by mercury-free processes[75, 76].

The PARCOM decision 90/3 of 14 June 1990 recommends that all chlorine-alkali electrolysis facilities in Western Europe using the amalgam process should be decommissioned by 2010 for reasons of environmental protection.

4.2.1 Chlorine-alkali electrolyses plants in the East German ‘chemistry triangle’

The region between the Buna works in Schkopau and the close-by chemical factories in Leuna and Bitterfeld located in Saxony-Anhalt is also known as the ‘Chemiedreieck’ (chemistry or chemical industry triangle).

4.2.1.1 Chlorine plants in the Electrochemical Works in Bitterfeld

The history of Bitterfeld as one of the most important centres of the chemical industry in Germany started in 1894, when even two electrochemical companies autonomously established chlorine electrolysis facilities on this location at the same time:

- CFE: ‘Chemische Fabrik Elektron AG’, founded in 1892 as a subsidiary company of ‘Chemische Fabrik Griesheim’, and
- EW: ‘Elektrochemische Werke’ (Electro-chemical works), founded in 1893 as a part of AEG.

The first industrial-scale chlorine-alkali electrolysis plant was commissioned by CFE in Bitterfeld Werk Süd (Works Area South) as ‘Elektrolyse I’ using asbestos-cement diaphragm cells, so-called Griesheim cells, followed in 1895 by ‘Elektrolyse II’ which later was called ‘Chlor I’.

The ‘Elektrochemische Werke’ commissioned in Bitterfeld Werk Nord (Works Area North) another chlorine-alkali plant with 300 numbers of so-called Rathenau cells[3]. The name traces back to Dr. Walther Rathenau, the later German minister of foreign affairs and first managing director of the Elektrochemische Werke GmbH. In 1921 EW was taken over by CFE and in 1925 the Elektrochemische Werke Bitterfeld were owned by IG Farben.

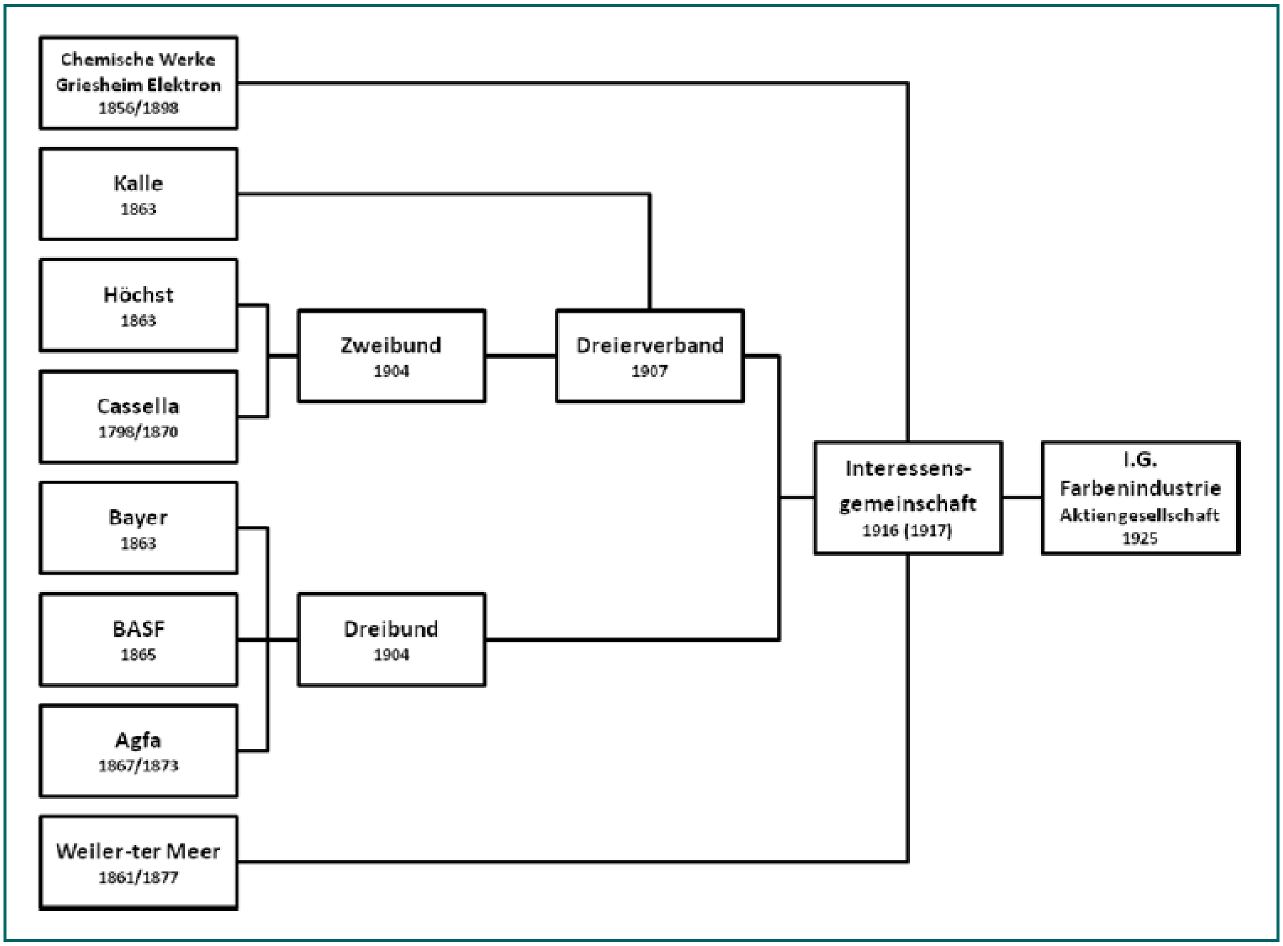


Figure 4-3: History and genesis of the origin of the ‘I.G. Farbenindustrie AG’[77]

The Interessengemeinschaft Farbenindustrie (I.G. Farben) AG, as the German Dye Industry Syndicate, existed already as a trust since 1916 and was founded 1925 as a merger involving a number of major chemical companies such as BASF, Bayer, Hoechst, Agfa, Griesheim-Elektron and Weiler Ter Meer[78]. At this time the IG Farben AG was the world’s largest group of consolidated companies in the chemical industry.

Figure 4-4: Chlorine-alkali electrolysis plant ‘Chlor III’ in Bitterfeld, East-Germany, built in 1917; closed in June 2000; demolished and dismantled in 2003 (40,000 tons of mercury-contaminated soil and rubble)[xviii]

The chlorine-alkali electrolysis plant ‘Chlor III’ in Bitterfeld was already built in 1917. The last asbestos-cement diaphragm cells of the ‘Griesheim-type’ were taken out of service in 1931. Chlor I and Chlor III were converted to the more efficient amalgam process during the late 1930s.

During GDR-time the chlorine plants belonged to the people owned ‘Chemisches Kombinat Bitterfeld’ (CKB). Chlor III was re-commissioned with mercury cells in 1950. Between the years 1965 and 1968 Chlor III was subject of a big expansion project, in order to double the production capacity. Between 1978 and 1982 also the reconstruction of Chlor IV was performed. In 1988/89 270,000 t of chlorine were produced in Bitterfeld. The chlorine-alkali electrolysis facility Chlor III in Bitterfeld was in operation until 30 June 2000.

Following German reunification the eight former East German chlorine plants and the acetaldehyde facility F44 were dismantled between 1998 and 2003 during the course of the major ecological superfund projects ÖGP Buna and ÖGP Bitterfeld (Ökologische Großprojekte) in Eastern Germany’s ‘chemistry triangle’. All remediation activities were financed and professionally managed by the for this purpose established ‘Bundesanstalt für vereinigungsbedingte Sonderaufgaben – BvS’ (Federal Agency for Reunification Operations).

The abandoned plants of the German Democratic Republic were in a highly neglected and decrepit state owing to their age and damage during World War II. This condition bore no comparison with, in particular, the degree of contamination of other western European or international facilities of a newer design.

[xviii] The author was involved in the remediation of both chlorine alkali electrolysis projects (Chlor I and Chlor III) in Bitterfeld as Site Manager covering a wide range of technical responsibilities.

4.2.1.2 Chlorine plants of the Buna Works in Schkopau/Germany

In April 1936 the IG-Farben AG commenced construction of Germany's first synthetic rubber facility in Schkopau to provide tire rubber for the incipient 'Volksmotorisierung' (increase of national motorisation), after a test plant for 2,400 tons of rubber per year was successfully operated already in 1935.

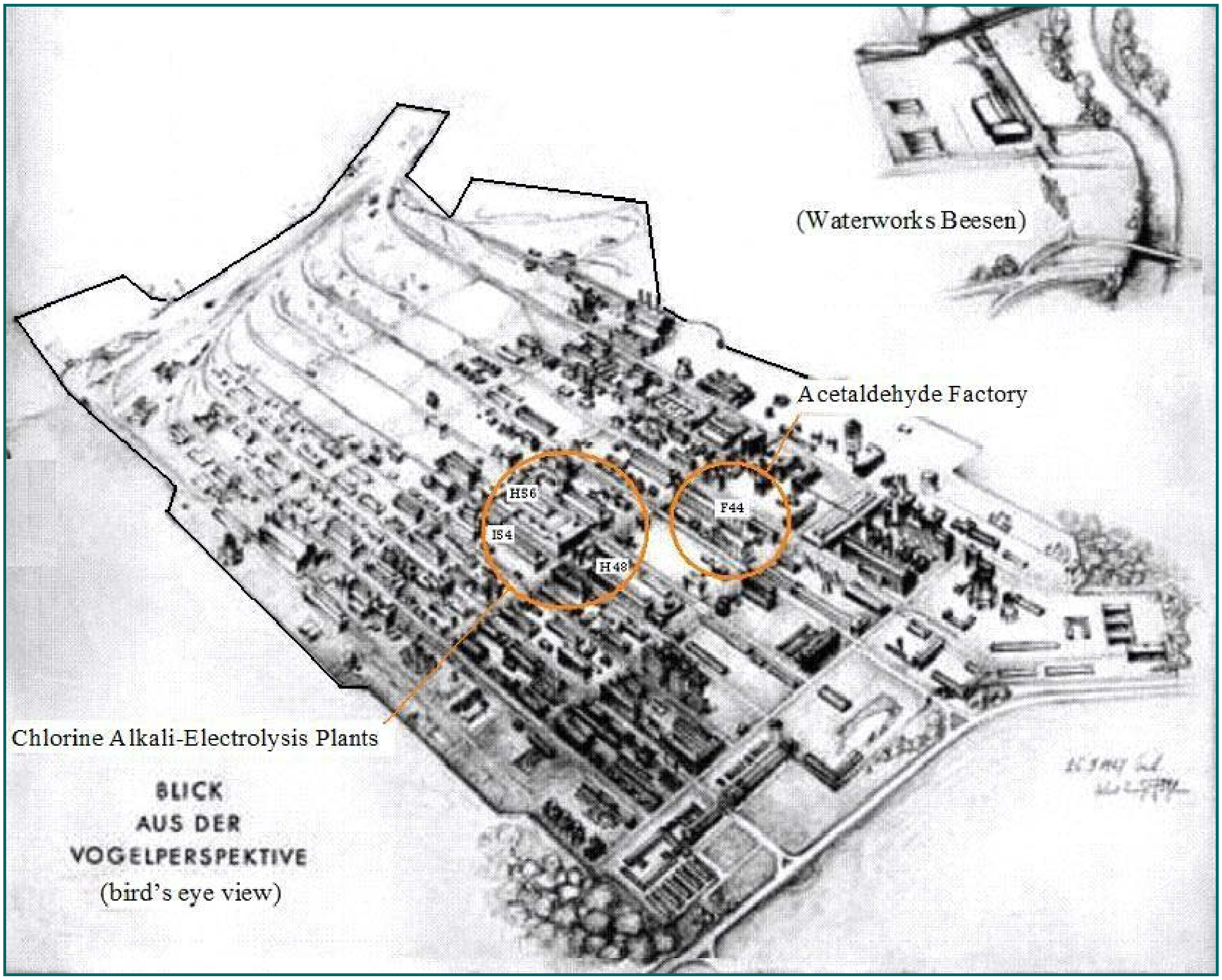


Figure 4-5: Buna Works Schkopau in the year 1947 with chlorine plants I54/H56 and the acetaldehyde factory F44 (source: Buna Schkopau)

The alkali metal sodium (in German: "Natrium") produced by electrolysis served as a catalyst for fabricating synthetic rubber from the gas butadiene. These two main components were eponymous for the 'BuNa-Werke'. During this time the chlorine-alkali electrolysis facilities Units H 56 and I 54 were constructed at the Buna works in Schkopau.

The IG Farben established in total four Buna factories in particular 1938 in Hüls near Recklinghausen, in Ludwigshafen (1940–42), and the last one, located in Upper-Silesia (Monowitz), was started in 1941 and never finally commissioned. Such as in all Buna factories, the 680 ha large Buna area in Schkopau was designed as a tessellated grid square system (fig. 4-5). The size of each grid square was approx. 100 m x 200 m. The original chlorine plant complex in Buna Schkopau including the chlorine plants I54 and H56 and the associated buildings was located in grid squares H-K/4-5:

Table 4-1: The buildings of the original chlorine plant complex H56 and I54 in Buna Schkopau

Building No.	Technical use/ generated products	Further description
H56 and I54	Chlorine-alkali electrolysis plants	Wide-spanned multi nave frame work halls from on-site casted reinforced concrete (fig. 4-6). Main structures highly contaminated due to war damages, age and lack of maintenance. Auxiliary buildings and equipment were contaminated due to process media such as backflow of Hg-containing brine and technical problems with filtration.
H46	Gas drying and compression	
H48	Caustic soda storage tanks	
H62	Brine processing plant	
H66	Salt dissolving plant	

The buildings were mostly erected as on-site casted reinforced wide-spanned concrete framework constructions with a minimum of tree naves and an overall width between 75 and 80 metre. The electrolysis cell level was established on the same elevation as the surrounding surface. All piping and infrastructure of the cells, the amalgam decomposers and the mercury pumps were installed in the supply cellar below.

Soil investigations have been performed with soil samples from the Buna Works in Schkopau. Methyl mercury compounds also result from the production of acetaldehyde.

Table 4-2: Total Hg and organic mercury compounds analyzed in soil from CAP areas in Buna Schkopau (GKSS)

Chlorine Plant Area	Total mercury [mg/kg] DM	MeHg+ [µg/kg] DM	MeOEtHg+ [µg/kg] DM
Buna H56	**190 – 3.000**	**4 - 48**	**Not determined**
Buna I 54	**45 - 550**	**8 - 14**	**1 – 17**
Buna L66	**100 – 5.900**	**24 - 400**	**3.5 – 18**

As a result of their solubility they may be found in high concentrations in the waste water of such plants. Groundwater contaminated by organic mercury compounds is a very serious problem, because very small concentrations may have a toxic effect.

Constitutive for the assessment of the contamination of soil is the condition of the floor of the basement used for the supply installations of the electrolysis facility. In most chlorine-alkali electrolysis facilities this is constructed as a concreted bottom plate (ferroconcrete/reinforced in-situ concrete) sloping towards a centrally located gutter. The circulating mercury could be discharged into this gutter in case of emergency shut-down. In some old facilities the floor sealing (bottom plate) has been heavily damaged during the war.

In H56 the damage of the floor slab in combination with an uncontrolled release of caustic soda caused an extreme swelling of the clayish soil below resulting in extensive irreparable uplifts of the subsoil (of more than 1 meter) which led also to extraordinarily high mercury-contaminations of the building ground located below. Depending on the degree of contamination of soil it had to be provided for that tremors resulting from the dismantling process do not cause a relocation of mercury to lower soil horizons. The structural design of the chlorine alkali-electrolysis plants I54 and H56 allowed a very flat and uncomplicated foundation system (see fig. 4-5) which was proven to be beneficial in order to perform selective demolition work.

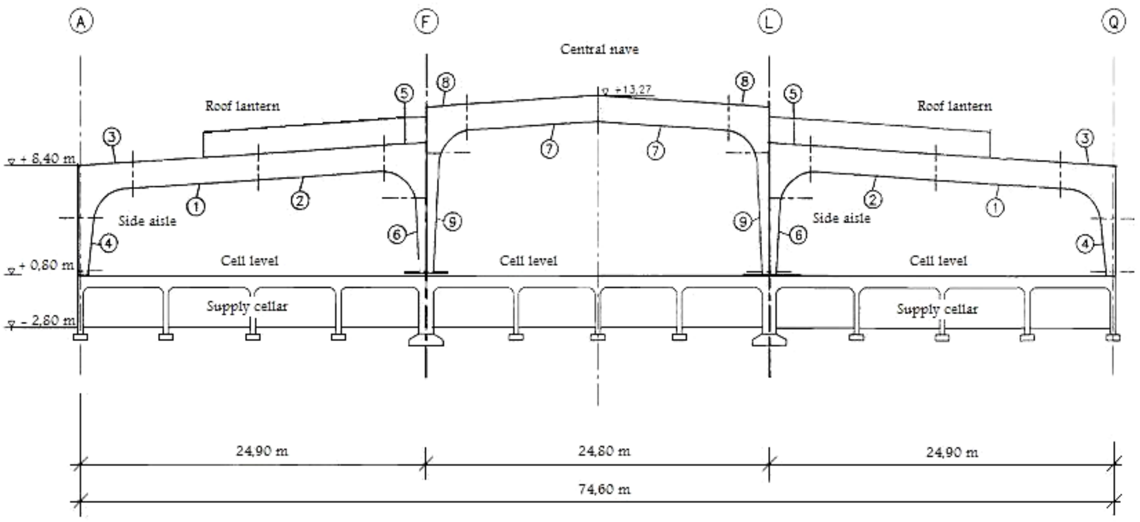


Figure 4-6: Sectional view of the chlorine-alkali electrolysis building H56 in Buna Schkopau (source: Lahmeyer)[xix]

During the 1960s the chlorine production in Buna Schkopau was extended by building an additional chlorine plant L66, using prefabricated reinforced concrete elements according to the single-span beam as a basic structural element. In contrast to the above mentioned constructions these constructions were statically determined and could be dismantled in reversed order of the construction. However, the span width was limited compared to the above mentioned ingeniously designed framework constructions.

The L-complex including the buildings L66, L56, L76, M77 and M74 was located in grid square L-M/5-6:

Table 4-3: The buildings of the chlorine plant complex L 66 in Buna Schkopau

Building No.	Technical use/ generated products	Further description
L66	Chlorine-alkali electrolysis plant	Built from prefabricated reinforced concrete elements based on deep sleeve foundations (fig. 4-6). Excessive soil contamination due to Ground slab leakage and sandy sub soil. Auxiliary buildings and equipment were contaminated due to process media such as in H56 and I54.
L56	Hydrogen purification plant	
L76	Caustic soda storage tanks	
M77 and M74	Salt dissolving and brine processing plant	

Another great difference of L66 compared to the much older chlorine plant buildings was the highly more complex foundation such as enormous sleeve foundations made of reinforced concrete had to be dismantled (see fig. 4-7). This entailed serious technical problems and an unforeseen delay of the time schedule and excessive higher costs.

[xix] As a technical consultant for the Buna mercury remediation project the author was in charge for the approval of the deconstruction planning for the mercury-contaminated buildings (mostly statically undetermined structures)

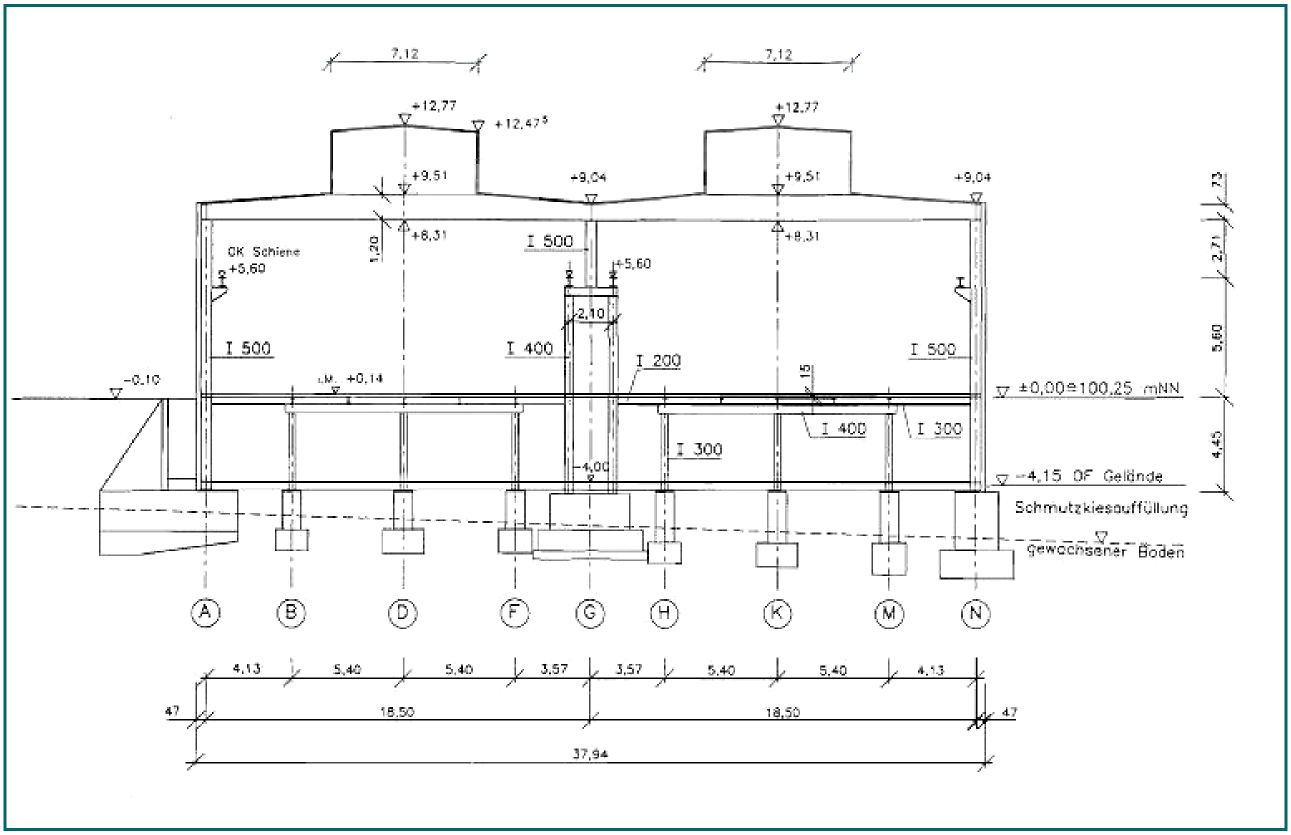


Figure 4-7: Sectional view of the chlorine-alkali electrolysis building L66 in Buna Schkopau (source: Lahmeyer)

4.2.1.3 Demolition of mercury-contaminated building structures in Buna and Bitterfeld

Next to contaminated soil the main mercury waste from chlorine-alkali electrolysis plants and acetaldehyde factories is the rubble generated by demolition from the building structure itself. Owing to this the 'destruction strategy' plays an important role for the classification of the waste independent whether the waste is foreseen for treatment or discarding in different classes of landfills or underground mine disposal[xx].

In consequence of this, the chlorine-alkali electrolysis plant remediation projects in Bitterfeld and Buna Schkopau the main emphasis of the site remediation was on the demolition (selective destruction) of the chlorine plant buildings. The supporting structure of chlorine-alkali electrolysis facilities mostly consisted of wide-spanned naves flanked by lower aisles. The supporting frameworks, either designed as reinforced, on-site casted concrete or steel framed constructions. The infill between the reinforced load-bearing concrete frames was established as brickwork. In longitudinal direction the frames were supported on both ends by so-called 'Kopfbauten' (head buildings) such as shown in fig. 4-2, built as stack-bonded massive multi-storey masonry structures, including the electrical supply and control rooms but also gas washing units, filters and other process related equipment.

[xx] For the mercury remediation superfund projects in Buna Schkopau and Bitterfeld (ökologische Großprojekte) all technical documents with regard to the chlorine-alkali electrolysis such as in particular dismantling and demolition procedures including structural calculations and chemical analysis reports were reviewed and approved by the author, either as consultant of the BvS as a superfund authority, or later as a site manager of the Project Management Company (PMC). For Chlor III Bitterfeld the author was providing the demolition strategy and the structural calculation of the building for the demolition permit.

Knowledge of the technical construction and estimation of the bearing capacity of load-bearing building parts (frame strut, binder, longitudinally stiffening bracings) is important for wide-spanned contaminated supporting frameworks of halls, as a failure of construction parts may occur due to possible static intermediate situations resulting from the necessary selective or partly selective dismantling. Thus selective dismantling considering contamination issues is limited to a certain extent as the structural (static) interests of the supporting framework inevitable determine the dismantling strategy and technology.

The stability in longitudinal direction is provided for by introducing the longitudinal forces from one massively stonewalled front section serving as a final skewback to the next. In this case the dismantling is carried out from one front section to the next while the dismantling apparatus hydraulic excavator or cable dredger mostly advances bay-wise by driving directly on the basement floor. A key feature of chlorine-alkali electrolysis buildings following the amalgam process is the supply cellar beneath the cell hall level. On ceiling of the supply cellar the electrolysis cells are located mostly at grade with the surrounding area. Besides bearing the load of the process equipment (electrolysis cells) this intermediate ceiling often absorbs tensile or secondarily also compressive forces in transversal direction. This horizontally stiffening intermediate level is not capable for being driven on with heavy mobile equipment.

Figure 4-8: Demolition (controlled destruction) activities performed on chlorine plant I54 in Buna Schkopau in 2001

Apart from corrosions on the supporting framework such as in particular acid corrosion on the reinforcement bars the controlled (selective) dismantling is hampered by the statically indeterminacy of the construction itself as the necessary separation of statically in-determined frameworks (typically at the calculated zero crossing of the bending moments) sometimes necessitates complex auxiliary constructions or additional supporting mobile equipment to take up the retention force for the intermediate steps during deconstruction such as shown in fig. 4-9.

Complete enclosures are neither technically or economically feasible due to the vast dimensions of the chlorine-alkali electrolysis buildings. Following the demolition sequence in longitudinal direction, as shown in fig. 4-8, helps to keep the open areas of the naves as small as possible. Practical experience gained in Buna has proven that spraying a water curtains is sufficient to reduce emissions. The disadvantage of this method is on one hand an additional structural load due to wind from inside and the fact that the emissions can increase abrupt, after the water curtain is stopped up.

Accumulation of mercury on the outer walls and in particular on roof constructions were apparently due to condensation as thermal insulation was not provided for in the early ferroconcrete buildings. It is recommendable to lift off the roof parts as careful as possible before the dismantling of the main structure occurs and to collect them separately for sampling purposes.

The accruing dismantling materials from the chlorine-alkali electrolysis facilities and the acetaldehyde plant of the former Buna-Works in Schkopau altogether amounted to approximately 400,000 t. The estimated amount of mercury released due to war-caused damages and the operational process ranges in the dimensions of several hundred tons of mercury.

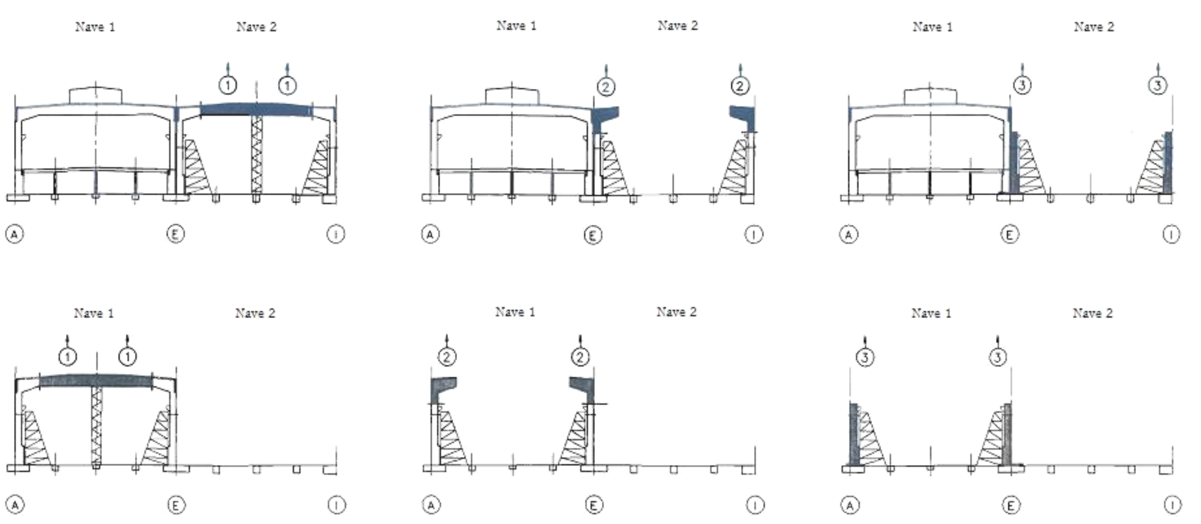


Figure 4-9: Sequence of the controlled destruction of the chlorine-alkali electrolysis building I54 in Buna (Lahmeyer)

While the contamination of the demolition waste, such as bricks and concrete rubble at the above mentioned old industrial sites was in the multi-digit gram-range per kilogram due to war damages, obsolescence and neglected investments, the following table shows the contamination situation (pre-sampling data) of a relatively small chlorine-alkali electrolysis facility with an enclosed space of about 14,000 m³ made of ferroconcrete which has been ordinarily used over a period of about 20 years. It was constructed at about 1980 according to the state of the art (spot sample of core holes).

Table 4-4: Contamination of a chlorine plant cell building in the Emirate of Abu Dhabi after 20 years of use

Building Part	Random Sample Size	Average Value [mg/kg] DM	Cubature [m³] (solid material)	Comment
bottom plate	16	660	790	0,4 m thick
pump sump /channel sediment	3	6420	10	preparatory separation
wall in general	11	14	400	Max. 46.4 mg/kg
roof cell hall	4	$\leq$ 10.00	350	Max. 16.0 mg/kg
cell level slab	17	11.50	150	Max. 92.8 mg/kg

The mercury contamination of walls, roof and cell level is rather low and only scarcely above the assignment criteria Z 2 (Zuordnungswert 2) being Hg ≤ 10 mg/kg in dry matter according to German LAGA (Bauschutt). With regard to the sampled building matter the average contamination is Hg = 350 mg/kg in dry matter. For this it proved to be essential that the walls had an intact and a regularly renewed coating of epoxy resin lacquer in full height of the walls above the cell level.

4.2.1.4 Dismounting and decontamination of equipment parts

Generally, the dismounting of a facility should be preceded by a proper decommissioning of the technical equipment including emptying, draining and cleaning. In Germany this happens usually according to § 19 l WHG (Wasserhaushaltsgesetz – Federal Water Act) conducted by so called WHG expert companies (Fachbetrieb nach WHG § 19 l).

The mercury contamination of the electrolysis cells is located on or rather in the steel surface. Surface samples of mercury contaminated metal parts have been accomplished by the X-ray diffraction spectroscopy. In the scope of a smaller scale sampling the considerably more complex and precise aqua regia extraction with a subsequent analysis (cold vapor atomic absorption spectroscopy) would be sensible, as thus also the mercury that is incorporated into the steel is measured. The sampling needs to be conducted by the cold separation process though.

Target value for utilization in most of the German steel works is Hg ≤ 5 mg/kg. Therefore decontamination of the technical equipment (in particular of the cell floors) is technically and economically reasonable. For decontamination of mercury-contaminated technical equipment following methods are available:

- wet chemical
- dry mechanical
- wet mechanical or a combination of the above mentioned methods

Investigations performed with wet chemical demercurization of various metals (copper, aluminum, stainless steel, construction steel) with washing solutions showed the best cleaning results in laboratory scale with iodine solutions[79].

Dry mechanical procedures such as sand blasting etc. have not proved themselves for decontaminating equipment due to the considerable amount of shot to be disposed additionally. However, it can be used for severely corroded constructions out of steel (girders and bearers) where mercury is often attached to corrosion products.

Wet chemical procedures using high pressure jet washing (with or without abrasive additives), sometimes supported by mechanically operating brushes were applied in practice in many cases. Good results were achieved by using a patented ultra high-pressure water blasting technology with up to 2,500 bars. Thus several hundred tons of steel parts with mercury contaminations in a range of 5,000 mg/kg but also 1,000 m² of cell bottoms could be cleaned in Buna Schkopau to the target value of 5 mg/kg[80, 81].

However, it has to be noted that cleaning of metal surfaces of small containers and piping (sometimes contaminated with dioxin containing chlorine sludge) is not economically worthwhile. In general, the amalgam decomposer, the downstream mercury pump and the mercury recirculation pipe have to be classified has highly contaminated (Hg >> 300 mg/kg in dry matter), so are large parts of the hydrogen passage.

Water jet surface decontamination requires a water treatment plant on the site recovering the washing water in a closed cycle. Chlorine-alkali electrolysis facilities using the amalgam process mostly possess an own water purification facility. It is wise to continue using it during the dismantling process for cleaning the waste water of the high-pressure jet washing.

4.2.2 Chlorine-alkali electrolysis in Waldshut-Tiengen (Old Lonza Works)

Since 1888 the AEG had established in close cooperation with the “Schweizer Metallurgische Gesellschaft” the “Aluminium-Industrie AG (AIAG)” in “Neuhausen am Rheinfall” in Switzerland, later known as “Alusuisse” provinding their technical ‘know how’ about electrolysis also to EW in Bitterfeld[3].

LONZA electrical works, another company from Swizzerland established in 1914 the ‘Lonza works’ on the German side of the River Rhine in Waldshut-Tiengen.

From the end of the thirties till to the late sixties the ‘chemical factory’ in Waldshut-Tiengen produced various chemicals based on ethyne (acetylene), using mercuric oxide as a catalyst which was generated by anodic oxidation of elemental mercury by electrolysis.

In the year 1974 Lonza was taken over by Alusuisse and in the mid nineties the production was finally shut down.

Between the years 1990 and 1995 soil investigations were performed on the site by the engineering company Lahmeyer International.

Figure 4-10: Location of the Old Lonza Works in Waldshut-Tiengen (map and aerial photograph, source: Lonza)

During soil remediation commenced a representative soil sample was taken by the author in order to perform soil washing and flotation tests.

4.2.3 Chlorine-alkali electrolysis plant in Ústí nad Labem (Aussig a.d. Elbe)

In the first half of the 19th century in the region around Aussig in Northern Bohemia (today: Ústí nad Labem/Czech Republic) more than 60 collieries were in operation. Located on the rivers Elbe and Bilina, Aussig was also connected to the main trade routes, in particular to the important railway from Teplitz to Prague.

In 1857 representatives of the Austrian peerage, in particular the Princes of Schwarzenberg, Clary-Aldringen and Fürstenberg founded the “Verein für chemische and metallurgische Produktion Aussig/ Elbe”. Incipiently producing only sulfuric acid and soda ash (sodium carbonate) by using the Leblanc process, the chemical factory in Aussig grew horrendously under the leadership of Max Schaffner (1830–1907). Beneficial was also the early relationship to Ernst Solvay, using his process for the production of soda and establishing an early alliance with Solvay & Cie. followed by the erection of the soda factory in Ebensee.

Establishing chlorine-alkali electrolysis facilities for the production of caustic soda and hypochloric acid under Schaffner the more efficient bell shaped Aussig cell (Aussiger Glockenzelle) was developed and was even used by their competitors in Bitterfeld.

The amalgam process was established in Aussig before WWII when the “Aussiger Verein” was taken over by the German dye syndicate “IG Farben” and the “Chemische Fabrik von Heyden”.

After the Second World War the chlorine-alkali electrolysis plant was operated by ‘Spolek pro chemickou a hutní výrobu (Spolchemie)’ till 2001.

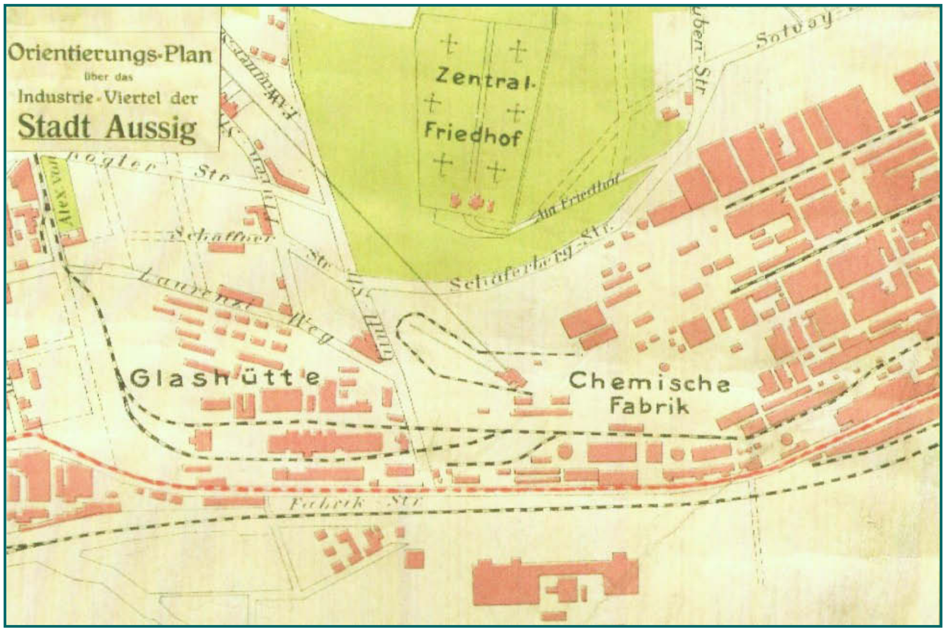


Figure 4-11: The industrial area of Aussig before WWII (collection of the author)

The ‘Spolchemie’ Chemical Factory is identified as the major source of pollution to the Elbe River, which is currently one of the most polluted aquatic ecosystems in the Czech Republic[82].

The mercury contamination under the concerned facilities was estimated (SEDLÁČEK, 1998) in a range of 267 up to 445 metric tons[83]. The entire volume of subsoil to be excavated was calculated with 223,000 m^3, which amounts to more than 310,000 metric tons. The mercury concentration in soil was estimated in a range between 10 and 10,000 mg/kg

In July 2002 the Fond of the National Property of the Czech Republic (FNM)[xxi] released a tender for the remediation of the Spolchemie area including the mercury-contaminated chlorine plant areas I and II and the location of the hydrogen storage tank, area V accordingly.

Currently the treatment of mercury-contaminated soil and rubble is ongoing by means of a thermal treatment plant installed on the Spolchemie area (compare to fig. 5-8)[84]. A soil sample was taken by the author at the 27 Oktober 2009 from the bunker area of the treatment plant. The results of the wet screening tests performed by the author are shown in App. A-3 in comparison to earlier conducted tests by Banske Projekty Teplice A.S. and Ergo Umweltinstitut GmbH.

[xxi] Fond národního majetku České republiky

4.2.4 Chlorine-alkali electrolysis plants in South-West Taiwan

Investigations concerning the bio-concentration of metals in terrestrial biotica, recently performed by Hsu et al.[85] around Kenting National Park have confirmed very high concentrations of Hg found in invertebrates such as for example in earthworms and snails, but also in amphibian and reptiles in particular in lizards and in snakes.

The Environmental Protection Administration of Taiwan has highlighted recently that its investigation into five underground water and soil pollution cases has located considerably high pollutant levels. The investigation was done by the Taiwanese EPA as a follow-up action with regard to a study Anshun plant of China Petrochemical Development Corporation's (CPDC) in Tainan and is part of a wide-ranging investigation into polluting industries and abandoned factories. Taiwanese EPA has confirmed hat abandoned factories at five locations were seriously polluted by heavy metals, particularly mercury, pentachlorophenol and PCDD/F which had severely affected the soil and underground water in the surrounding areas.

Figure 4-12: South Taiwan Overview Map showing locations of former chlorine plants in Tai-nan and Kao-hsiung

The other four factories belong to Ho Cheng Metal Industrial Corporation in Kaohsiung County, Taiwan VCM Corporation in Kaohsiung city, Kaohsiung Ammonium Sulphate Company in Cianjhen and CPDC in Cianjhen. The mercury concentration in the soil at CPDC's Cianjhen plant site detected by Taiwanese EPA was 580 times greater than the limit[86].

4.2.4.1 Formosa Cianjhen Plant in Kaohsiung City (Chien-Chen site)

The Chien-Chen site consists of a former pesticide factory located in downtown Kaohsiung City, Taiwan. The plant was operated after the Castner-Kellner process using metallic mercury as a circulating bed electrode. Two sources of contamination were identified at the site - the plant itself as the primary source, and the construction material backfill and the soil as the secondary source.

Figure 4-13: Chien-Chen Site; location and side map of the former Formosa Chianjhen Plant in Kaosiung (source: Golder Assoc.)

The total area of the site is 20,000 m^2 and all industrial buildings at the site have been demolished. The major contaminant of concern (COC) is mercury. Investigators of the Taiwanese EPA stated that the mercury pollution there has made the soil shine. The report also revealed that the other factories had contaminated the surrounding area with copper, zinc, arsenic, and mercury, while the groundwater was contaminated by organic chlorine, and vinyl chloride. Houjin River, Love River, Cianjhen River, and Fongshan River all share the same upstream.

Figure 4-14: Panorama view of the former Formosa Chianjhen plant site in Kaosiung (industrial facilities demolished)

Most contaminated soils and backfill were excavated and currently stored on site. The average mercury concentration in soil is 500 mg/kg, but mercury can be present in its pure form in some of the excavated soil. The remediation objective negotiated with the local Environmental Agency is 5 mg/kg.

Table 4-5: Mass of mercury-contaminated soil at the Chien-Chen site as a function of concentration (source: Golder)

Hg-range [mg/kg]	< 20	21-100	101-260	261-400	401-1000	> 1000	Total
Mass [mt]	15,800	27,600	17,100	5,100	6,100	6,100	77,800

4.2.4.2 Anshun Plant Case in Tainan City

The Anshun (安順) chlorine-alkali electrolyses plant is located in the North West of Tainan City/Taiwan between the Lu-Er-Men Stream and the Chu-Fa-Gun Steam and was built by the Japanese company Kanegafuchi Soda in 1942. The plant used also the mercury cell process after Castner-Kellner and was taken over after WW II by the state-owned Taiwan Alkali Industrial Corporation (TAIC) in 1964. The required mercury was most probably delivered by the German allies, originally producing hydrochloric acid, caustic soda, liquid chlorine, but most probably also noxious gas for the Japanese navy.

The plant was taken over by the state-owned Taiwan Alkali Industrial Corporation (TAIC) in 1964. In 1969, a pentachlorophenol plant was added, and the entire plant remained in operation until1976. In 1982, TAIC merged with China Petrochemical Development Corporation (CPDC), which then was privatized in 1994, inheriting TAIC and all of its properties. On 19 March, 2004, Taiwan EPA declared the Anshun area (38.4 ha) a “contaminated soil remediation site”.

The plant was taken over by the state-owned Taiwan Alkali Industrial Corporation (TAIC) in 1964. In the year 1969 a Pentachloro-phenol plant was added to become Asia’s biggest producer of the pesticide dichlorodiphenyltrichloroethane (DDT). The company was requested by the Ministry of Economic Affairs to shut down in 1976. In 1982, it merged with China Petrochemical Development Corporation (CPDC), which then privatized in 1994, inheriting TAIC and all its property.

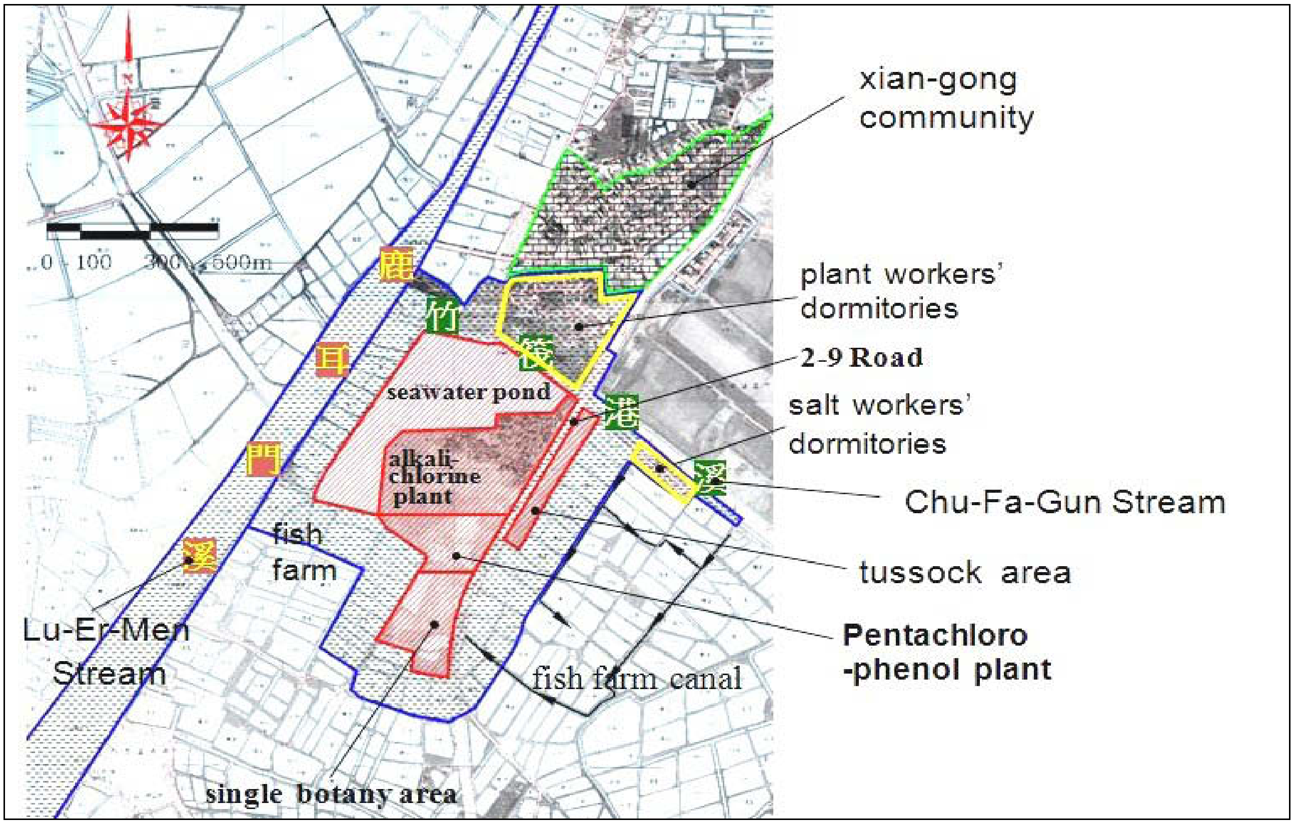


Figure 4-15: Site map of Anshun (安順) showing chlorine-alkali electrolyses and pentachloro-phenol plant (CPDC)

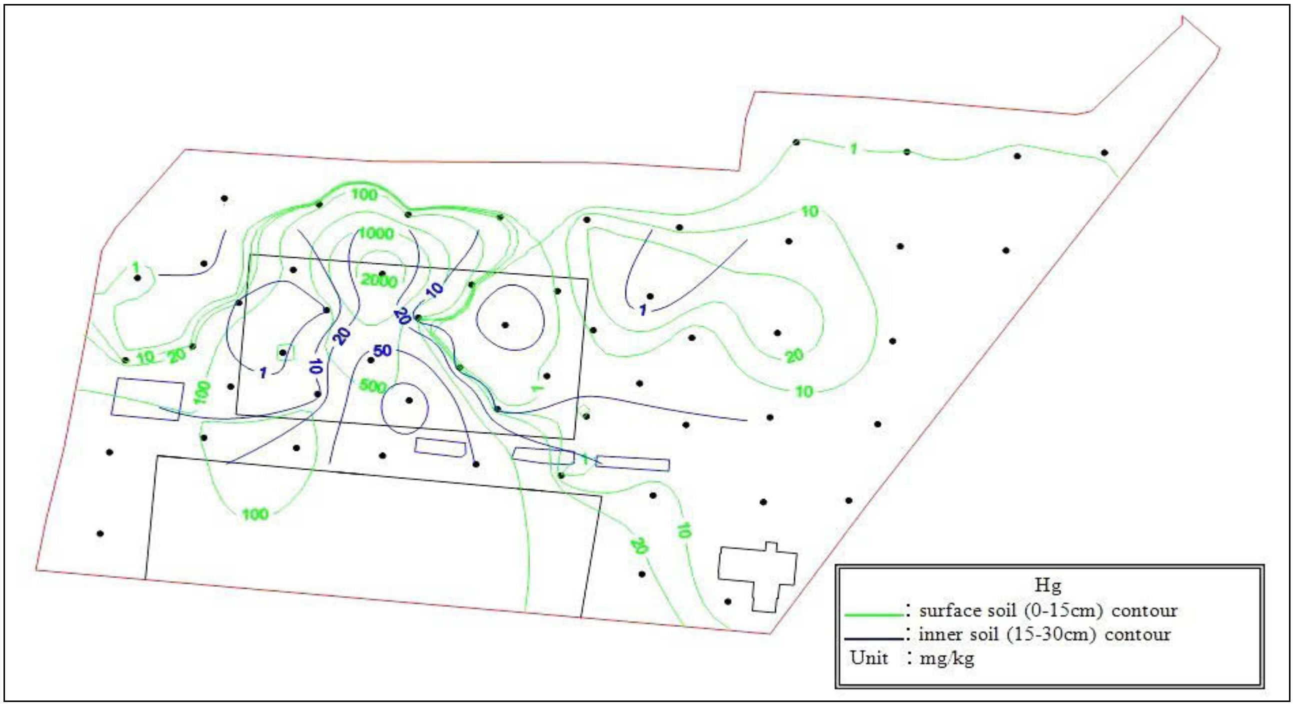


Figure 4-16: Mercury concentrations determined in the surface soil and inner soil in the surrounding of the former cell plant at Anshun (安順); source: China Petrochemical Development Corp. [CPDC]/ Montgomery Watson Harza [MWH]

On 19 March 2004 Taiwanese EPA declared the entire Anshun area (38.4 ha) a 'contaminated soil remediation site'. The highest concentration of mercury in the surface soil and inner soil at Anshun (安順) was determined close to the surface level at the location of the former cells and outside the gate, where maintenance work was performed. The highest single measurement of total mercury is in the range of 3,370 [mg/kg]:

Table 4-6: Anshun Site; highest contaminant concentrations in soil and sediments (Chao et al. 2008)

Contaminant	**Concentration in soil**	**Concentration in sediments**	**Soil control standard**
Mercury total	3,370 [mg/kg]	1,410 [mg/kg]	20 [mg/kg]
PCDD/F	64,100,000 [ng TEQ/kg]	6,560 [ng TEQ/kg]	1,000 [ng TEQ/kg]
PCP	51,400 [mg/kg]	Not determined	Not determined

Mercury and dioxin concentrations overlapping in particular in the sediments of the sea water pond associated to the former cell plant (see App. B-1). The occurrence of two contradictory types of contamination in parallel currently creates difficulties in finding an adequate and capable overall treatment technology for both contaminants.

Since the Anshun site in Tainan and the Formosa Cianjhen Plant in Kaohsiung belongs to the same owner the author suggested a remediation conception considering the remediation requirements of both abandoned sites. In particular a physico-chemical pretreatment with a main emphasis on flotation was recommended for both sites because of economical reasons followed by an adequate, individual thermal treatment of the generated contaminant-enriched filter cake.

4.2.5 Chlorine-alkali electrolysis plants in Melbourne and Sidney/Australia

In Australia recently two chlorine plants in Yarraville/Melbourne and in Botany/Sidney became subject of necessary mercury remediation activities. Both plants were established originally by ICI Australia and owned in our days by ORICA.

In 1926, as a complement to the German dye syndicate IG Farben, the British 'Imperial Chemical Industries' was founded. The Australian daughter companies and local agents of the four founder companies Brunner, Mond & Co., Nobel Industries, United Alkali and British Dyestuffs Corporation[87] were united to Imperial Chemical Industries of Australia and New Zealand Ltd (ICIANZ) only two years later.

4.2.5.1 The chlorine-alkali electrolysis plant in Yarraville/Melbourne/Victoria

The first activities of the chemical industry in Victoria tracing back to the year 1874, when Orica as the oldest chemical company in Australia was established by Jones, Scott and Company. Orica started manufacturing at Deer Park near Yarraville/Victoria (today Melbourne) under the name Australian Explosives and Chemical Co. Ltd. and was sold in the mid of the 1920s to Nobel Industries as part of the merger forming Imperial Chemical Industries[88].

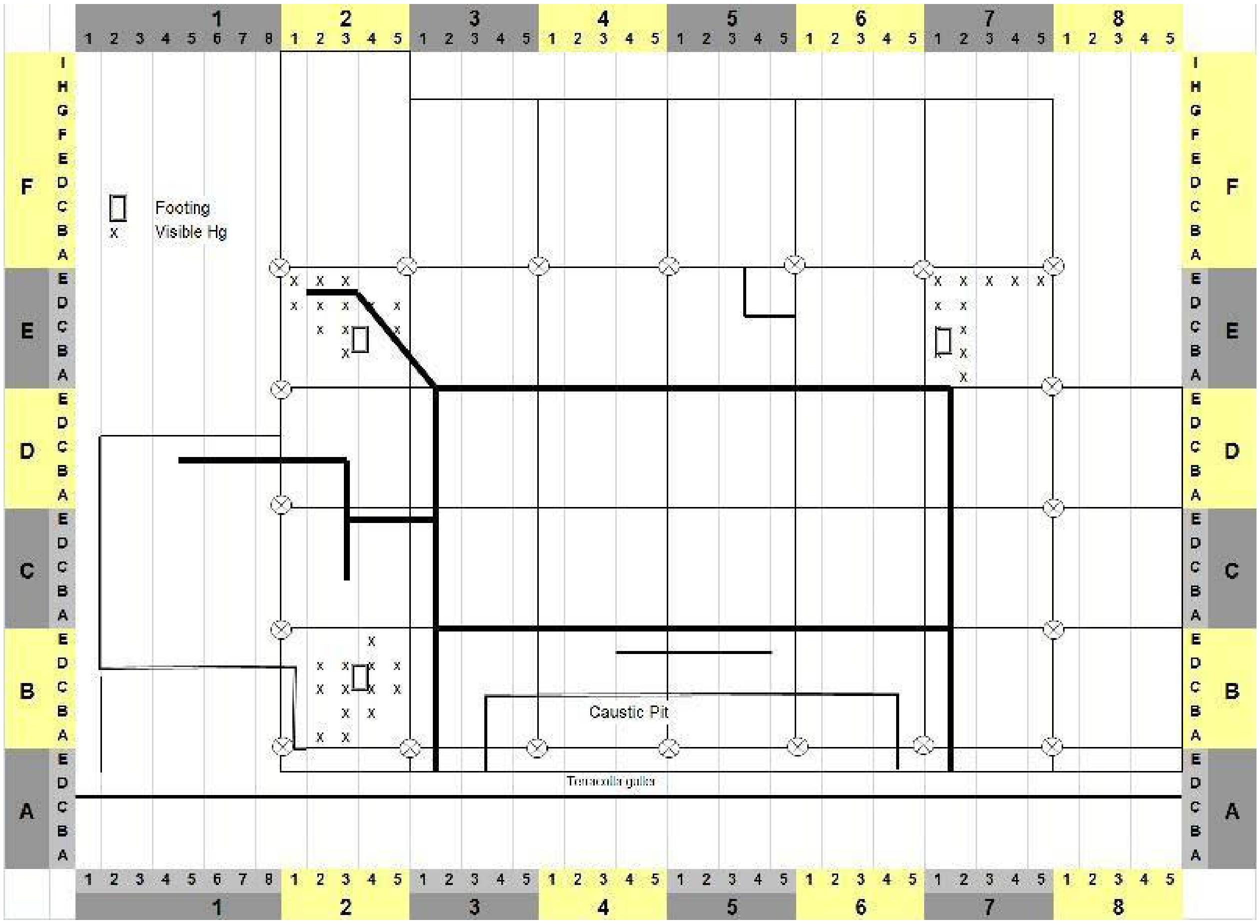


Figure 4-17: Schematic ground view of the Yarravile chlorine alkali electrolysis plant in Melbourne/Australia

Later also other chemicals were produced on this location and in the late 1920s ICI Australia commenced in Yarraville operation of a chlorine manufacturing plant in Yarraville/Victoria benefitting from the practical experience gained with the Caster-Kellner Process in Runcorn/UK. The Yarraville plant had been in operation for almost 80 years producing chlorine by the amalgam process.

Golder Associates (including the author) was commissioned in early 2006 to provide assistance in developing a strategy for the remediation of mercury impacted soil and construction materials associated with a former Chlor-Alkali Plant. Treatment technologies and remediation strategies assessed included[89]:

- Thermal (both batch and continuous) treatment
- Soil Washing (chemical leaching and water based washing)
- Immobilisation (chemical immobilisation)
- Direct disposal to landfill (and disposal with prior immobilisation)
- On-site encapsulation (after treatment)

The remediation option selected after the undertaking of pilot scale trials for soil washing and chemical immobilisation was encapsulation within a mono cell at an existing prescribed waste landfill.

In 2007 GGE Projects, the project delivery division of Golder Associates was appointed project manager and managing contractor involving the author as a consultant for the remediation works. The scope of works included completing the design of the remediation works, preparation of works packages, procurement of the works and supervision and administration of the works.

The environmental and civil engineering services provided by GGE projects for the project involved[91]:

- Demolition of existing mercury impacted concrete features and removal of infrastructure
- Remediation through excavation of mercury impacted soil to achieve the cleanup targets, validation testing program and Regulator liaison
- Program of environmental, health and safety management and monitoring
- Loading and transport of the mercury impacted materials to the encapsulation mono cell
- Backfilling and shaping of the excavation to design levels including cutting and filling of existing ground level surface to form a suitable subgrade surface
- Stormwater drainage system reinstatement

The results of the remediation planning (developed by involvement of the author) such as in particular the ‘Soil Remediation Technology Selection’ is attached to this thesis as App. D-1 showing a combination of soil washing and solidification/stabilization as the ultimate option.

Remediation works were completed on time and to budget, a total of 6,000 metric tons of mercury impacted soil were successfully remediated. The project was completed within 8 weeks

4.2.5.2 The chlorine-alkali electrolysis plant in Botany/Sidney

The Botany chemical complex was established by ICIANZ in 1940 just south of Sydney/New South Wales to become soon the centre of Australia's chemical industry making ICI the Australian market leader for polyethylene and PVC production for following two decades[90].

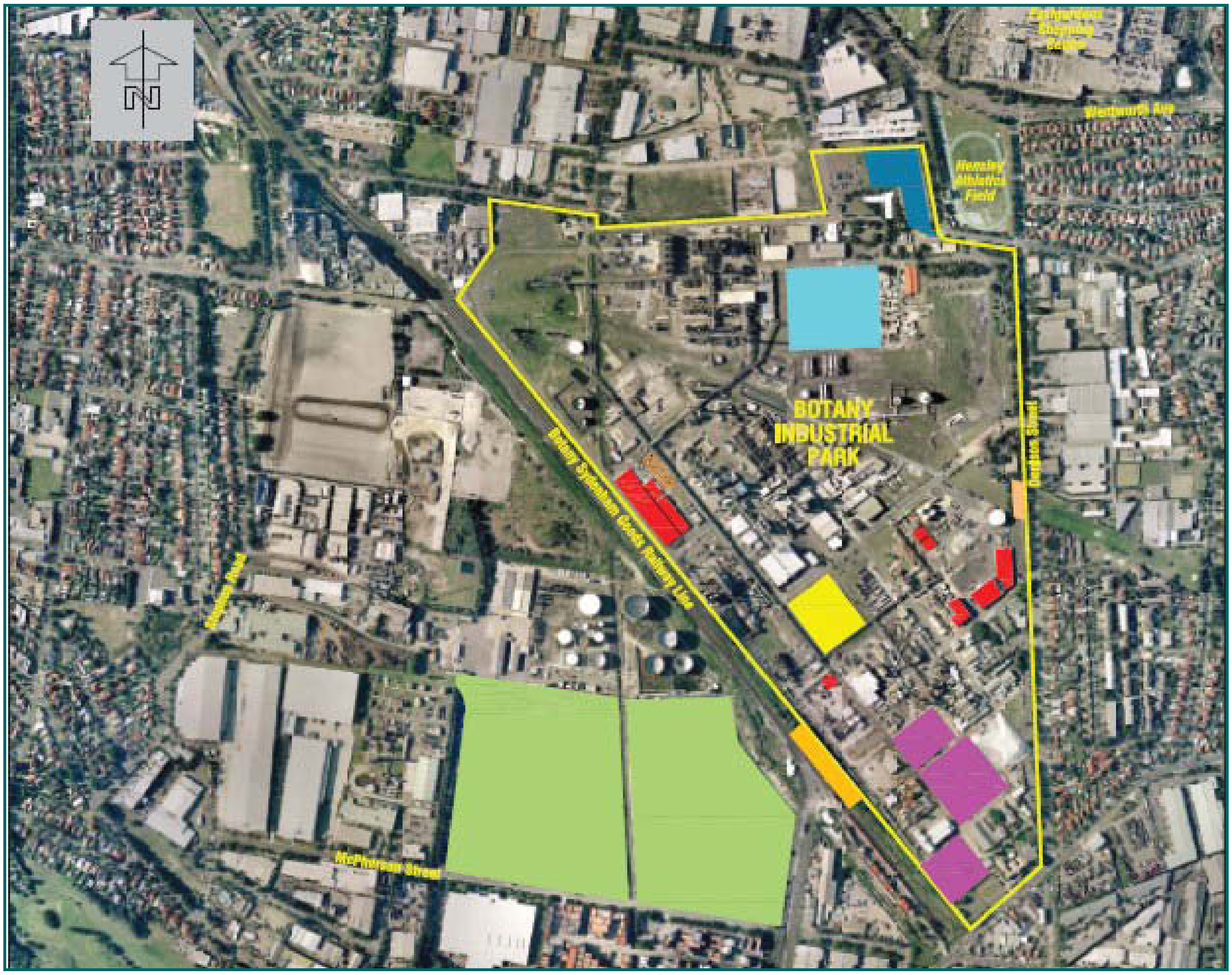


Figure 4-18: Side map of the Botany Industrial Park showing the FCAP locations in purple (source: Golder Associates)

In 1941 a mercury cell chlorine alkali-electrolysis plant to produce chlorine and caustic soda made from salt, shipped from Queensland, was commissioned at Botany. This chlor-alkali plant with a production capacity of about 81 000 metric tons of chlorine and 86 000 metric tons of caustic soda formed the basis for the progressive development of a broad range of chemicals.

The chlorine was used to manufacture chlorohydrocarbons (carbon tetrachloride, tri- and per-chloroethylene [tetrachloroethylene]) but also insecticides, herbicides and solvents, and after 1962 to produce PVC synthetic resin. The co-produced caustic soda by-product to chlorine was less valuable to ICI but, contributed to the chlor-alkali plant being a profit source and important business for Botany for several decades. In 1997 the mercury cell chlorine plant was finally closed down[91].

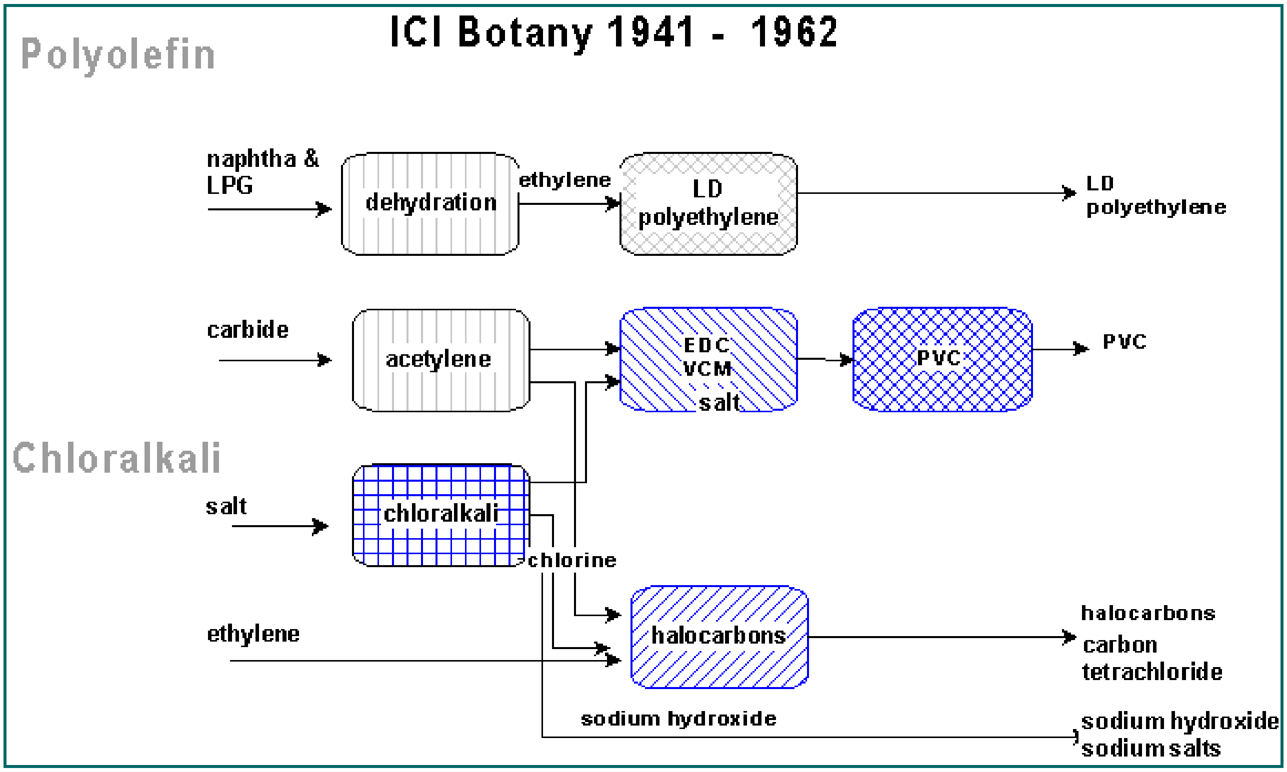


Figure 4-19: Schematic of the Botany chemical complex in the years from 1941 up to 1962 (source: Chemlink Pty Ltd)

The Australian Company Thiess Services was recently awarded a major mercury clean-up contract by Orica Australia. The project involves remediation of over 20,000 metric tons of concrete and soil contaminated by mercury at the site of Orica's former Chlorine alkali Plant at Botany. All excavation, sorting, separation and treatment (soil washing undertaken by Highlands Remediation – see also section 5.1.3) will be performed inside a ventilated enclosure over the entire work site, an area of 9,400m^2 which was completed in January 2011[92].

4.2.6 Olin Saltville Chlorine Plant in Western Smyth County/Virginia/USA

The Olin Saltville Site Project concerning the waste disposal ponds 5 and 6 was one of the first chlorine plant remediation projects in the US and is currently again subject of remediation activities.

The Olin Saltville Chlorine Plant in Western Smyth County/Virginia was developed and operated as a manufacturing facility over a period of 78 years from 1894 to 1972. Originally operated by the Mathieson Alkali Works until 1954, when Mathieson merged with Olin Corporation, the Olin Saltville Site was used for various chemical manufacturing operations. A soda ash plant was constructed in 1894 and began operations in 1895. Settling ponds were constructed to receive slurries and solid wastes from soda ash manufacturing by the Solvay process.

The first development of the area apparently started in 1918 with the construction of a cyanide plant for the government's war effort. Later, a "By Product" plant was constructed that included a cell room, boiler and engine rooms, an evaporator room and pot room. Plans, dated 1920 with revisions in 1925 and 1932, show relocation of the NFHR channel from the base of the limestone bluff on the south side of the river to an alignment adjacent to the FCPS.

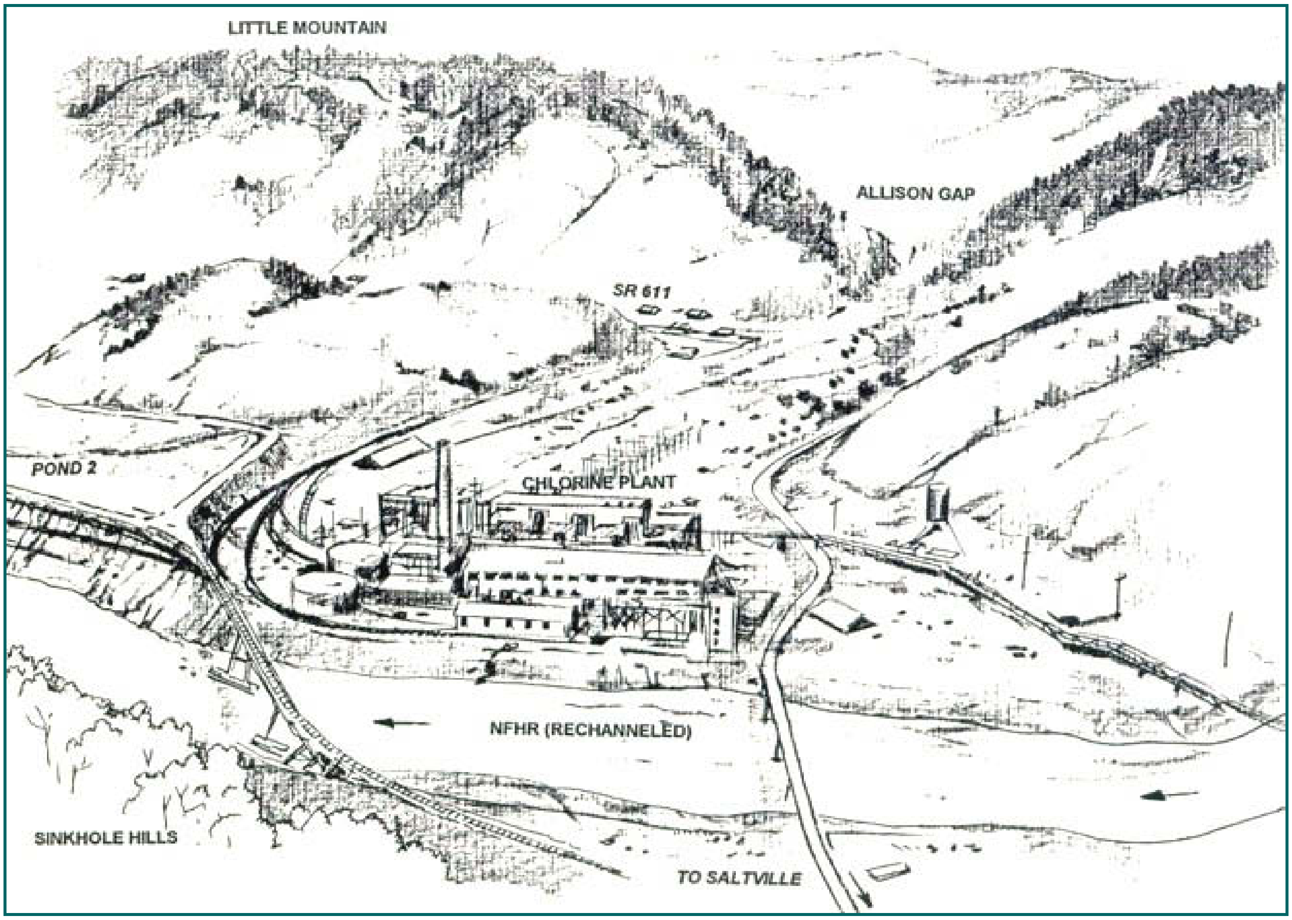


Figure 4-20: Mercury cell chlor-alkali plant constructed by Mathieson Chemical Corporation in 1950 (Source: Golder)

In 1950 Mathieson Chemical Corporation constructed a mercury cell chlor-alkali plant on the site of the "By-Product" plant (fig. 4-20). The chlorine plant was operated from 1950 to 1972. Olin shut down Saltville plant operations in 1972, and began demolition activities of the FCPS soon thereafter. Demolition of the process equipment was completed in June 1973.

Liquid mercury was drained from the equipment and shipped to Olin plants in Georgia and Alabama for re-use. The equipment was cleaned with wash water, which was allowed to percolate into the soils at the FCPS. Specific information regarding where the equipment was washed down does not exist, but the location was in the plant and now lies under the clay cover. The process equipment was then shipped to other sites for re-use or placed on the slope forming the easternmost end of Pond 6, along with building demolition debris, and covered with clean fill. Erosion control measures at the FCPS and riverbank stabilization measures along the NFHR and RBC were constructed in 1978-1979. The FCPS was re-graded, capped and site security measures installed as part of a remedial action completed in 1983-1984.

In June 1987 a Record of Decision (ROD) was issued for the Saltville Waste Disposal Site by the United States Environmental Protection Agency (EPA), which identified mercury as the contaminant of concern affecting mainly the near-by North Fork of the Holston River. Olin agreed to implement the ROD and entered into a Consent Decree with the EPA in September 1988. A contract was awarded to Golder Associates in order to conduct of a Remedial Investigation/Feasibility Study (RI/FS) concerning the Former Chlorine Plant Site and the associated Saltville Waste Disposal Ponds[93]. After the study was completed in February 1994 US EPA announced already in January a Proposed Remedial Action Plan[94].

On-site construction activities were performed between April 2001 and the end of the year 2002 basically including the capping the both waste disposal ponds (fig. 4-21).

Figure 4-21: Capping activities performed at Saltville Waste Disposal Ponds 5 and 6 in 2001/02 (source: Golder Assoc.)

Currently the selection of a cleanup plan for the abandoned chlorine alkali electrolysis plant site and the river is under progress[95].

4.3 ACETALDEHYDE FACTORIES

In acetaldehyde factories mercuric sulphate (Kucherov reaction), later also mercury oxide under the presence of sulphuric acid was used as a catalyst for the transformation of ethyne to acetaldehyde (ethanal).

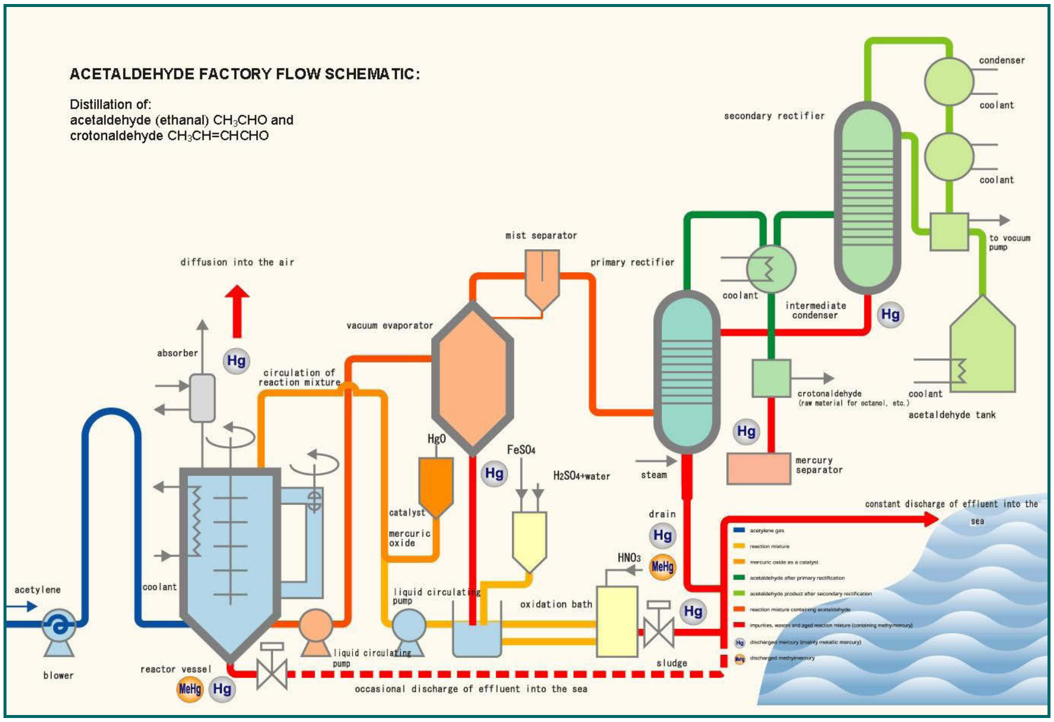


Figure 4-22: Schematic of an acetaldehyde factory (after: www.nimd.go.jp/archives/english/tenji/image/plant.gif)

Acetaldehyde factories became famous because of the already earlier mentioned Minamata disease, which was documented for the first time in the Japanese towns of Minamata and Nigata (see also section 3.3: Hazards and Toxicity of Mercury and its Compounds).

4.3.1 The acetaldehyde factory F44 Buna Schkopau (Germany)

The first pilot plant in Germany for the production of synthetic rubber (Zahlen-BuNa) was established in the "BuNa-Werke Schkopau" already in the second half of the year 1935. Since Sodium (Natrium) was produced in the following years by the already described Chlorine Alkali-Electrolysis Plants, the gas butadiene was produced in the ostensible 'four-step-process':

Ethyne (acetylene) => acetaldehyde (ethanal) => butylene glycol => butadiene

Acetaldehyde was produced in Schkopau in the acetaldehyde production Units F 44/F 44a by direct hydration, where mercuric sulfate was used as a catalyst for the transformation of ethyne to water and acetaldehyde. In the course of this reaction small quantities of elemental mercury but also methyl mercury $[CH_3Hg]^+$ were generated. Other unwanted mercury-containing by-products from the acetaldehyde generation process were contact acid regeneration sludge

The facilities were located along the F-road in grid square F-G/3-4 and were extended in length over several decades and reached finally an entire length of more than 200 m.

Table 4-7: Facilities associated to the acetaldehyde production plant F44 in Buna Schkopau

Building No.	Technical use/ generated products	Further description
F 44 and F 44a	Gas generator units, pressure gas scrubber and distillation of acetaldehyde	The main building was several times laterally extended; finally reaching an entire length of 200 m without any support for the increased longitudinal forces. The structure was classified as seriously collapse-endangered.
F 34	Distillation of acetaldehyde and crotonaldehyde	
F 34a and b	Storage tanks for acetaldehyde, crotonaldehyde and raw aldehyde	Concrete structure; building height 14 m
G 39 and G 39a	Contact acid regeneration and acid recovery	Concrete structure, diameter 5 m, height 15 m.
G 41	Mercury recovery	Bricks and concrete, building height 16.7 m

4.3.2 The carbide/acetaldehyde factory (ЗАВОДА «КАРБИД») in Temirtau/ Kazakhstan and the 'Nura River clean-up project'

The 'Karaganda Synthetic Rubber Factory' started operations in Temirtau (Karaganda Oblast/ Republic of Kazakhstan) in August 1950 and had a design capacity of 43,200 metric tons per year, expanded to 65,000 tons per year by 1964, and to 76,500 tons per year by 1975. The plant became the joint stock company 'AO Karbide' in the early 1990s. By 1995 output had been reduced to 36,000 metric tons per year due to a decrease of demand for acetaldehyde and equipment wear. Production at the acetaldehyde unit ceased in 1997, and in 1998 'AO Karbide' was split into three independent plants. The acetaldehyde unit was retained by state-owned 'AO Karbide'[96].

4.3.2.1 Description of the acetaldehyde process as a source of excessive pollution

The carbide factory (ЗАВОДА «КАРБИД») including the acetaldehyde plant in Temirtau was originally erected as a part of the Buna works in Monowitz and transferred as reparation of war after WW II by the armed forces of the Soviet Union to Temirtau. Whilst the Buna works in Ludwigshafen (1940-1942), the butadiene production was already designed for the application of the more efficient Reppe-process[xxii]:

Ethyne (acetylene) => butinediol => butylene glycol => butadiene,

the acetaldehyde factory in Buna IV (Monowitz) was still designed analogous to the above described Acetaldehyde factory F44 in Buna Schkopau using the above described less efficient "four-step-process", but having already an option to switch to the Reppe-process at a later stage[97].

Nevertheless the direct hydration of acetylene to acetaldehyde after transferring the plant to Temirtau was performed by the Kucherov process, which was implemented in four hydrator columns of about 17 meters height, filled with contact acid, which was a mixture of sulfuric acid, iron(III) and mercury(II) sulfate. Environmental pollution occurred due to metallic mercury generated during the acetaldehyde reaction which was transferred with the acetaldehyde through the entire process and gaseous mercury emissions to the atmosphere. Main wastes generated were waste water entered via the 'AO Karbide' waste water and contact acid regeneration sludge. Mercury sludge containing a settling of organic materials, the mercury salts and metal mercury were treated by dry distillation, and from 1976 onwards had been sent for mercury recovery to 'Nikitovski Mercury Combine', where also mercury ores from the nearby deposit where processed[98].

Waste water from the acetaldehyde process was released untreated directly to the Nura River and mercury-containing sludge was discharged till to the end of the 1960s directly into the Zhaur Swamp , a low-lying depression of 1 km^2 area close to the factory where waste sludge and wastewater with very high concentrations of mercury were disposed, resulting in an entire Hg content of 62 tons. Sludge filtration beds were established later. The sewage was then transferred into treatment tanks where it was chlorinated and silt from the bio-filters settled. The overflow was discharged to the main drain through an underground collecting channel, and from there into the Nura River[90].

[xxii] Walter Reppe (1892-1969), was one of the leading acetaldehyde chemists in the BASF main laboratory and member of the supervisory board, later also professor at the University of Mainz and at the TH Darmstadt.

Figure 4-23: Carbide and acetaldehyde factory in Temirtau, Kazakhstan (Source: Posch & Partner/Golder Associates)

The abandoned carbide and acetaldehyde factory in Temirtau included various highly mercury-contaminated building structures as shown in figs. 4-22, 4-23 and tab. 4.8.

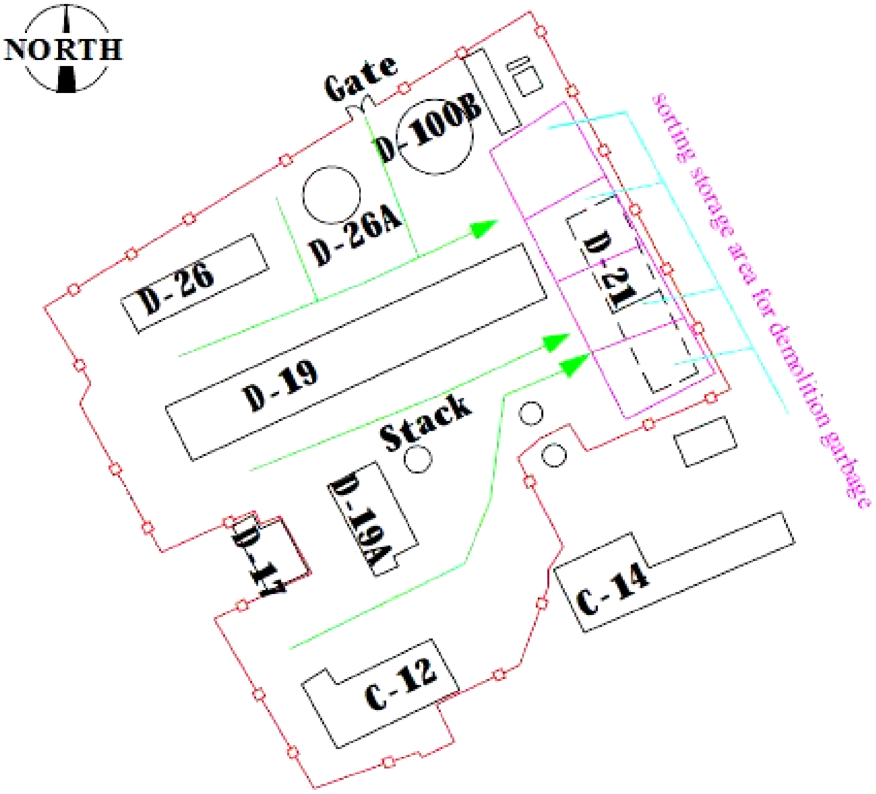


Figure 4-24: Ground plan of the Temirtau acetaldehyde factory demolition site

Most of the buildings of the former carbide factory in Temirtau are combined structures of either steel frameworks or reinforced concrete frames infilled with brick work nogging similar to the previously described buildings in Buna Schkopau and Bitterfeld. Fig. 4-23 above is showing the location of the acetaldehyde factory D 19 and the associated buildings as explained in greater detail in tab. 4-8 as follows:

Table 4-8: Facilities associated to the acetaldehyde production plant in Temirtau /Kazakhstan

Building No.	Technical use/ generated products	Further description
D 19	Acetaldehyde factory	Building height approx. 31 m; heavily contaminated with mercury
C 12	Distillation of acetaldehyde	Combined steel and concrete structure; building height 30.6 m
D 26	Storage tanks for acetaldehyde, crotonaldehyde and raw aldehyde	Concrete structure; building height 14 m
D 26 A	Mercury recovery/ sedimentation cell	Concrete structure, diameter 20m, height 6m, wall thickness 0.5 m
D 21	Contact acid regeneration	Main structure collapsed
D 19A	Contact acid recovery	Bricks and concrete, building height 16.7 m
D 100B	Cooling tower	Concrete structure, diameter 5 m, height 15 m.

4.3.2.2 Contamination of the Zhaur Swamp and the Nura River

In the years after the final shut-down of the acetaldehyde factory from 1997 up to 2004 numerous investigation programs were carried out in the course of the international project INCO Copernicus and by various companies such as BCEOM, Ramboll, Posch & Partner (P & P) and Kazgidromet. More than 8,300 samples were taken along the Nura River and ash analyses were performed accordingly[99].

The riverbed sediments (463,000 to 550,000 m^3) located in the 75 km stretch of the river between Temirtau and the Intumak Reservoir contain about 10 tons of mercury. About 4 tons of mercury are contained in the river embayment sediments (160,000 m^3), and about 2 tons of mercury are contained in oxbow lake sediments and floodplain soils (290,000 m^3)[100].

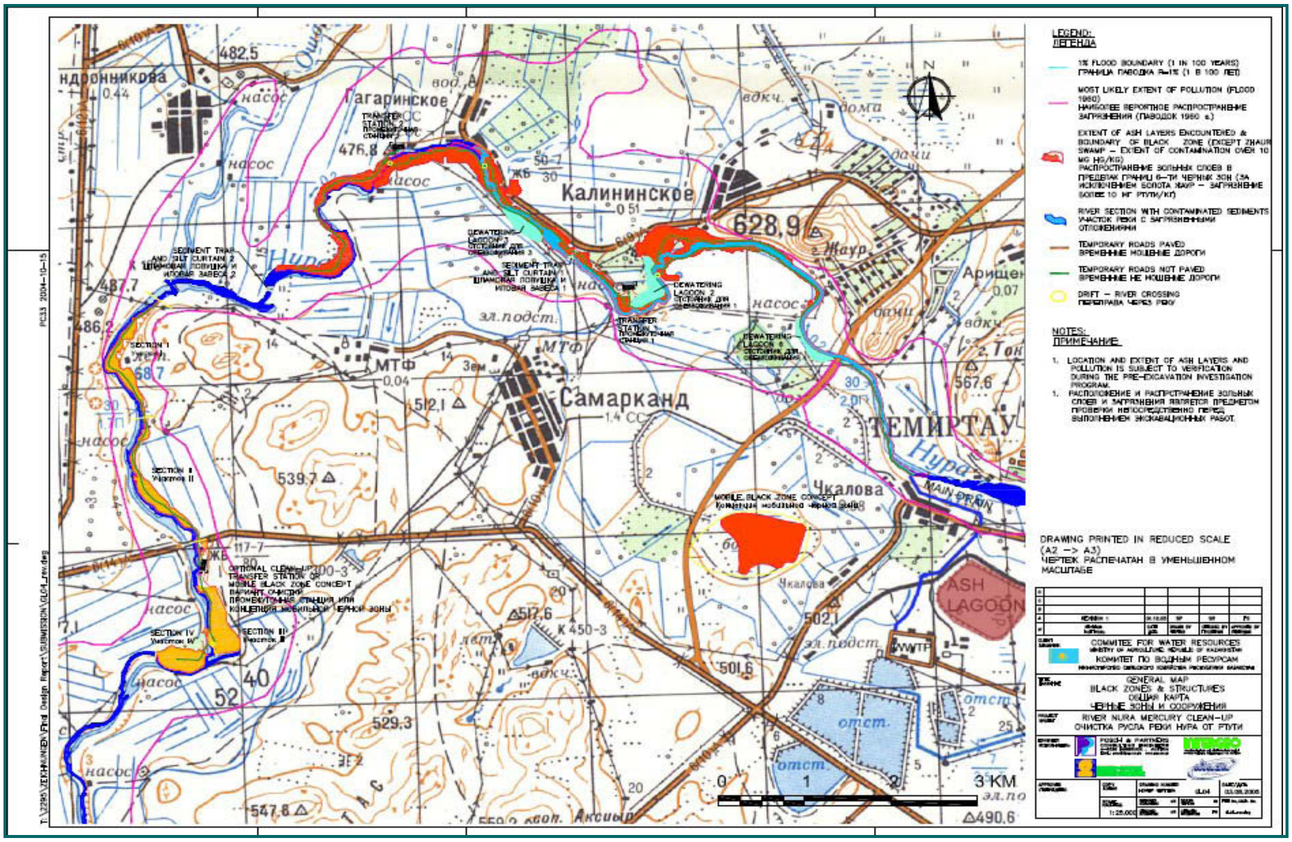


Figure 4-25: Nura river clean-up project overview map (Source: Posch & Partner)

Correspondingly the majority of the mercury-containing floodplain soil is located within the first 25 km stretch of the river downstream of Temirtau. It is estimated that there are about 53 tons of mercury in the floodplain soil, about 70% of which is located within the first 25 km downstream of Temirtau. Approximately 5.8 km^2 of the floodplain has mercury concentrations over 10 mg/kg, resulting in 880,000 m^3 of contaminated soils. Another 1,720,000 m^3 of silt deposited on the river bank is estimated to contain about 65 metric tons of mercury[101].

In 1942 also the first turbo-unit of power station KarGRES-1 was commissioned in Temirtau. High ash-containing power-generating coals (ash content up to 50%) and flotation wastes of Karaganda coal-cleaning factories were used as combustible in the power station, which had reached an entire power production of 271 000 kW already in 1950. In the following years up to the 1960s the capacity could be tripled. Until 1968 the power station discharged the fly ash to the Nura River at 1 km upstream wastewater outlet of the carbide factory. Until 1968 in total 6 million metric tons of fly ash was released directly to the Nura River[102].

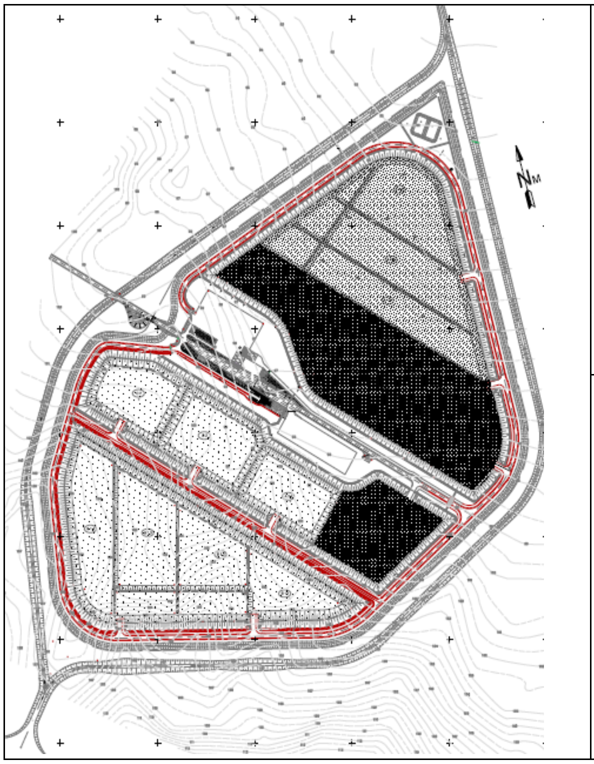
Consequently a large majority of the contamination in Temirtau is characterized by mercury adsorbed to the fly ash. Mercury-containing sludge had also been deposited throughout plant operations in the 'old' ash lagoon of the KarGES-1 thermal power plant, located on the banks of the Nura River. There were numerous failures in the KarGRES-1 lagoon, which lead to periodic uncontrolled discharges of power plant ash and mercury-containing sludge to the Nura River. The HPS 1 old ash fill contains another 32 tons of mercury[90].

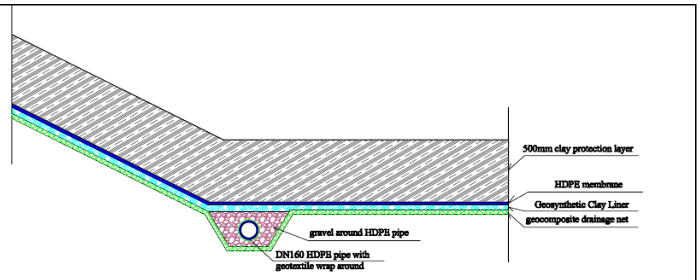
Since the threshold value for land utilization and re-use of soil in Kazakhstan (same as in Russia) is relatively low (Hg < 2.1 mg/kg) and the amount of mercury-contaminated soil/sediments and in particular ash is in the range of several million metric tons disposal in landfills was selected as the most economic and practicable technical solution.

4.3.2.3 Site remediation and the 'Nura River clean-up project'

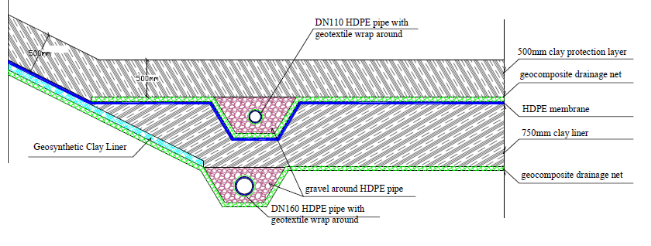
The 'Nura River clean-up project' initiated by the Republic of Kazakhstan and supported by the World Bank was planned for a time frame of four years and includes the following tasks[103]:

- Construction, commissioning and operation/disposal of secure hazardous waste landfills
- Remediation of the AO Karbide plant site including removal of Hg-contaminated soil and sludge and transportation to the landfills
- Clean-up of the river bed, the river banks and the flood plains of the Nura River and the highly contaminated Zhaur Swamp; excavation of the materials and transportation to the landfills





Cell type A1 for 10 [mg/kg] ≤ Hg ≤ 1500 [mg/kg]



Cell type A2 for 1500 [mg/kg] ≤ Hg ≤ 30000 [mg/kg]

Figure 4-26: Nura river clean-up project; landfill arrangement and cell design (Source: Posch & Partner/Golder Assoc.)

In 2007 the project was started with Posch & Partner[xxiii] as project management company (PMC)/site consultant and contractors from China, in particular KitayStroy Ltd and CGC Overseas Construction Co. Ltd. In September 2008 the landfill in Apan were ready to be commissioned. The place was selected because of a naturally occurring clay layer in the underground.

The Temirtau Nura river clean-up project is the third project worldwide where a specific landfill was designed as a mono dump type for mercury-contaminated waste. Whilst for the demolition residues of the chlorine plants in Alexandria/Egypt and in Abu Dhabi/United Arab Emirates[xxiv] multi-layer asphalt dumps were constructed the Temirtau project sticks to a more or less conventional landfill design with HDPE liners, which is linked to the huge amount of waste to be disposed.

Basically 3 cells of the A1 type with one single HDPE liner were constructed in Apan. In cell A1.1 the contaminated materials from the Nura river and Zhaur swamp was going to be disposed and the cells A1.2 and A1.3 were designed for other mercury waste in a range of 10 [mg/kg] ≤ Hg ≤ 1,500 [mg/kg]. The cell A2.1 with two HDPE liners was reserved for highly contaminated wastes up to a mercury-concentration of 30,000 [mg/kg] such as in particular rubble from the acetaldehyde site.

One of the technical problems identified in the course of the project was the very poor compactibility of the mercury-contaminated power station ashes, which causes considerable problems in the landfills. See also section 5.2.4 of this thesis.

[xxiii] In the Temirtau project P & P is currently supported by personnel from Golder Associates Germany. The author procured this subcontract for Golder and was in charge as a home office consultant and project manager for this project till to his resignation as an Associate and Project Manager in Middle East in 2009.

[xxiv] The author was in charge as a site consultant for the construction of an asphalt-lined mono dump in Abu Dhabi and supervised in particular the civil works.

4.3.3 The Chemical Factory Marktredwitz (CFM)

Since the CFM was the first large-scale remediation case in Germany and the contamination profile is similar to the above described acetaldehyde factories, it should be mentioned here for the sake of completeness.

The Chemical factory in 'Markt Redwitz' in today's Government District Upper-Franconia was founded in 1788 by Wolfgang Caspar Fikentscher (1770-1837), a young pharmacist and native of Redwitz, educated in Nuremberg.

Although the CFM is known in our days as the first chemical company in Germany the town of 'Redwitz' belonged as a part of the 'Egerland' before 1816 to the 'Habsburg Austrian Territories', providing for Fikentscher a more economical access to necessary raw materials such as in particular mercury.

Figure 4-27: View of the Chemical Factory Marktredwitz in 1860 after an oil painting from a contemporary unknown artist (Marktredwitz, city archive)

At the beginning the 'Company W.C. Fikentscher' was running in 'Redwitz' a laboratory for supplying their own glass factory in the nearby located town Brand with chemicals. In his early years, still under the influence of the alchemists, Fikentscher tried to fabricate in his laboratory gold. After starting with the production of phosphorus, nitric acid, benzoic acid and various mercury compounds such as particularly red mercuric oxide [xxv] and synthetic cinnabar[xxvi] the company became within a few years a successful supplier for chemicals on the European and international market[104].

[xxv] Mercury(II) oxide HgO was generated by pyrolysis of mercury(II) nitrate at temperatures above 300 °C.

[xxvi] The first artificially manufactured cinnabar was prepared by Gottfried Christoph BEREIS (1730-1809) by converting ammonium sulfide $(NH_4)_2S$ into HgS. Bereis studied in Jena and later in Helmstedt, where he was Professor for physics, chemistry and medicine.

In August 1822, the celebrated poet and chief of the cabinet of ministers[xxvii] of the Grant-Duchy Saxe-Weimar-Eisenach Johann Wolfgang von Goethe (1749-1832) visited the chemical factory and the glass works in Brand and even performed some experiments in the associated laboratory.

In 1889 the CFM was purchased by the brothers Oskar Bruno and Curt Bernhard Tropitzsch. In the following years the company increased the fabrication of mercury-containing products was increased. In the year 1907 the Hg-containing seed stain 'Fusariol', which is a phenyl mercuric acetate ($C_6H_5HgOOCCH_3$) was invented and since 1912 successfully produced in the CFM.

After 1971 cases of occupational disease became public and control by the supervisory authority became more frequent. Nevertheless it took another one and a half decades till the chemical factory was finally shut down In July 1985 by the permitting authority 'Landratsamt Wunsiedel' because of serious environmental violation. In October 1989, an investigation committee was established by the Bavarian State Parliament in order to verify responsibilities and the reason for the excessive environmental pollution. The final report was published by the Bavarian state government in July 1990[105].

Immediately after the closure of the factory a contract for the clean-up of the CFM was awarded to the Kemmer-Harbauer Group Berlin (Kemmer GmbH/Harbauer GmbH & Co.KG)[xxviii], a specialized contractor for site remediation and waste treatment from. The first phase of remediation activities included the removal of stored chemicals and residues from operation followed by a systematic dismantling of production equipment and controlled demolition activities under heavy personal protection equipment.

The scope of work also included the construction of a specifically designed decontamination plant, which was established by Harbauer in 1992 outside of the city of Marktredwitz in Wölsau. The plant as a 'proto-type' included two major treatment steps, such as soil washing and thermal desorption and will be discussed in greater detail in one of the following sections[xxix].

[xxvii] The Privy Councilor von Goethe as the state minister of Saxe-Weimar-Eisenach was furthermore the highest-ranking mining official of his country and made the visit to Marktredwitz for professional reasons. Goethe was seeing himself as a natural scientist and estimated his 'Farbenlehre' as much more important than all his lyrics. Besides this he was the initiator of the first chair of chemistry in Germany at the University of Jena and understood the benefit of using scientific methods in the mining and chemical industry very early.

[xxviii] The Kemmer-Harbauer Group belonged at this time to the larger Philip Holzmann Group in Frankfurt/Main.

[xxix] The Marktredwitz plant was planned, mechanical completed and commissioned in 7 months only. The author was in charge as a Deputy Project Manager for the entire project and in particular as a Commissioning Manager for the thermal part of the plant.

5 LIMITATIONS AND CONCERNS REGARDING CURRENTLY USED STATE OF THE ART TREATMENT AND DISPOSAL TECHNOLOGIES FOR MERCURY-CONTAMINATED SOLID WASTES (SOIL)

The best demonstrated available 'ex-situ Environmental Restoration Technologies' for the treatment of metal-contaminated wastes are currently represented by the following 'state of the art' decontamination processes/treatment technologies:

- Physico-chemical treatment (soil washing and extraction/leaching processes)
- Stabilisation/solidification and immobilisation
- Thermal treatment processes such as thermal desorption (vacuum distillation)

Physico-chemical and thermal processes, but also ex-situ bioremediation are commonly used for the treatment of contaminated soils. In Germany about 40 % of such wastes are treated by physical/chemical processes in soil washing plants[106]. Biological methods are only relevant for bio-degradable material and not easily applicable for the treatment of 'high mercury waste'. The low acceptance threshold value for conventional biological remediation processes derives here from, as the biological procedures do not present a pollution reduction possibility. On the other hand the various mercury compounds may be cross-transformed by biological processes or may thus be accumulated in the biomass. These processes can be used for the separation or accumulation of mercury from contaminated soils and/or waters in a certain range of low mercury wastes and therefore is not subject of this thesis, same as some promising in-situ technologies[107] such as electro-reclamation[108], in-situ stabilization/solidification[109] and in-situ thermal desorption[110] currently discussed in the more recent literature.

From the above listed technologies/processes physico-chemical treatment such as particularly soil washing is currently not a widely-used treatment technology for the processing of high mercury waste and it is subject of this thesis with the intention to discuss options for reliability improvements concerning the treatment of such wastes, specifically by application of flotation techniques.

By comparing different standards of waste treatment equipments in different countries, it is necessary to consider the difference between 'soil (solid waste) treatment centers' such as established successfully in Austria, Germany and Switzerland but also in the United Arab Emirates[xxx] and 'site treatment facilities', in order to be shifted directly from one contaminated site to another such as practiced preferably in the USA. The technical term 'mobile plant' describes mainly the ability of easy dismantling in modules and is widely used even for plants on fixed locations. Some Asian industrial countries such as in particular Taiwan is currently lacking adequate treatment facilities, but also in Australia soil treatment plants are not available, but it is also very difficult to import such equipment. Besides this thermal treatment plants for mercury wastes are not easily permitable by the Australian Environmental Authorities.

Besides treatment as a preferable option in some desert countries such as in the United Arab Emirates and in Egypt the disposal in so-called 'mono dumps' was performed as a solution for discarding high mercury waste from the demolition and dismantling of abandoned chlorine-alkali facilities and should be mentioned for the sake of completeness as an economical alternative to underground waste disposal, in case of adequate treatment technologies as mentioned above are not available. An exception is the disposal of mercury wastes in conventional landfills as currently practiced in the 'Nura River' clean-up project in Temirtau/Kazakhstan.

[xxx] In the United Arab Emirates the ADNOC group of companies is operating a waste treatment center for hazardous wastes from the oil- and gas industry, currently managed by the author.

5.1 Physical-chemical treatment of high mercury wastes

At present soil washing pertaining to mercury is either applied as a leaching technology such as currently practiced in the United States or in combination of the above listed technologies, as it was performed for example in the Marktredwitz plant by combining physical-chemical treatment with thermal desorption (vacuum distillation), as discussed in greater detail later.

In the following the contemporary state of the art soil washing and leaching processes applied in Europe and the US/Canada will be reviewed, based on typical examples of currently existing or former plants or projects.

5.1.1 Soil washing in the Netherlands and Belgium

The origin of soil washing technology was in the Netherlands. Wet mechanical treatment was applied by 'Mosmans Mineral Tekniek bv' already in the early 1980s. It is remarkable, that 'Mosmans' and 'Jaartsveld Groen en Milieu bv' (JGM), as the pioneers of physico/chemical solid waste treatment used flotation as an essential part of their plant design already in the early beginning.

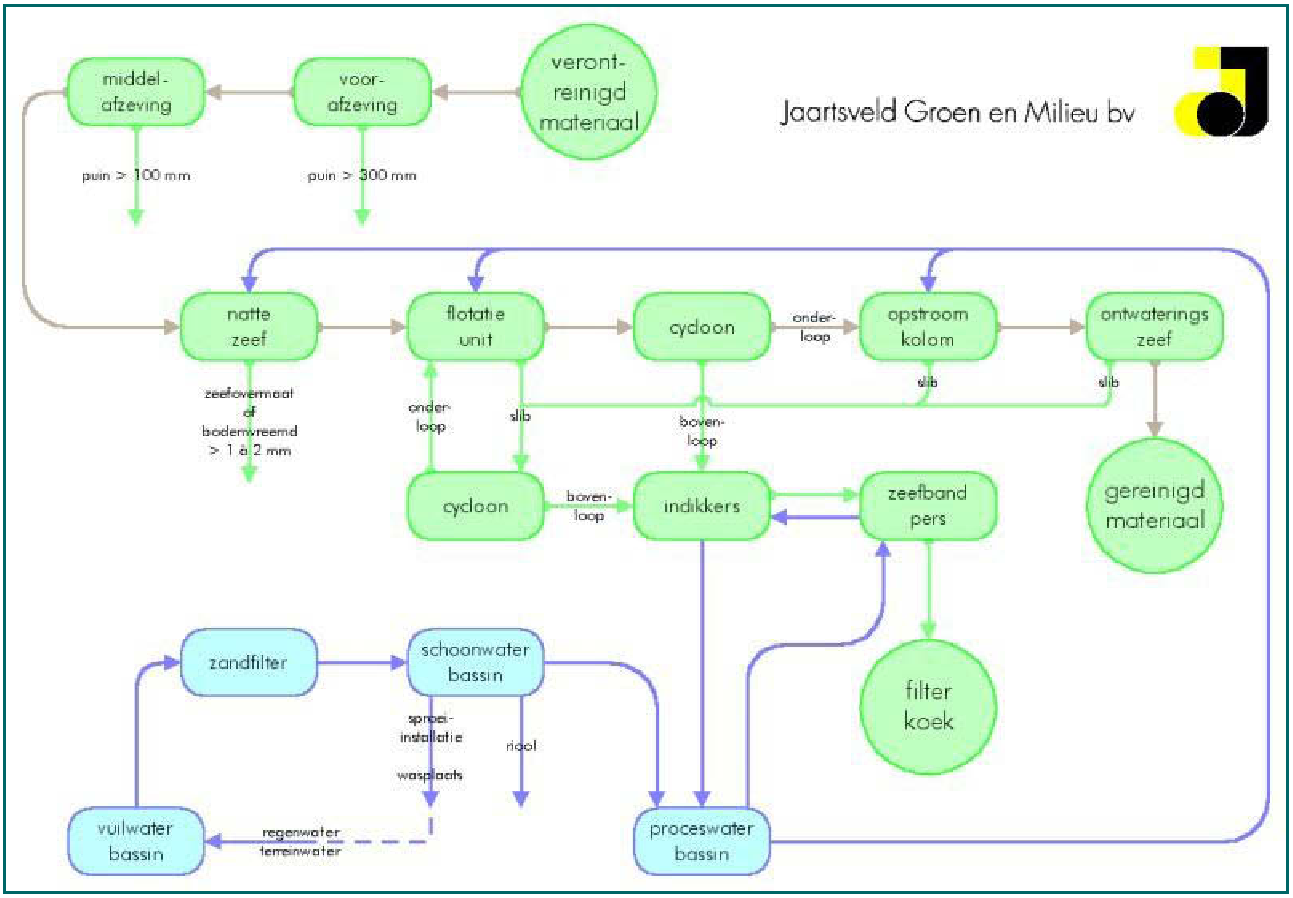


Figure 5-1: Process schematic of the Jaartsveld soil washing plant in Steenbergen/Netherlands (Source: JMB)

The JGM plant in Steenbergen/Netherlands was designed and commissioned by Metso Minerals and already equipped with a battery of 'Denver-type' D-R cells[111]. Fig. 5-1 shows that the underflow of the first hydro cyclone < 1mm (2 mm) was fed into the downstream flotation unit (flotatie unit). The effluent is undergoing another hydro cyclone treatment separating fine sand from froth. The tailings (slib) are sent to a downstream arranged mono sizer (opstroom kolom) before the treated material is finally dewatered (ontwaterings zeef).

The process water circuit of the plant as an overflow from the thickeners (indikkers) after flocculation is not undergoing any further water treatment using rainwater after sand bed filtration (zandfilter) for upgrading the process water quality. The design of the entire plant is simple but efficient and representative for the majority of soil treatment plants from the Netherlands and Belgium.

Other well-known soil washers from Belgium and the Netherlands are for example Aclagro, AWS, A&G Milieutechniek, Boscalis Dolman, De Bree, DEC, Heijmanns, Heidemij and Sita. Boscalis Dolman[112] is running next to facilities in Belgium also a soil washing centre in Schiedam and on some other locations in the Netherlands. After cleaning successfully the Miami River in Florida just recently Boscalis Dolmans was awarded with another contract for the cleanup of the 'Lower Fox River' in Wisconsin/USA, which is currently one of the world's largest river sediment remediation projects[113].

Companies from the Netherlands and Belgium were also able to transfer their soil washing technology oversees such as Heidemij bv, established with ARCADIS Geraghty & Miller/USA the Alternate Remedial Technologies Inc. (ART) on the US American market[108].

DEC as the soil treatment branch of the world wide operation DEME[xxxi] group operates next to others in Brugge and Zolder one of the largest soil washing centers in Europe, called GRC Kallo in the harbor of Antwerp/Belgium using flotation as an essential part of their soil washing technology:

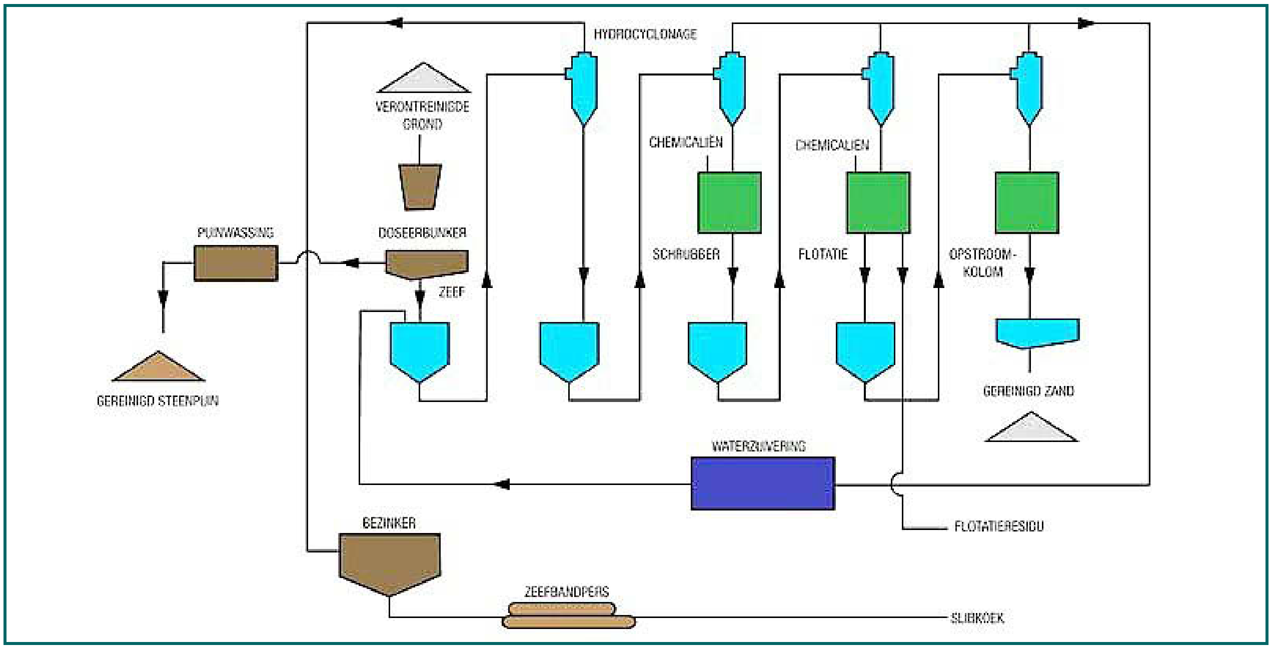


Figure 5-2: Process flow diagram of soil treatment center GRC Kallo, Antwerp/Belgium (Source: DEC)

One of the largest soil remediation projects in Europe currently is ongoing in the UK performed by the British branch of DEC. In order to treat nearly two million metric tons of contaminated soil in the course of the build-up for the 'London 2012 Olympic Games' five soil-washing plants were working on the location in parallel.

In a just recently given presentation, the business development manager of DEC UK mentioned as one of the future challenges in soil washing mercury from chloro-alkali plants[114]. This statement indicates clearly that currently even the worldwide operating Dutch and Belgian soil washing industry has no adequate treatment

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[xxxi] Dredging Environmental & Marine Engineering

technology for high mercury wastes from former chlorine alkali electrolysis facilities available.

5.1.2 Soil washing plants in Austria, Germany and Switzerland

In the first generation of wet mechanical soil washing plants applied in Austria, Germany and Switzerland the treatment was based on the physico/chemical principle only. The soil was liberated by mechanical energy input with the intention of shifting the contamination merely from the coarse fraction to the fines. The contaminant/soil separation was conducted by applying a sequence of classifying and separation processes.

This method of soil treatment with a high emphasis on the associated water treatment has been proven to be an appropriate treatment technology for other than mercury-contaminated soils for the period of more than 25 years.

In Austria presently only one full-fledged soil washing facility exists, operated by ABW [xxxii], formerly PORR Umwelttechnik, in the 11th city district of Vienna.

Figure 5-3: Bird’s view of the physico-chemical soil processing plant in the 11th city district of Vienna (Source: ABW)

The soil remediation process for this plant originally was designed by Miljøvern Umwelttechnik (MUT) in cooperation with Harbauer GmbH & Co. KG, Berlin, which was at this time the German market-leader in soil treatment technologies and plant operation, as a subsidiary company of the former construction contractor-group Philip Holzmann AG, Frankfurt/Main.

Initially the plant was established in March 1991 by PORR[xxxiii] for the Vienna Trade Promotion Fund in order to perform the remediation of the cyanide-contaminated soil and rubble of the ‘Chemical Factory Victor Alder’

[xxxii] Abbruch-, Boden- und Wasserreinigungsgesellschaft m.b.H. (Demolition, Soil and Water treatment Ltd.)

[xxxiii] PORR Ges.m.b.H was established as an affiliated company of Grün+Bilfinger, Maculan, Hinteregger and Kemmer/Harbauer)

in the so-called 'Alder-Gründe' in Vienna-Oberlaa. Over a period of many decades the synthetic pigment 'Prussian blue $Fe_7(CN)_{18} \cdot 14H_2O$' was manufactured on this location.

The soil washing process of the original plant was very much based on the chemical properties of Prussian blue. Because iron hexacyanoferrate is soluble in alkaline liquids, precipitation as Berlin white under acidic conditions by reaction with Iron(III) ions is possible[115]:

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 12OH^- \rightarrow 3Fe^{II}(CN)_6^{4-} + 4Fe(OH)_3 \downarrow ....pH8-12 \quad (5\text{-}5)$$

$$4Fe^{3+} + 3Fe^{II}(CN)_6^{4-} \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3 \downarrow .....pH3 \quad (5\text{-}6)$$

After the successfully performed remediation of the site in 1993 the plant was technically up-graded and established as a 'waste treatment centre' in order to receive solid waste and particularly contaminated soil and rubble from various waste generators from entire Austria. The investment for the complete ABW plant, including the temporary waste storage facility for approx. 10,000 m^3 and a bench scale test washing plant, was in a range of 10.9 million Euros. The permit for operation was provided by the magistrate department 22 of Vienna excluding soil and other solid wastes, contaminated with volatile chlorinated hydrocarbons and in particular with mercury[116].

Short time later Harbauer established based on the same design two other soil treatment facilities such as in Berlin-Britz (formerly Pintsch oil site) and in the Bavarian district town Marktredwitz for the remediation of the CFM, as the first large scale global mercury remediation project.

The world's first large-scale facility for the treatment of mercury containing solid wastes was also erected by the company Harbauer in Wölsau, outside the city centre of the Upper-Franconian district town Marktredwitz, for the remediation of the "Chemical Factory Marktredwitz" aka CFM. This abandoned chemical manufacturing facility was founded already in 1788 and was considered to be the oldest in Germany. Remediation of the plant comprised selective dismantling of the highly mercury-contaminated building structure, dismantling and packing of highly contaminated plant components and erection of a physico-chemical/thermal (distillative) soil and rubble cleaning plant.

Construction of the treatment plant started in mid-1992. Operation commenced in October 1993 including the first optimization phase. 50,000 metric tons of mercury-contaminated solid wastes were treated successfully between August 1993 and June 1996. Unfortunately the Marktredwitz plant is often misunderstood in the literature as a pilot-scale plant only[117]. The permitted facility design (see fig. 5-4) comprised as pre-treatment step for the entire sand and gravel fraction the Harbauer soil washing process, whereas at Marktredwitz solely attrition cells were used. Froth flotation was not part of the design.

The mercury enriched hydro cyclone overflow < 100 μm was dewatered in downstream arranged chamber filter presses and transferred via the filter cake storage bunker to the second main treatment step "vacuum distillation" performed by a three-stage thermal desorption rotary system, which will be described in greater detail later. Pertaining to the "Marktredwitz plant", the main emphasis of the entire waste treatment facility was on the thermal desorption part, not requiring any specific physico-chemical mercury separation devices in the in the soil washing section at this time, but making the plant from a present day's view unnecessarily expensive, since the investment for the entire plant was in a range of 42 million DM.

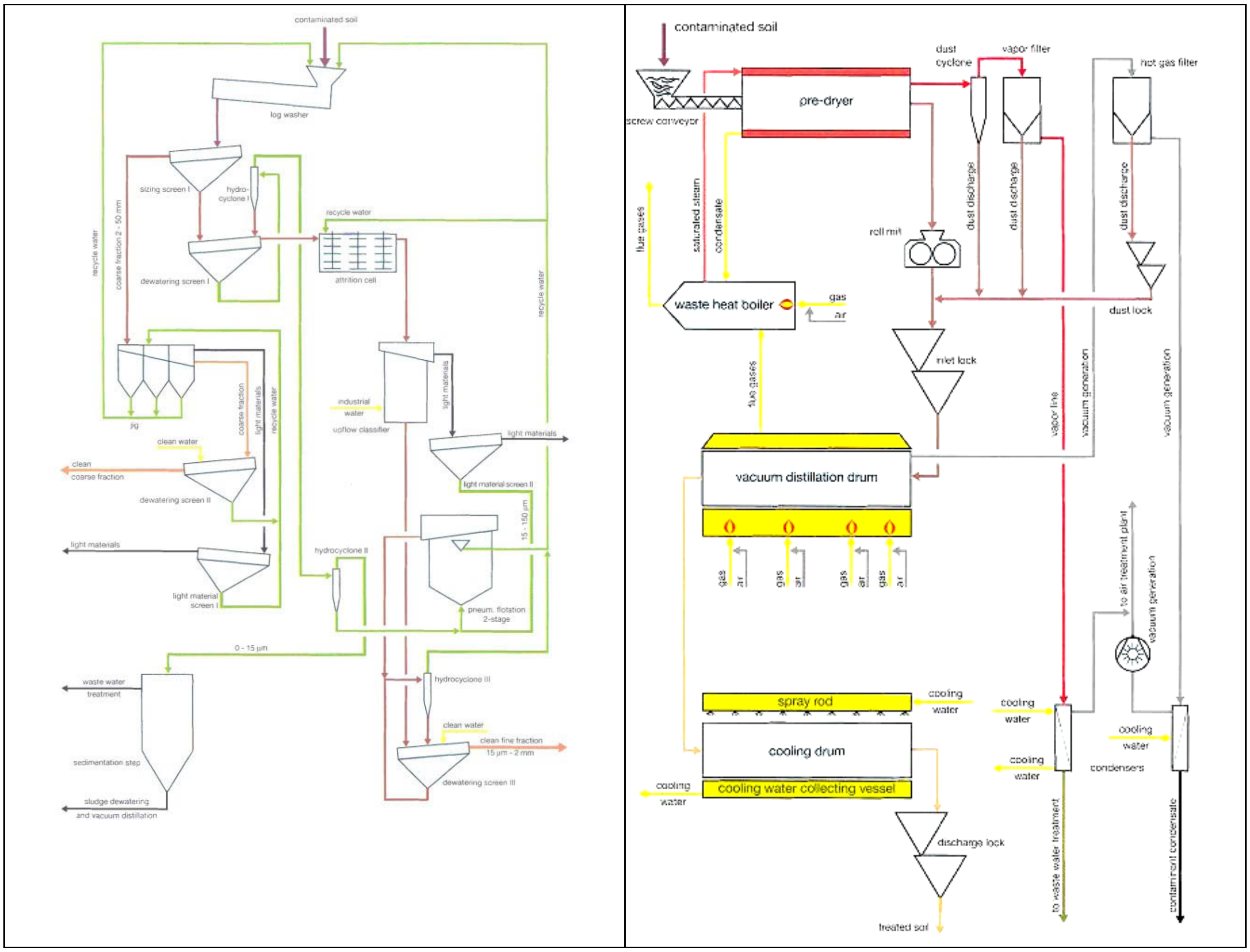

Figure 5-4: Flow diagram of the Marktredwitz treatment facility including soil washing and thermal desorption/vacuum distillation, 1992 – 96 (Harbauer GmbH & Co.KG)

Nevertheless the Marktredwitz plant, as a proto type was the first successful mercury remediation facility of its time and besides this also one of the largest soil treatment plant in the world and in some ways of a much higher technical level than many other solid waste and particularly mercury treatment plants today. In the official information brochure about the remediation case provided by the Supreme planning commission in the Bavarian ministry of inner affairs is mentioned by the authors SCHWEIGER AND WITTMANN[104], that the treatment plant as the first plant of its kind worldwide is the same pioneer work as the foundation of the Chemical Factory 205 years earlier.

One of the more focused plants for the treatment of highly metal-contaminated solid wastes is the physico-chemical soil washing plant 'Berlin-Gradestrasse', also erected and commissioned by Harbauer GmbH & Co. KG (now GBAV GmbH) in Berlin/Germany (fig. 5-5). The facility can treat organic and metal-contaminated excavated soil, demolition rubble and other mineral wastes. The throughput capacity is currently about 150,000 metric tons/year. The plant is completely encapsulated and equipped with an off-gas treatment system.

Upon delivery the material can be subjected to size reduction of oversized grains > 80 mm in a mobile single-toggle jaw crusher before being fed to the soil washing facility. This is particularly useful for the treatment of soils interspersed with scoria and contaminated brick and concrete rubble. The integration of an impact mill into the process facilitates further crushing where required[118]. According to the original design of the facility the wet mechanical disintegration of mineral wastes of all particle sizes takes place via two log washers arranged in series. Results from the use of a new, patented washing and sorting drum on a technical scale have been published just recently.

The disintegrated gravel and sand fraction is separated at 2 mm and 20 mm on a two-deck screening machine. The gravel sand fraction > 2 mm is detached from the contaminated low density material by a membrane jigging machine. Both material flows are drained on dewatering screens and discharged separately. For further treatment of the sand fraction < 2 mm several hydro cyclones with different diameters are available as an option. The hydro cyclone underflow (0.1 mm up to 2 mm) can be transferred to a coarse particle size flotation machine based on modified agitator cells arranged in series. After flotation the treated sand can subsequently be de-carbonised in a down-stream mono sizer.

The cyclone overflow sludge < 0.1 mm is further treated in a multi-stage hydro cyclone unit and subsequently treated in a two-state pneumatic flotation. The ultra-fine grains < 0.02 mm separated in the cyclone overflow are coagulated in a round coagulator by means of a relatively complex water purification process. Together with the contaminant concentrate of the flotation states this is dehydrated in chamber filter presses.

Highly contaminated soils from former tar and gas works and coking plants have been treated successfully in this soil washing plant. The soils and demolition rubble from these sites are highly contaminated with polycyclic aromatic hydrocarbons (PAH) and other organic contaminants.

Prior to the rearrangement of the soil washing plant Berlin-Gradestrasse (fig. 5-5) a pneumatic flotation (EKOF Freistrahlflotation) was already subject of the original design, same as in the ABW plant in Vienna. During operation it was identified, that pneumatic flotation cells are very sensitive regarding sand accumulation. Consequently the pneumatic flotation was run as a part of the water treatment circuit, only. After equipping the Gradestrasse plant with Denver type (impeller-supported) sub aeration cells the pneumatic flotation could be operated successfully as a cleaner unit for the effluent from the mechanical flotation.

Even before up-grading occurred, as per operating license the Gradestrasse plant was officially allowed to accept mercury-contaminated waste up to a limit of 3,700 mg/kg DW. After equipping the plant with mechanical cells for PAH treatment the plant was still lacking a ‘reliable separation process’ for the treatment of high mercury wastes. Owing to this, quicksilver as a contamination remained a treatment problem due to uncontrolled accumulation of mercury in various upstream equipments causing high risk operation and maintenance hazards.

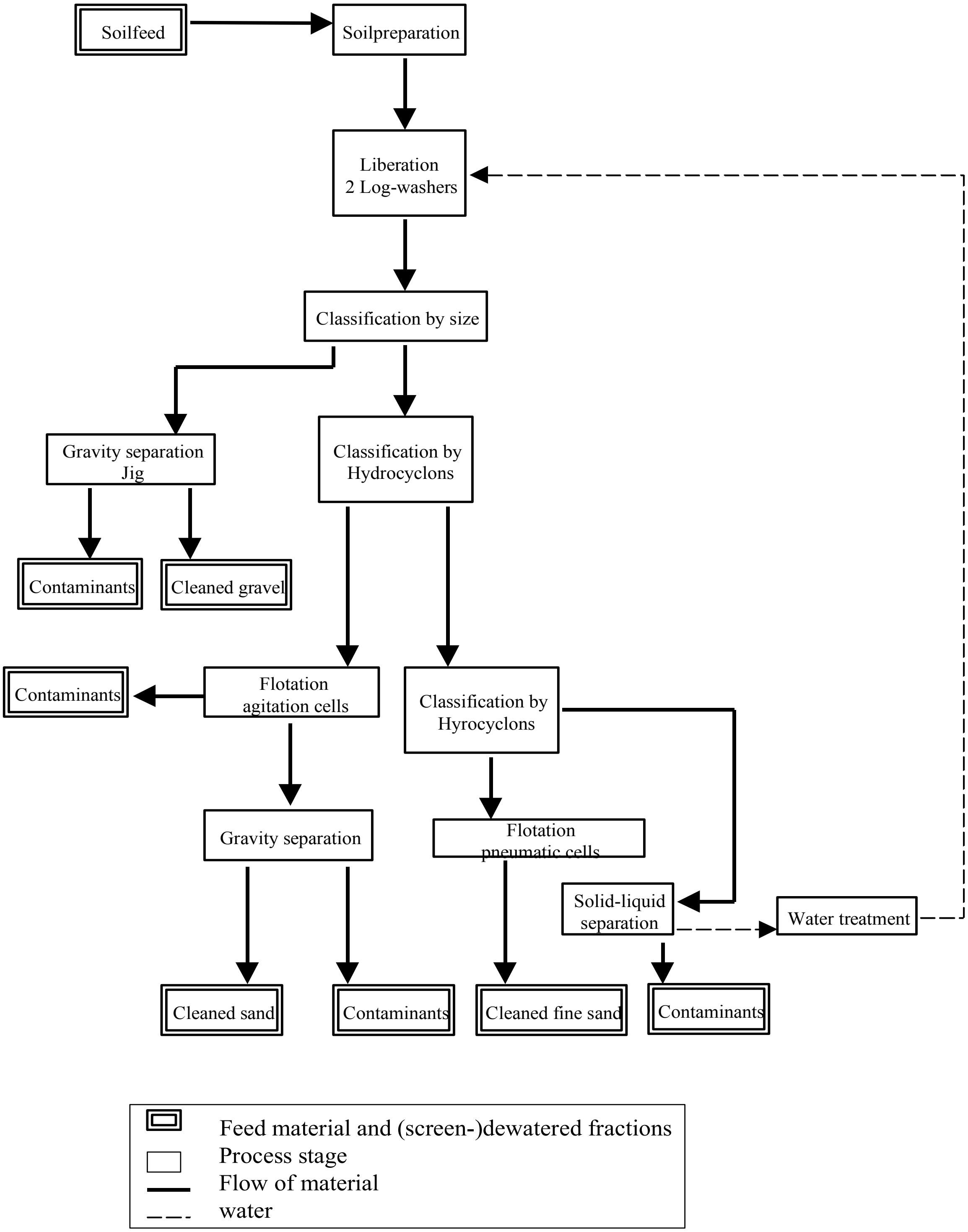

Figure 5-5: Flow diagram of the soil washing plant Berlin-Gradestrasse (System Harbauer) after the rearrangement in 1996 (planned and conducted by the author)

Compared to the technical level of the already described soil washing plants in the neighbour countries in Switzerland the soil and gravel washing plant Rümlang, called ESAR near Zürich-Klothen, operated by

Eberhardt Recycling AG shall be mentioned here. The plant was recently upgraded with two pneumatic flotation cells. ESAR works very close together with the thermal treatment plant in Herne, which was previously involved in the mercury remediation cases Alusuisse/Lonza (Waldshut/Tiengen) and Buna Schkopau (acetaldehyde factory F44).

5.1.3 Physico-chemical soil treatment in the USA and Canada

In the USA 77% of the National Priority List Superfund sites (50×10^6 m³ of soil), 72% of the contaminated sites of the Department of Defence sites and 55% of the industrial sites from the Department of Energy are metal-contaminated[119].

From a total number of 977 US EPA Source Control Treatment Projects, performed in the United States in the years between 1982 and 2005, considerable 18 % were treated by ex situ stabilization/solidification (fig. 5-6)[120], because in the USA and Canada soil washing is still not a widely accepted technology and has been synonymously described by US EPA as an acid leaching technology.

Therefore soil washing projects are amounting with 6 out of 966 lower than 1% and demonstrating that soil washing within the US compared to Europe is clearly underrepresented.

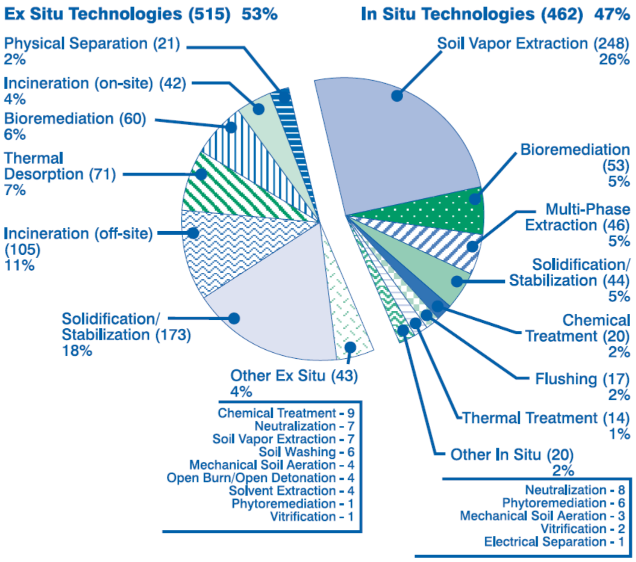

Figure 5-6: US EPA Source Control Treatment Projects between the years 1982 and 2005[117]

Fig. 5-7 presents a schematic of a bench-scale remediation process, including particle size classification and oxidative leaching, demonstrated by COGNIS Inc. of California on two different batches of highly mercury-contaminated soil[121, 122].

Alkaline leaching with regard to recovery of mercury was first introduced in the mining industry after WWI in the Canadian cobalt district[123], where low-grade amalgamation mills were operated for the separation of silver in particular by the McKinley-Darragh Mining Company and the Buffalo Mine since 1907[124].

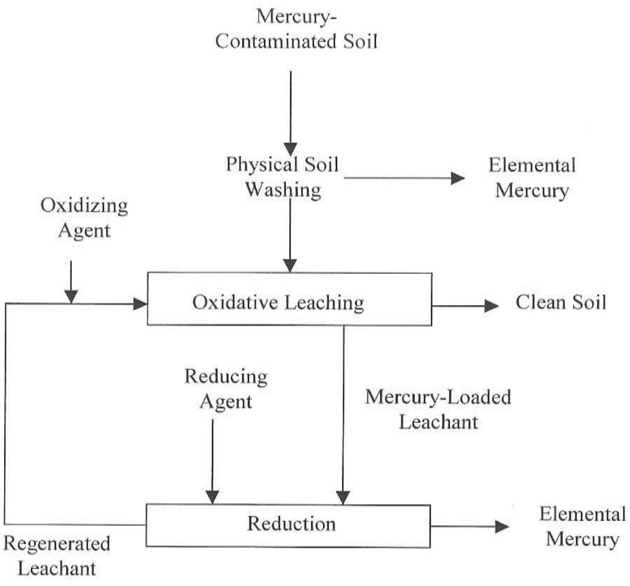

Figure 5-7: Typical US soil washing technology including particle size classification and oxidative leaching (source: COGNIS Inc.)[118, 119]

Using the property of mercuric sulfide to be soluble in an alkaline sodium sulfide solution consisting of sodium sulfide and sodium hydroxide[125], alkaline leaching was performed as follows:

$$HgS + S^{2+} \Leftrightarrow HgS_2^{2-} \qquad (5\text{-}1)$$

The occurrence of various mercury sulfide species in aquatic systems will be discussed in greater detail in section 6.3 of this thesis. The recovery of mercury from the generated sulfur mercuric ion HgS_2^{2-} as a leaching product as per equation (5-1) was usually performed with powdered metallic aluminum[120]:

$$3HgS_2^{2-} + 2Al^0 \rightarrow 3Hg^0 + 6S^{2-} \qquad (5\text{-}2)$$

The acidic leaching of cinnabar traces back to a patent granted to W. GLAESER in 1927[126] suggesting the use of hypochlorite ions as a solvent. Target was to transform the insoluble HgS into the soluble tetrachloro-complex $HgCl_4^{2-}$:

$$HgS + ClO^- + 2H^+ + 3Cl^- \rightarrow HgCl_4^{2-} + S + H_2O \qquad (5\text{-}3)$$

HgS also can be dissolved in Aqua Regis:

$$3HgS + 12Cl^- + 2H^+ \rightarrow 3HgCl_4^{2-} + 2NO + 3S + 4H_2O \qquad (5\text{-}4)$$

Another acidic leaching method also applicable to mercury-contaminated solids, was developed by the US Bureau of Mines and applied to low-grade manganese-silver ores from various US mining districts in a semi-pilot test plant using the dithionate anion ($S_2O_6^{2-}$)[127] derived from dithionic acid $H_2S_2O_6$ aka $[O_3SSO_3]^{2-}$.

As mentioned in section 5.1.1 of this thesis, the Dutch company Heidemij bv, established in close coorporation with ARCADIS Geraghty & Miller/USA the Alternate Remedial Technologies Inc. now ART Engineering, LLC in the United States, located in Tampa/Florida.

Figure 5-8: Soil washing plant for the King of Prussia (KOP) Superfund site in New Jersey (Source: Metso Minerals)

ART was applying for the first time in the US a full-fledged 'soil washing technology'[xxxiv] at an US Superfund site, which is known as the 'King of Prussia Superfund Site' (KOP), in Winslow/New Jersey.

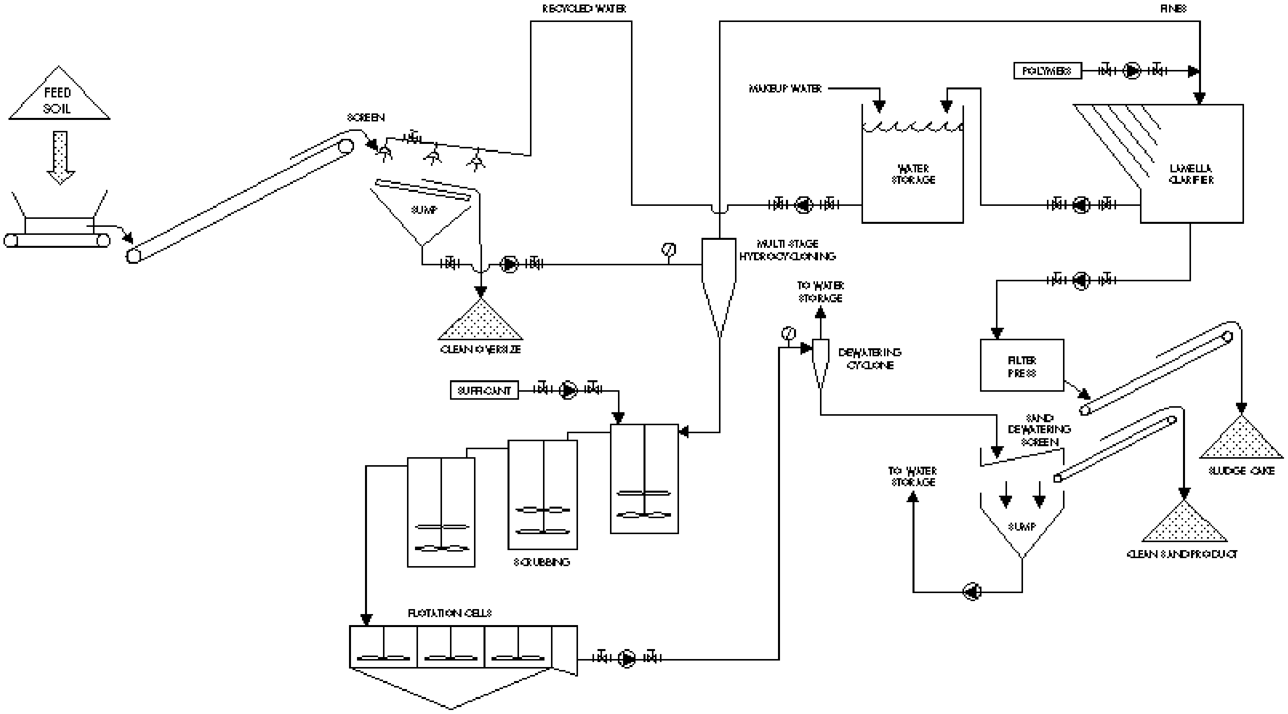

Figure 5-9: Process schematic of the ART (mobile) soil washing plant at King of Prussia Superfund site (US EPA)[125]

The soil found at the King of Prussia Technical Corporation Superfund Site in Winslow Township was mainly contaminated with heavy metals from a former waste recycling company such as chromium at 8,010 mg/kg, copper at 9,070 mg/kg, and mercury at 100 mg/kg (max. values found). Metal-containing sludge stored formerly in ponds showed in some points high concentrations of chromium at 11,300 mg/kg, copper at 16,300 mg/kg, lead at 389 mg/kg, and nickel at 11,100 mg/kg[128].

The plant as shown in fig. 5-9 is equipped with attrition cells and a mechanical froth flotation. Metal-contaminated fines from the hydro cyclone overflow and the froth product (not shown in fig. 5-9) are treated in a lamella clarifier. The sludge is leaving the plant as dewatered filter cake. After flotation the cleaned sand is dewatered on a vibrating screen. In less than four months (from end of June till to beginning of October 1993 almost 20,000 metric tons were successfully treated with the (mobile) soil washing plant at the site.

Since the concentration of mercury as an associated metal contaminant was relatively low in this remediation case, the above described mobile soil washing plant most probably is not straight away applicable for high mercury waste without the right chemical regime and some technical modifications required.

Another small but knowledgeable company, specialized in physico-chemical treatment of mercury-contaminated soil, is Highlands Remediation from Canada. Former experience gained in the Syracuse remediation project, New York (see fig. 5-10), the company currently is involved in projects in Australia, such

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[xxxiv] The design is tracing back to Metso Minerals providing a turnkey plant for this project[108], but also to the involvement of the current ART Vice President and Project Manager of KOP, Mr. Erik Groenendijk, a mining engineer (Technical University of Delft) and expert in mineral processing technology applied to waste treatment.

as in the chlorine plants in Yarraville (Melbourne)[xxxv] and in Botany (Sidney) as mentioned before in section 4.2.5 of this thesis.

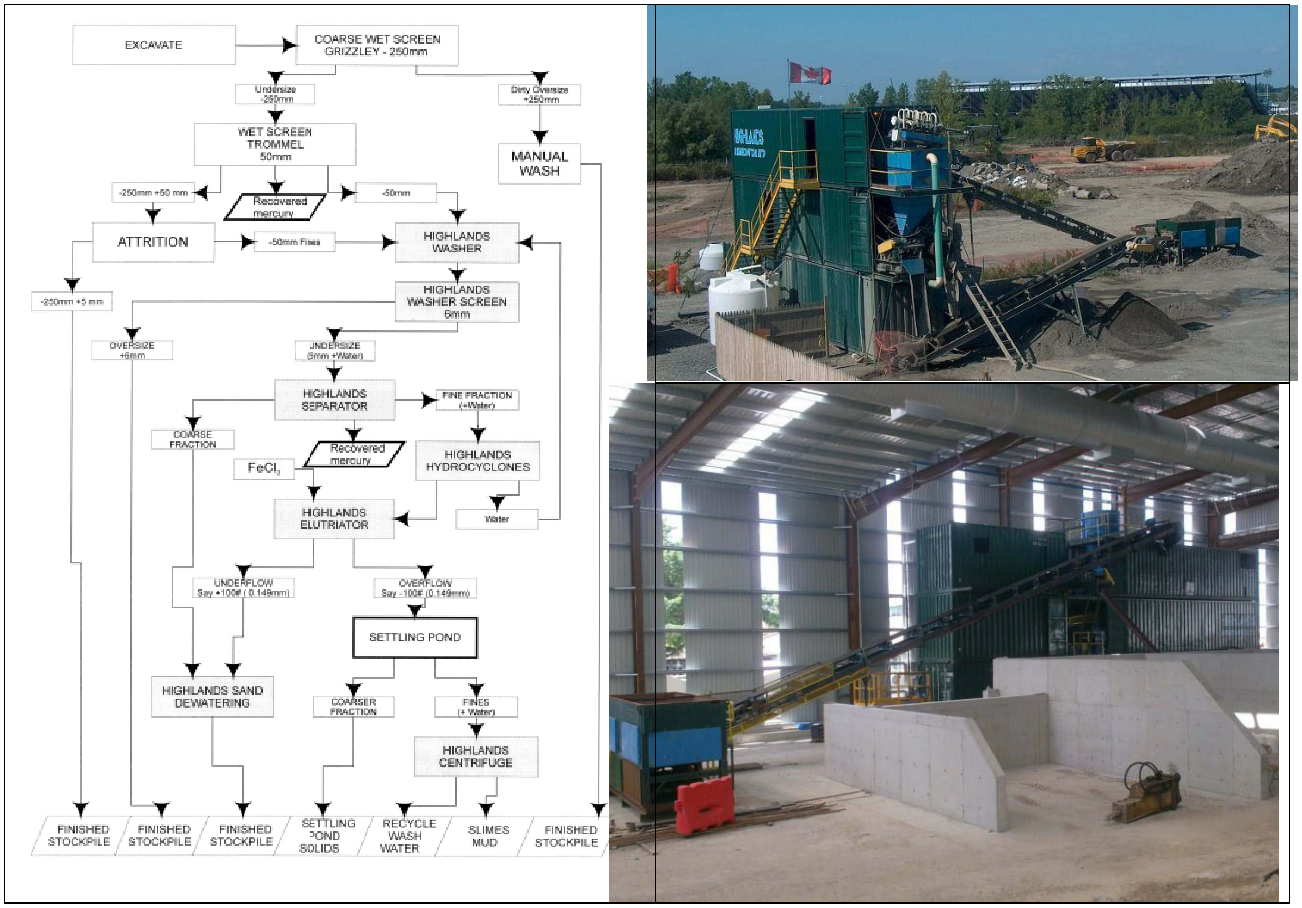

Figure 5-10: Mobile soil washing plants of Highlands Remediation in Syracuse/New York and in Botany (Source: courtesy of Highlands Remediation)

The plant of Highlands Remediation is equipped with attrition and a 'central device', called 'Highlands separator', which is understood as a kind of specifically designed upstream sorter with a strong affinity to a pneumatic flotation or a column flotation apparatus.

[xxxv] In Yarraville soil washing did not fully succeed as a main treatment technology because of various reasons (see fig. D1-1 and D1-2 in the Appendix)

5.2 Solidification and immobilization of mercury-containing wastes

Immobilization, solidification or encapsulation processes ex-situ pursues the objective to produce a stable storage product with the smallest possible leaching potential. Immobilization is a chemical fixation of soluble substances and their conversion into a less soluble compound, such as into a heavy metal hydroxides or heavy metal sulfides. Solidification on the other hand is the bonding of a substance to an encapsulating matrix.

Solidification/stabilisation in the USA is the most commonly used technology, even for wastes contaminated with mercury[129]. The method, with or without sulfidization, is using hydraulic binding agents such as cements or puzzolana is a common procedure most notably in the USA, where a US patent was granted on the subject of stabilization of mercury in mercury-containing materials to KACZUR ET AL. in 1982[130]. Stabilization of mercury-containing waste is subject to US Patent No. 4,844,815 (ADER ET AL., 1989) in order to reduce the amount of leachable mercury in the waste to environmentally acceptable levels[131]. The patented method uses elemental sulfur and cement kiln dust (CKD) in the presence of strong bases such as in particular caustic soda. Disadvantages of this method are also clearly stated in the patent. So the authors are concerned, that the large excess of sulfide in an alkaline environment will form the soluble mercuric sulfide complex HgS_2^{2-}.

Consequently stabilisation/solidification, as a treatment option, is considered by US EPA for low mercury wastes only ($Hg \leq 260$ mg/kg). As per Austrian landfill ordinance, in case mercury is present as hardly soluble sulfured compound and has been solidified, disposal is allowed up to a maximum of 3,000 mg/kg in dry matter. Whilst in Germany immobilisation including stabilisation/solidification is still not an accepted treatment technology for hazardous wastes and specifically not for mercury-contaminated soil.

However, the “German” landfill ordinance uses the terms “solidification” and “stabilization” and states that stabilization processes reduce the hazardousness of waste components and thus convert hazardous waste into non-hazardous waste. Solidification processes in terms of the landfill ordinance solely change the physical character of the waste (e.g. liquid to solid or compact) by means of using additives but does not influence the chemical properties. In Germany the disposal of stabilized waste formerly requiring special supervision on landfills of the categories I and II is only permitted if a “complete stabilization” can be proved, in which case the European Waste Code Numbers 190304 or 190306 or most commonly 190305 can be assigned to this waste[132].

Stabilizing procedures, in contrast, have to chemically modify hazardous substances in order to convert them into non-hazardous substances or to encapsulate them permanently and irreversible in a matrix. The conversion of soluble heavy metals into hardly soluble sulfides is a typical example for such a stabilization process. This may be done by sulfured heavy metal precipitation using sodium sulfide or comparable reagents. The proof of permanence or the complete stabilization have to be furnished by carrying out appropriate procedures such as an elution according to the pH_{stat}-procedure at pH 4 and pH 11 on the basis of directive EW 98p, No. 5. However, solidified and partly stabilized wastes are excluded from an assignment to landfill categories I and II unless they already complied with the respective assignment criteria previous to the treatment.

The immobilization (stabilization) by sulphidisation of heavy metals is mostly done with a sodium sulfide solution. By now, organosulfide compounds, such as trimercapto-s-triazine trisodium, which have hitherto only been used in water purification techniques, are used increasingly[133]. Several other mercury-binding agents on a sulfide basis are available on the market. The established complexes are often susceptible to pH-value fluctuations and oxidation. The 1,3-benzenediamidoethanethiol dianion ($BDET^{2-}$) is supposed to not exhibit these disadvantages. Experiments with this reagent have been conducted with mercury contaminated soil of a gas pipeline route of the Appalachian region[134].

In the German-speaking regions and particularly in Austria the solidification of wastes contaminated with heavy metals has been conducted using standard cement according to DIN EN 197-1, in order to immobilize waste as a pretreatment procedure ahead of the landfill[135].

5.2.1 Difficulties by using conventional Portland cement

The necessary sulphidisation of metals (metal contaminants), which not forming insoluble hydroxides (such as mercury and cadmium) in conjunction with common types of Portland cement has proven to be difficult. Particularly non-sulfate resistant cements with more than 3 mass-% tricalcium aluminate ($3CaO \cdot Al_2O_3$) tend to expand their volume aka. ‘sulfate blowing’ under certain circumstances. This effect has already been acknowledged during the concrete production at the end of the 19th century and has been ascribed to the mineral ‘ettringite’ $[Ca_6Al_2(0H)_{12}](S0_4)_3 \cdot 26\ H_20$[136], which was identified for the first time by Michaelis, who called it ‘Zement-Bazillus’ (cement bacillus)[137]. The composition of ettringite is described in technical terms of the cement technology often also as $C_3A \cdot 3CaSO_4 \cdot 32\ H_2O$[138].

Minerals of the calcium-aluminum-sulfate-hydrate-group such as ettringite, but also portland cement reaction products with iron sulphate ($FeSO_4$) such as Ca-Fe Ettringite: $9Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3 \cdot 26\ H_20$ and also Pharmacosiderite: $(K,Na)(Fe,Al)_4(AsO_4)_3(OH) \cdot 6\text{-}7H_20$, bind significantly high amounts of water in their lattice and thus enlarge their volume by many times, accordingly[139]. This leads to a mechanical destruction of the cement matrix[140].

Apart from the effect of sulfate blowing, the formation of a crystalline calcium-silicate-sulfate-hydrate named ‘thaumasite’ with an approximate structure $[CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O]$ also poses considerable problems[141]. While the forming of the mineral ettringite may be largely limited by using sulfate-resistant cement and avoiding the exposure of the cement-bond product to high ambient temperatures, the destruction by thaumasite nevertheless occurs as long as carbonate[142, 143] instead of aluminate is available. Recently it was observed on concrete, that thaumasite damages occurred on locations, where previously a ettringite attack had taken place[144]. The forming of thaumasite leads to a disintegration of the cement matrix, so that products already solidified on a concrete basis may again dissolve. Thus encapsulated metals may again be released, in the worst case even in a more soluble species. From this point of view the use of portland cement as a hydraulic binder for stabilization/ solidification deems not to be a capable solution.

Excluding the destruction of the immobilization wrapping by undesirable blowing or destructively working sulfate-hydroxide-mixed minerals, the effect of remobilization of already sulphidised, i.e. insoluble mineral mercury wastes, occurs when using conventional Portland cements and calciferous flue ashes. Mercury sulfide HgS may be conveyed into the soluble mercury(II)-oxide and as an intermediate stage the highly mobile sulfuric mercury hydroxide ion $[HgS(OH)_2]^{2-}$ my form. Solely kiln dust of the cement production showed good results during experiments[145]. This is most probably due to the higher alkaline content, as the transformation of Portland cement $Ca(OH)_2$ into gypsum leads to a higher pH-value in the pore fluid[146]:

$$Ca(OH)_2 + K_2SO_4 \rightarrow [CaSO_4 \cdot 2H_2O] + 2KOH \qquad (5\text{-}7)$$

This excessive alkaline microenvironment is mostly going in parallel to the unwelcome generation of soluble mercuric sulfide complexes

It is recommend to only use increasingly sulfate resistant cements, i.e. standard cement rich in granulated cinder or cement types rich in alkaline or kiln dust, when solidifying sulfidized mercury- and cadmium wastes. These need calcium hydroxide solely as stimulation for hydratization.

5.2.2 Solidification with magnesia binders

There is a possibility of increasing the sulphate compatibility by adding sodium silicate and/or Sorel[xxxvi] cement aka magnesia cement (magnesium oxychloride cement). The disadvantage of magnesia MgO, is that the catalyst magnesium chloride $MgCl_2$ remains to be existent soluble after the setting occured. By the sole use of magnesia binders the thus produced disposable material is consequently not long-time stable because of its poor water resistance.

$$\mathrm{MgO} + \mathrm{H_2O} + \mathrm{MgCl_2} \rightarrow \mathrm{Mg(OH)_2} + \mathrm{MgCl_2} \qquad (5\text{-}8)$$

The advantage over hydraulic binding agents is that by adding magnesia binder not ‘ettringite’, but only the far less problematic mineral ‘magaldrate’ $[Mg_{10}Al_5(OH)_{30}](S0_4)_2 \cdot H_20$ can be formed. Magaldrate became mainly known as a gastric acid binder in the medical practice.

In particular in Australia, where the import of soil washing plants is problematic and where the permitting of thermal treatment plants is difficult due to the legal situation, the solidification procedure with a subsequent landfilling, under compliance with to the TCLP-criteria, is an option for the treatment of mercury wastes. The author participated in projects in New South Wales and Victoria where solidification procedures were successfully conducted using appropriate binding agent on the basis of magnesium.

[xxxvi] Stanislas T. M. Sorel (1803-1871), French engineer of Polish descendent, father of hot-dip galvanizing and inventor of the Sorel cement

5.2.3 Systems Engineering for Immobilization and Solidification

Solidification plants are designed simply. The central component is the mixing machine, either constructed as plough or double shaft paddle mixer, that is operated continuously or in batches.

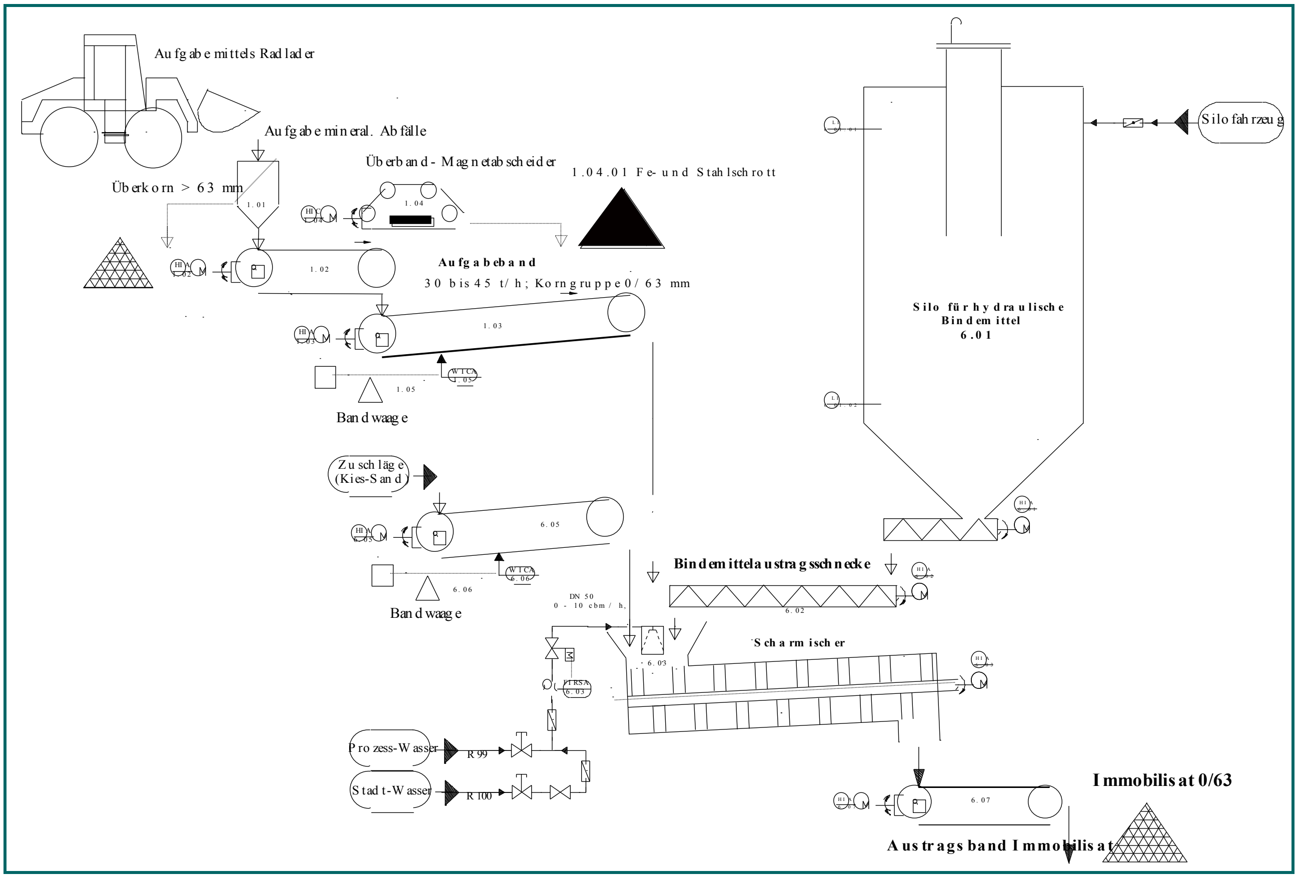

Figure 5-11: Process Flow Scheme of a conventional immobilization and solidification facility

The periphery consists of binding agent silos and conveyor belts or spiral conveyors with corresponding weighing cells. When hydraulic or pozzolanic binding agents are used, such as cements, fly ash or hydraulic lime, the ratio between water and binding agents is of importance for the leach stability of the stabilized waste. This is due to the fact that the water content defines the porosity of the hardened cement paste, as well-known from the cement technology.

Solidity testing methods are mostly borrowed from the concrete technology. Dispensing with concrete additives of early strength (such as sodium silicate) the generated leach stable product reaches is final solidity only after 28 days. Pressure tests and leaching tests, however, can already be carried out after 2 to 7 days. For a subsequent land filling yield strength of 5 N/mm^2 proved to be sufficient. Additionally it is of vital importance for the production of a stable disposable product that waste and supplements are at least rudimentary of one grain-size. Gag grading and too much water content, that would lead to unwanted cavities and porosity, increase the lixiviation behaviour and are thus to be strictly avoided.

The author is currently in charge as a plant manager for a hazardous waste treatment facility in the Emirate of Abu Dhabi. One of the treatment Units is a solidification/stabilization plant, where various low mercury wastes such as in particular Hg-contaminated catalysts are treated. The plant is designed similar to fig. 5-11, but the stabilized output is poured in cubic blocks to be used as a supporting and construction material in the associated landfills.

5.2.4 Solidification by pelletization (agglomeration)

Ultra-fine grained wastes such as filter dust or filter cake of band or chamber filter presses are not suitable for the above described solidification for the mentioned reasons. However, fly ash and filter dusts are sometimes suitable as a binding agent supplement for cements due to their pozzolanic properties.

Mercury has mostly been removed from the exhausts by a downstream countercurrent gas scrubbing in combination with activated carbon filters. However, newer technologies such as entrained-flow processes inject appropriate adsorbents in the upstream flow of the filter plants (bag filter), whereby, apart from the increased content of organic pollutants, the content of mercury in the accruing filter dusts increases considerably, particularly when sulfurized activated carbon is used[147].

Filter dusts from large combustion plants (coal-fired power plants) often exhibit elevated mercury concentrations and can be even in a range of 1,000 mg/kg[148]. Mercury as a coal utilization by-product (CUB) adsorbs onto fly ash following either the ‘model of Langmuir’ or the ‘model of Freundlich’[149]. A special case is for example the mercury from an acetaldehyde factory in Temirtau/Kazakhstan adsorbed on the power station fly ash in the previously described ‘Nura River clean-up project’, where the mercury-contamination occurred after the disposal in the river.

Pelletizing processes that agglomerate by means of pelletizing mixers or disks have proven successful for the solidification of ultra-fine grained, dust-like or paste-like wastes[150]. By forming seed crystals and by rolling on a rotating contact surface spherical aggregates with a high stability build up.

The advantage of the pelletizing procedure is the significant reduction of volume, the easer transportability of the pellets as bulk material and in particular the fact, that due to the lower water content less hazardous minerals are formed. However, the filter dust pellets are not long-term stable with regard to a subsequent landfilling and require a supplementary encapsulation by a multistep pelletization or by embedding pellets in a cement matrix.

Pelletization of various fly ashes from different incineration and combustion processes was already subject of a research project performed by the author in the year 1992. For wastes with a higher leachability a multi-step pelletizing process was developed.

This pelletization process in combination with a suitable sulphidisation agent also could be applicable in particular for the higher mercury-containing power station ashes from the Nura River clean-up project.

5.2.5 Other Immobilization and Solidification Methods

Apart from amalgamation procedures with tin or zinc dusts, that are neither of economic nor of technical significance, several other immobilization alternatives can be found on the basis of sulphidisation. The “Sulfur Polymer Stabilization” of the Brookhaven National Laboratory (BNL) appears to be particularly noteworthy. Hereby, mercury containing wastes are embedded in a mixture of so-called sulfur-polymer-cement, which consists of 95% elemental sulfur and successfully retains wastes with a mercury content of up to 5,570 mg/kg[151].

5.3 Thermal treatment of mercury-containing wastes

Thermal processes offer another possibility for the treatment of highly mercury-contaminated mineral wastes and also for a further treatment of concentrated output materials from other processes, such as sludge or filter cakes. Currently used thermal treatment as general technologies are:

- Thermal desorption/vacuum distillation,
- incineration/combustion and
- plasma based thermal treatment.

US EPA recommends for high mercury inorganic subcategory waste with a total mercury content greater than or equal to 260 mg/kg roasting/retorting (RMERC) and for high mercury-organic subcategory wastes incineration (IMERC). The only plasma plant ever was commissioned in Germany is the new GEKA plant in Munster, which was designed for destroying explosives and noxious weapons.

5.3.1 Thermal desorption

Roasting/ Retorting (RMERC) includes also thermal desorption and in particular vacuum distillation, which can also be operated as a stand-alone soil remediation/solid waste treatment process. The main advantages of using vacuum distillation technology are:

- Small flows of process gas,
- operation is poor on oxygen (restricting the generation of PCDD/F and the risk of explosion),
- leaks do not lead to an uncontrolled escape of process gas,
- comparatively low process temperature and, because of this, low energy consumption,
- high decontamination effect and
- the technology is less sensitive with regard to fines (depends very much on the filter type and design).

Disadvantages are the relatively low throughput and high treatment costs.

The technology of thermal desorption as a proven state of the art technology is based on the fact that contaminants are transferred into the gas phase for re-condensation/recovery, which makes the off-gas treatment the technically most demanding part of the plant. Particularly mercury, arsenic and cadmium indicate a good applicability for a thermal distillation process, which is more efficient under vacuum. The following table shows the boiling points of arsenic and the most common metals:

Table 5-1: Boiling points of the most common metals under atmospheric pressure

Metal (name)	**Boiling point [°C]** at 1013 mbar	**Metal (name)**	**Boiling point [°C]** at 1013 mbar
Mercury	356	Lead	1730
Arsenic	633	Copper	2320
Cadmium	767	Chromium	2400
Zinc	907	Nickel	2980

Specifically thermal desorption applied mostly as vacuum distillation plants, designed either as one or two step processes, is used in waste processing since more than twenty years. One of the more common applications is the processing of oil well drill cuttings and other spade-able slurries primarily from the oil and refinery industry all over the world (fig. 5-12).

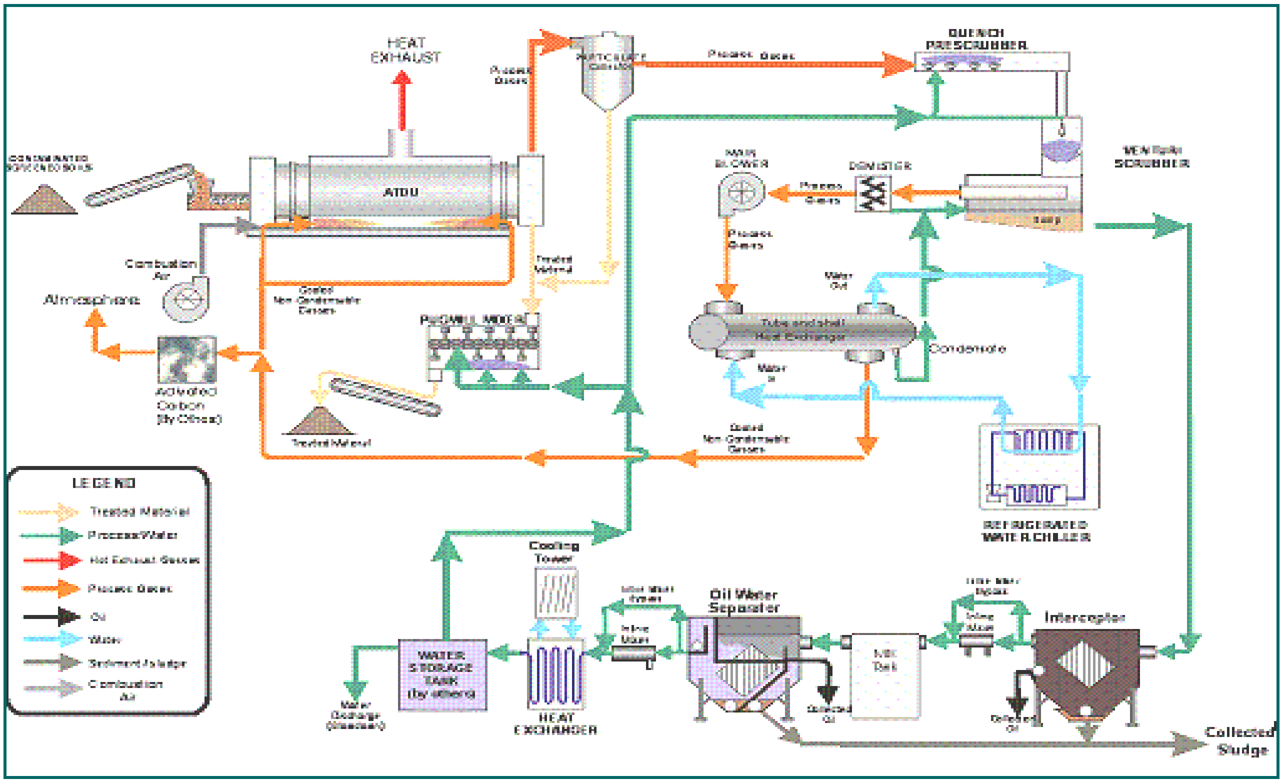

Figure 5-12: Thermal desorption as it is commonly used for the treatment of HC-containing wastes such as oil well drill cuttings; Source: RLC Ltd, USA

Thermal desorption is also applied for the treatment of organically-contaminated soils and for the contaminant-enriched output of fines (filter cake) from other treatment processes such as centrifugation or soil washing and applied for solid wastes containing a higher amount of fines, for which no other or more economic treatment or separation processes are technically available.

An alternative for the treatment of mercury-contaminated soil is the previously mentioned physico-chemical treatment (soil washing) as recently published by RICHTER, STAPELFELDT, FLACHBERGER AND ARAUJO, 2008[152]. One of the limiting factors of currently existing soil washing plants is actually the concentration of fines. Whilst in thermal desorption plants soils with a silt and clay concentration of 20 mass-% were found treatable without any problems. This was emphasized by CZETSCH, 2002[153,xxxvii] as the main difference between the two competing technologies.

For the sake of completeness it has to be mentioned, that the limitation regarding the amount of fines in soil washing plants is not so very much a technical, than more an economical restriction and so far as mercury is concerned, thermal desorption is almost unrestricted concerning the mercury concentration. Consequently thermal desorption is currently a most commonly used and widely accepted technology for the treatment of high mercury waste next to various disposal options. However the most obvious shortcoming is the high treatment

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[xxxvii] Czetsch, A: Managing Director of TechnoSan Umwelttechnik GmbH, lecture held at BayLfU conference Augsburg/Germany in 2002

price in combination with a low throughput rate and a lower technical availability compared to possible alternatives such as soil washing.

Vacuum distillation in order to decontaminate materials containing mercury was first applied in an industrial scale for the remediation of the already mentioned Chemical Factory Marktredwitz, using a three kiln system, where only the distiller and the cooling unit are operated under full vacuum conditions. In the vacuum distillation drum the waste material is heated up to a temperature of about 650 °C supported by a vacuum of 50 mbar generated by steam jet ejectors and water ring vacuum pumps. The mercury was converted into the gas phase and was re-condensed in a complicated system of quenches, mechanical mercury separators and gas scrubbers. 56,000 tons of mercury-contaminated solid wastes were treated successfully between August 1993 and June 1996 in this plant and 25 metric tons of mercury has been recovered.

Since the Marktredwitz plant was a 'proto type' (see Appendix F-1 and F-2), which was applied for the first time in an industrial scale various laboratory and bench scale tests with mercury-contaminated soil were performed before and during operation with the target of process optimization. The majority of these tests were executed in the Harbauer test plant stations, the so-called "Technikum" associated to the soil washing centre Berlin-Gradestrasse[xxxviii]. Also mercury-contaminated soil from the Buna works in Schkopau was tested in a bench scale thermal desorption plant. Tests carried out with material from the Buna works in Schkopau have shown that the product temperature is in a range between 86% and 88% compared to the skin temperature of the thermal desorption. The LAGA threshold value of Hg = 10 mg/kg could be reached only at a skin temperature of almost 650 °C and a residence time of 40 min at a vacuum of 50 mbar. Mercury enriched filter cake, as an output material of soil pre-treated in the Marktredwitz plant by soil washing reaches the 10 mg/kg already at a skin temperature of almost 440 °C and shows a steadier course of the distillation process. Results shown in Appendix E-1 were recently published by RICHTER AND SCHMIDT, 2011[154].

Based on the above mentioned bench scale tests in July 1996 an industrial scale test with soil and rubble from the Buna works chlorine plant site in Schkopau was successfully performed in the Marktredwitz plant reducing the mercury-contamination from more than 10,000 mg/kg to an acceptable level in a range close to 10 mg/kg. The results were not considered in the remediation planning of the Schkopau chlorine plant site for various reasons.

One of the more important issues with regard to proper design and operation of thermal desorption plants is the technical equipment for de-dusting the off-gas. Whilst in a treatment plant for oil well drill cuttings (fig. 5-12) a dust cyclone might be sufficient enough, most of the mercury waste thermal desorption plants are equipped with bag house filters. Since these filters ore operated under vacuum, excessive dust load and at temperatures in a range between 160 °C and 210 °C, high demands are made on these devices. Depending on the operation temperature of the distiller in particular clay minerals are subject of a more or less intensive thermal destruction which has an influence on the design dust load of the filters, accordingly. Also the cleaning cycle of the same is of high importance. Since the pulse jet cleaning system via Coanda nozzles is not working very well under vacuum conditions, especially large bag house filters should be cleaned preferably under atmospheric pressure. To withstand the temperatures mentioned above, mostly glass fibre coated with polytetraflouroethylene (PTFE) aka. Teflon[xxxix] is used as filter clothes for the bags. One of the essential disadvantages of this type of filters is the poor resistance against earth alkali metals, which is relevant for the soil treatment of abandoned chlorine alkali electrolysis plants, where sodium (Na) or potassium (K) is usually contained in such soils in considerable quantities.

Considering all this makes the filters an important key device adjudicating upon the entire process is either under control and well operational or not.

[xxxviii] The author was from 1994 up to 1997 Operations Manager and later Sr. Plant Manager of the soil washing centre Berlin-Gradestrasse and before Commissioning Manager of the Vacuum Distillation Unit in Marktredwitz

[xxxix] Teflon is a widely used brand name originally created by DuPont when PTFE was invented in 1938.

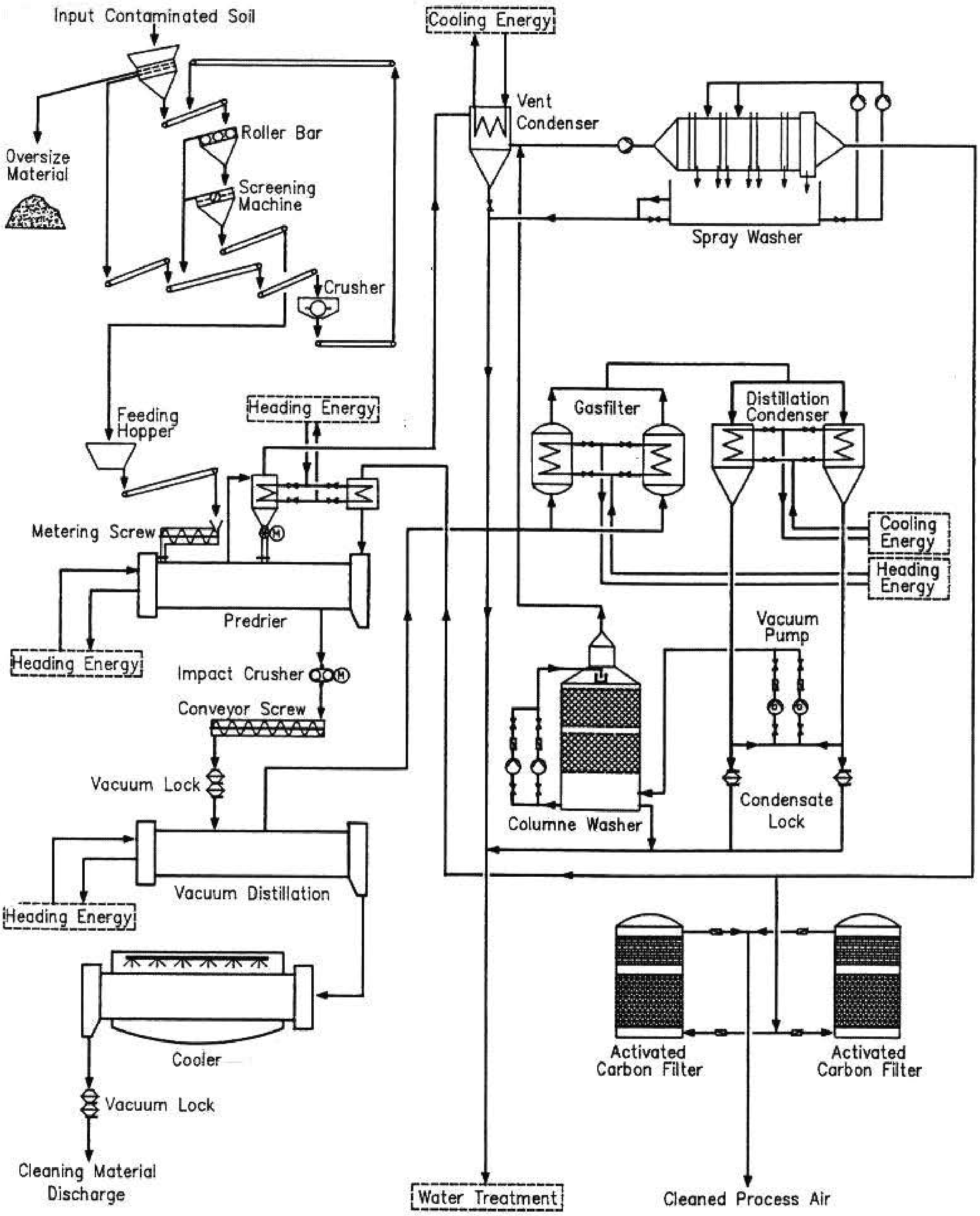


Figure 5-13: Thermal desorption (vacuum distillation section) of the Marktredwitz plant (source: Harbauer)

Another serious design issue is the necessity to condensate the mercury from the off-gas in one single location only and not to spread it across the entire off-gas treatment system, which normally includes quenches, gas scrubbers (packed columns) and activated carbon filters, filled either with iodized and/or sulfidized char coal.

Owing to the above described dust filter and off-gas demercurization, the Marktredwitz Plant (fig. 5-13) hat to undergo a design improvement and various alterations. In order to handle the large amount of dust for example a cyclone was installed upstream to the bag house filters. In addition their surface was increased, the material was changed, the cleaning system was modified and vacuum pumps were upgraded with larger steam injection pumps as pre-compressor device[xl].

Whilst in Marktredwitz a three step system with propane gas fired lance burners was applied, in the more recent years in Germany two step thermal oil thermal desorption plants were merely applied for the treatment of mercury-contaminated solid wastes (soil). Significant for this technology are the relatively low temperatures of about 300 °C.

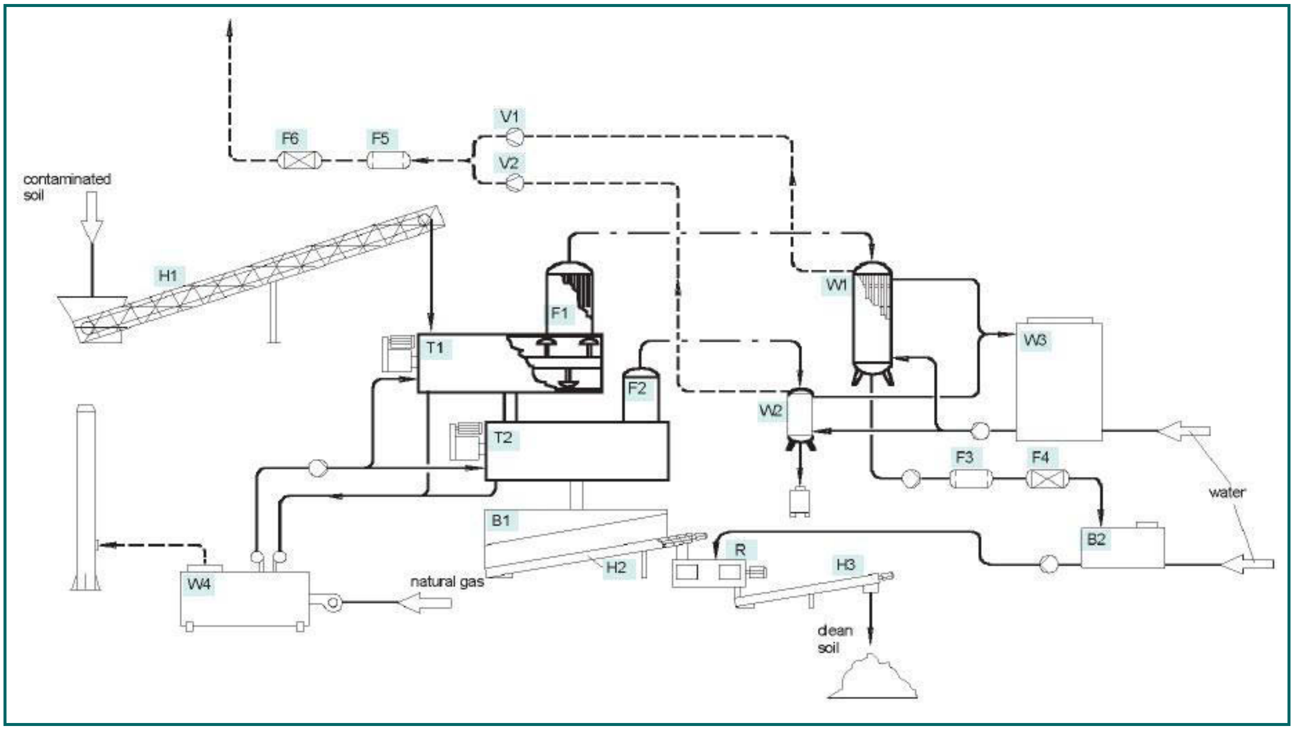


Figure 5-14: Vacuum distillation plant (thermal desorption) after the EcoSan-process (source: TechnoSan)

Fig. 5-14 above is showing a thermal oil plant, as it is currently operated by TechnoSan Umwelttechnik GmbH in Neuötting/Germany. The pre-drier (operated at lower temperatures 60 °C and 100 mbar) T1 and the vacuum dryer T2 are supplied by AVA econ industries Herrsching. Similar plants are currently operated in Rositz/Thuringia and in Ústí nad Labem.

[xl] `All necessary alterations in the thermal desorption of the Marktredwitz Plant were planned and supervised by the author. For the successful implementation of a mechanical mercury separation device the author was nominated for the Wilhelm Holzmann Prize

6. FLOTATION

Flotation in a narrower sense is understood in this thesis as 'froth flotation', which is known as a separation process, applied in general for the beneficiation of metallic ores, but also for various non-metallic raw materials provided by the mining industry such as coal, graphite, fluoride, potash or some clay minerals. More recent applications were also performed with regard to the decontamination of polluted soils and other hazardous solid wastes.

Flotation as a hydrometallurgical process is based on the physical and chemical properties of certain minerals after dispersion of the (comminuted) ore or contaminated soil in an aqueous pulp in order to be floated to the surface by means of gas bubbles as a transport media and organic promoting reagents as collectors.

6.1 TECHNICAL DEVELOPMENT OF FLOTATION

Early ore processing applications using the oiled-pulp kneading method in medieval Persia were reported by A.M. GAUDIN[155]. In 1877 a patent for the purification of graphite was granted to the 'GEBRÜDER BESSEL' in Dresden[156], the former owners of the graphite mine 'Kropfmühl'[xli], for the use of various oils, resins and tars as reagents for a batch process, where the graphite was cooked together with these ingredients and the required gas bubbles were generated by the cooking process itself. The first real 'gas bubble flotation' was described by C.V. POTTER in 1902[157] developing a method for processing a difficult zinc mean product from Australian Broken Hill Mine, where the flotation was accomplished in an acidic aqueous solution (Potter-Delphrat Process).

The use of organic reagents instead of oil-based collectors was one of the most important improvements in the following years. In 1921 a patent was granted on this subject to PERKINS[158] for the use of dipolar organic collectors containing hydrocarbons on one end and bivalent sulfur or trivalent nitrogen on the other such as in particular thiocarbanilide[xlii] $C_{13}H_{12}N_2S$, but also xanthates are matching to this description[159].

Xanthates initially were discovered by W.C. ZEISE in Copenhagen before 1815[160] as the salts and esters of the xanthic acid ROC (S) SH and finally rediscovered as a flotation promoting reagent in 1923 by C.H. KELLER. The issuance of an U.S. patent to KELLER on the use of xanthates as collectors for the flotation of heavy metal sulfide minerals followed accordingly in 1925[161].

6.1.1 Application of flotation techniques for the treatment of solid waste

Flotation of cinnabar and residues from mercury distillation such as 'stuff' and condensation slurries was practiced by some mining companies in California and in Nevada already in the early 1930s[162]. Results of flotation tests of a cinnabar-stibnite ore from the Red Devil mine, Alaska were reported by ERSPAMER AND WELLS (1956)[163]. The Flotation of beaded (metallic) mercury was described by LUYKEN AND BIERBRAUER (1931)[164] as very difficult even under consideration of a very fine dispersion in the pulp.

The first application of froth flotation in a physico-chemical soil washing plant in Germany was performed by RICHTER, SCHMIDT ET AL. (1997)[165] in a soil treatment facility in Berlin-Gradestrasse by up-grading the existing plant with modified Fahrenwald type sub-aeration machines provided by the German vendor SKET. Using common flotation reagents from coal processing several thousand metric tons of highly organically-contaminated soil with polycyclic aromatic hydrocarbons (PAHs) greater or equal 20,000 [mg/kg DW] were treated successfully in a soil particle range between 0 and 2 mm.

[xli] Kropfmühl (close to Passau) is the only German graphite mine and was founded in 1870. The current annual production is about 100,000 metric tons of the so-called "Hauzenberger Graphite"

[xlii] Thiocarbanilide aka 1,3 diphenylecarbamide is a derivate of thiourea by reaction of aniline with carbon disulfide

At that time soils contaminated with polycyclic aromatic hydrocarbons (PAH) were commonly treated by more expensive thermal processes such as in particular incineration. Thermal treatment of highly organically-contaminated waste is restricted very often, when the waste is contaminated in parallel by heavy metals because of off-gas treatment limitations of various thermal treatment facilities.

A similar situation exists presently with regard to highly mercury-contaminated soils and similar high mercury solid wastes. Currently thermal treatment is, as previously mentioned, still accepted in particular by the US EPA, as the 'best demonstrated available technology (BDAT)' by roasting/ retorting (RMERC)[166]. Unfortunately this technology cannot handle high mass flow rates because of low operational availability and throughput restrictions.

HUANG AND WILSON (1976)[167] removed HgS, CdS and $Cd(OH)_2$ from aqueous systems by a number of batch-type precipitative and adsorbing colloide flotation tests using $Al(OH)_3$, $Fe(OH)_3$, FeS and CuS as colloids and Sodium lauryl sulfate $C_{12}H_{25}NaO_4S$ (SLS) and hexadecyltrimethylammonium bromide $CH_3(CH_2)_{15}N(Br)(CH_3)_3$ aka ((HTA)Br) as collectors.

More recently published applications of flotation techniques or adsorption processes pertaining to the treatment of mercury-contaminated wastes are mostly constrained to 'Ion Flotation' by dissolved air flotation machines (DAFs)[168] and some very specific technical applications such as the removal of Thiomerosalfrom industrial process water[169] or the removal of mercury cyanide complexes from the processing streams of gold hydrometallurgical operations[170]. Next to required coagulants and auxiliary flocculants Dithiocarbamates (R–N (–R″)–C (=S)–S–R′) are used mostly for precipitation.

ABUMAIZAR AND SMITH (1999)[171] published results of their batch and column soil washing laboratory tests, treating successfully soils contaminated with heavy metals such as lead, zinc, copper, cadmium and nickel by using chelant extraction with different washing reagents, in particular the disodium salt of ethylene-diamine-tetraacetic acic Na_2EDTA and sodium meta-bisulfide $Na_2S_2O_5$.

Articles currently submitted, dealing with the treatment of metal-contaminated soils and sediments, lacking mostly an application with regard to mercury:

VANTHUYNE ET AL. (2003)[172] performed laboratory flotation tests with sediments of the Gent-Terneuzen Canal using either kerosene or 0.1 M potassium ethyl xanthate (KEtX) as collectors. The highest metal recovery could be performed at pH 12 showing slightly better results for kerosene, where the recovery of Zn, Pb and Cd was in a range of 90%. With KEtX in particular the recovery of Cd was in a range of about 80%. Earlier performed flotation tests with Gent-Terneuzen Canal sediments involving the same authors have shown that the results of flotation tests performed with the whole sediment range (0-2mm) were much better results than those for the fine particle fraction only. Such an effect also was observed earlier during the first industrial scale flotation tests performed with metal-contaminated soils in the physico-chemical solid waste treatment plant Berlin-Gradestrasse by STAPELFELDT AND RICHTER (1997 and 2202)[118, 173].

DERMONT ET AL. (2007)[117] reviewed worldwide the entire state of the art technology regarding 'soil washing for metal removal'. Also field demonstrations dealing mostly with pilot scale technologies applicable for mercury are highlighted, such as soil washing tests performed in Ústí nad Labem, Czech Republic in the year 2000 and a field demonstration using physical separation to remove mercury from soils conducted for US American EERC in 1994. Unfortunately the 'Marktredwitz plant', previously referred to, is misunderstood as a pilot scale site demonstration plant, only. Astonishingly in the same article is also stated, that froth flotation is a widely used technology, referring mostly to various laboratory scale applications and in particular not to the flotation of mercury-contaminated soil.

MOUSSAVI AND JAVIDNEJAD (2006)[174] conducted foam fractionation experiments in the acidic range separating mercury (II) species by using the effect of complexation.

6.2 PHYSICAL AND ELECTROCHEMICAL ASPECTS OF MERCURY FLOTATION

WEINIG AND PALMER suggested already in 1926 that in the theory of flotation physical and chemical phenomena merge into each other and that there is no way of drawing a sharp line between them[175].

In 1873 G. LIPPMANN[xliii] discovered in Kirchhoff's laboratory in Heidelberg, that the surface of mercury could be charged positive when exposed to an electrolyte for example diluted sulfuric acid. It was observed that mercury is releasing immediately mercury ions into the surrounding electrolyte, even in an aqueous pulp because of its extremely low dissolution pressure. VON HELMHOLTZ explained this effect later by the theory of the electrical double layer.

In consequence of the observed phenomenon, Lippmann postulated a causal relationship between the electric charges on interfaces between fluids such as diluted acid/mercury and the potential difference, which is known as the Lippmann Equation[176]:

$$dE_A = -\frac{d\gamma}{q_A};[V] \tag{6-1}$$

E_A is the electrical potential in [V][xliv] and q_A is the specific charge density per area in [C/m^2]. In particular γ is defined as the surface tension (interfacial tension), also often referred to as the specific surface energy:

$$\gamma = \left(\frac{\Delta W}{\Delta A}\right);\left[J/m^2\right];\left[N/m\right];\left[kg/s^2\right] \tag{6-2}$$

The surface tensions of liquids, in particular of mercury depends considerably on the temperature. The maximum surface tension of mercury (515±7 dynes/cm at 31°C) is reached when only mercury vapor is present[177]. The surface tension of water is becoming lower when the temperature rises. The values of surface tensions of 'mercury/water' and 'mercury/air' as present in the literature differ considerably. Most probably this deviation is caused by the influence of the purity of mercury, but also maybe by using different isotopes of mercury.

Table 6-1: Surface tension values[178, 179]

Name of liquid/ contact media	Surface tension σ in [mN/m]; [dyn/cm]	At temperature [^{o}C]
Mercury/Air	425.41[180]	20
Water/Mercury	415	20
Ethanol/Mercury	15.5	20
Water/Air	72.86 ± 0.05	20
Water/Air	71.99 ± 0.05	25
Ethanol/Air	22.39	20

Besides the above given equation also a thermodynamic derivation exists, considering temperature and pressure, where the surface tension σ is the partial derivative of the free enthalpy G with respect to the surface A:

[xliii] Gabriel Lippmann (1845 – 1921): Important pioneer in color photography (Nobel prize 1908) and inventor of the 'Lippmann electrometer', a mercury filled device with a capillary tube end based the above described surface tension effect

[xliv] The standard potential of mercury is $E^0 = 0.7973$ V, referring to the chemical equation: $2\,Hg \rightarrow Hg_2^{2+} + 2\,e^-$

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,p};\left[{}^{\mathrm{J}}\!/_{\mathrm{m}^2}\right];\left[{}^{\mathrm{N}}\!/_{\mathrm{m}}\right] \tag{6-3}$$

The important relationship of the surface tensions within the three phases' system 'mercury-water-air' and the contact angle θ can be explained in greater detail by means of fig. 6-1:

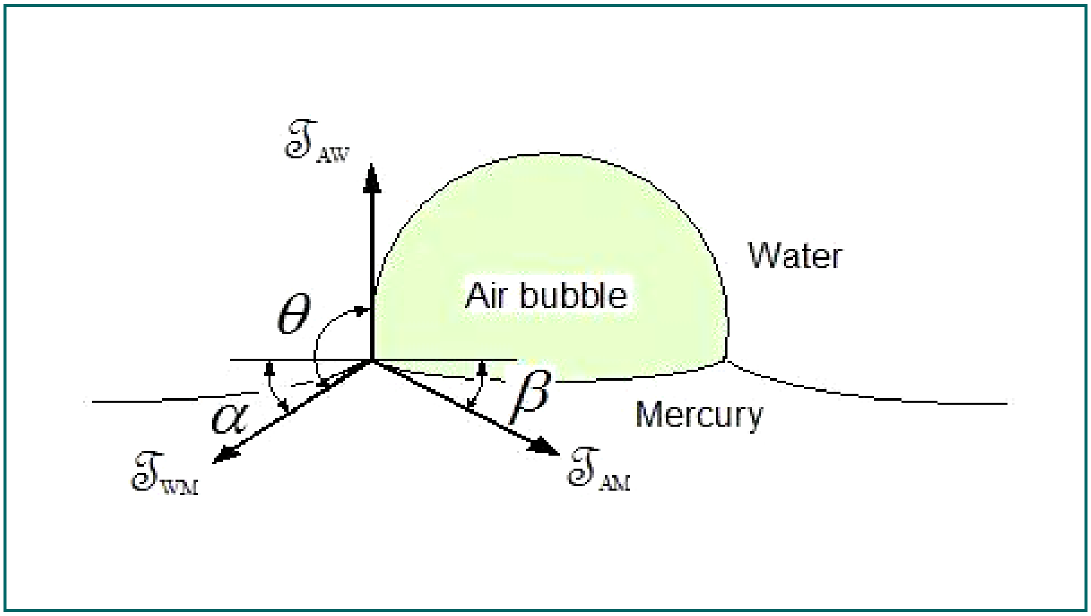


Figure 6-1: Tension forces in the system mercury-water-air showing the contact angle $\theta \approx 100^{o}$ (after A.M. Gaudin)

At equilibrium the vector sum of all tension forces $\vec{T}_i$ shall be nil:

$$\sum_{i=1}^{n} \vec{T}_i = \vec{T}_{WM} + \vec{T}_{AW} + \vec{T}_{AM} = 0 \tag{6-4}$$

The sum of all shear forces along the horizontal contact line in figure 3 at equilibrium shall be also zero:

$$\sum_{i=1}^{n} T_{hi} = \left|\vec{T}_{WM}\right|\cos\alpha + \left|\vec{T}_{AW}\right|\cos(\theta-\alpha) - \left|\vec{T}_{AM}\right|\cos\beta = 0 \tag{6-5}$$

Assuming that the angles α and β are negligible (means approaches zero) the simplified equation can be written as follows, since the forces are proportional to their tensions:

$$\cos\theta = \frac{T_{AM} - T_{WM}}{T_{AW}} = \frac{\sigma_{AM} - \sigma_{WM}}{\sigma_{AW}}; 0^{0} \le \theta \le 180^{0} \tag{6-6}$$

This term above is also referred to as 'Young's equation'. A contact angle of $\theta = 0^{o}$ such as for quartz characterizes non-floatability and vice versa a contact angle of $\theta = 180^{o}$ theoretically represents wetting of the mineral by air to the exclusion of water. GAUDIN pointed out clearly, that there is no mineral physically existing giving an air-water contact angle larger than about 110^{o} [181]. The contact angle θ for mercury at air-water contact is usually in a range of 100° and is directly linked to its hydrophobicity. By means of the figures given in the table above, a contact angle for mercury of around 91° could be calculated.

Since the influence of ethanol is entailing a reduction of the surface tension in water, this follows a rise of the contact angle and explains the necessity of the alkyl-groups in the most common promoting agents (collectors) for metal ore flotation. The very important force of adhesion F_A is becoming larger by increasing the contact angle:

$$F_A = T_{AW} \sin\theta \qquad (6\text{-}7)$$

6.2.1 Thiol Collectors applicable for mercury and its compounds

Figure 6-2 shows a variety of thiol (organic sulfidryl) collectors commonly used in metal flotation and in water treatment. These ligands are capable to form strong complexes with mercury.

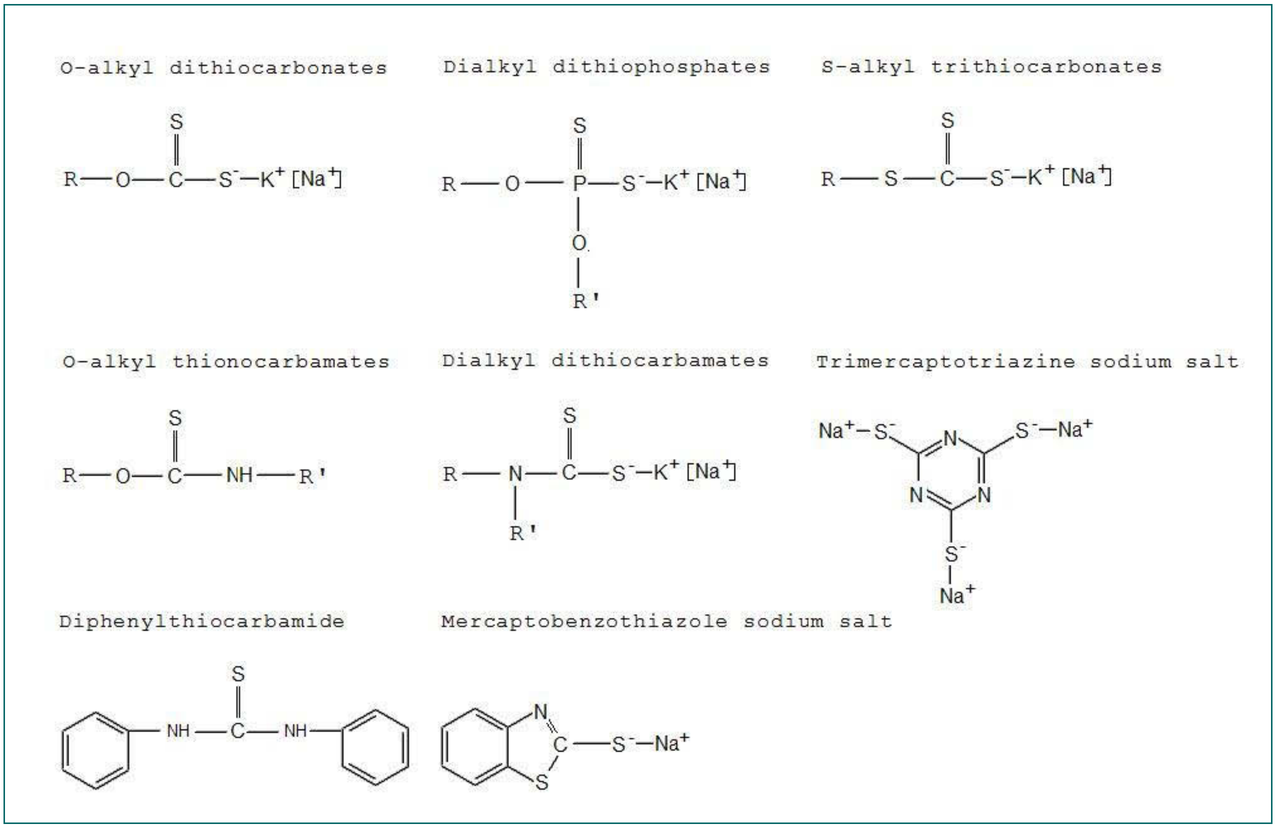


Figure 6-2: Thiol (organic sulfidryl) collectors commonly used in metal flotation and in water treatment

O-alkyl dithiocarbonates aka (Alkali)-Xanthates commonly are produced by the reaction of an alcohol ROH with caustic soda NaOH or kali lye KOH in presence of carbon disulfide CS_2:

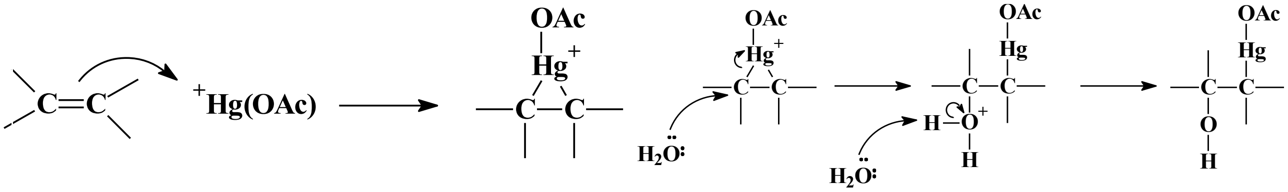
$$ROH + NaOH + CS_2 \rightarrow ROCS_2Na + H_2O \qquad (6\text{-}8)$$

This reaction also represents an intermediate step in the transformation of primary alcohols into alkenes, following the 'Olefin Synthesis' after Tschugaeff[xlv] aka 'Chugaev Elimination' where the xanthate is transformed into a thiol (xanthate) ester by using methyl iodide CH_3I removing also the Alkali metal[182]:

$$\mathrm{ROCS_2Na + CH_3I \rightarrow ROC_2S_2CH_3 + NaI} \qquad (6\text{-}9)$$

At a relatively low temperature of about 200 °C a thermal decomposition of the xanthate ester takes places receiving an alkene RC=CR and the by-products carbonyl sulfide COS and an alkane thiol such as in particular methane thiol CH_3SH[183], formerly known as methyl mercaptan [m-mercaptan]. Mercaptans[xlvi] (alkane thiols) RSH, first described by W.C. Zeise (1833)[184], are characterized by a very strong affinity to mercury due to their reactive sulfhydril group allowing them to form particularly with mercury water-insoluble mercury mercaptides such as mercury ethylmercaptide $Hg\ (SC_2H_5)_2$[185].

Alkenes react for example with mercuric acetate $Hg(O_2CCH_3)_2$ commonly abbreviated as $Hg(OAc)_2$. After dissociation the electrophile $^+Hg(OAc)$ attacks the C=C bond forming a mercurinium ion as an intermediate. –OH attacks the substituted carbon providing a planar mercury organic compound in Markovnikov orientation. This reaction is known as oxymercuration or alkoxymercuration used for the synthesis of ethers[186].



(6-10)

Collectors in particular xanthates are characterized by containing a polar and a non-polar group. The most efficient polar groups are:

- either the thiol group (sulfhydril group), characterized by a sulfur-hydrogen bond –SH
- or soluble sulfides such as those of alkali metals or alkali earth metals

A.F. TAGGERT found in his very early experiments, that the non-polar group of a xanthate collector shall not contain more than eight carbon molecules and the solubility of the collector preferably shall be in a range between 200 mg/l and 300 mg/l[187].

Aqueous Solutions of xanthates are subject to hydrolysis:

$$\mathrm{R-O-CSS^- + H_2O \Leftrightarrow R-O-CSSH + OH^-} \qquad (6\text{-}11)$$

At pH 5 the generated xanthic acid is breaking down to alcohol and carbon disulfide as it also could be verified in the preliminary tests performed in this thesis.

Xanthates are oxidized on metal sulfate surfaces by oxygen and stronger oxidizing agents such as:

[xlv] Lev Aleksandrovitsch Tschugaev (Лев Александрович Чугаев), 1873-1922, distinguished Russian chemist, professor of chemistry at the University of Moscow. He researched about platinum and nickel complexes, terpenes and xanthates (www.physchem.chimfak.rsu.ru/Source/History/Persones/Chugaev.html).

[xlvi] The name derivates from corpus mercurium captans (Zeise, 1833)

$$2\,X^- + \tfrac{1}{2}\,O_2 + H_2O \Rightarrow X_2 + 2\,OH^- \qquad (6\text{-}12)$$

X^- = Xanthate, and X_2 = Di-xanthate

This reaction is also applicable for solid mercury sulfide HgS, forming the much better soluble mercury (II) hydroxide HgO (see tab. 6-2) as an intermediate step before mercuric xanthate is generated.

$$HgO + H_2O \Leftrightarrow Hg^{2+} + 2OH^- \qquad (6\text{-}13)$$

Chemisorption on sulfide surfaces is generating a monolayer, because the interaction between the metal ions on the mineral surface and the xanthate ions is forming very slightly water soluble heavy-metal xanthates. Following the Schürman's[176] series determining the affinity of common metals to sulfur:

$$Hg > Ag > Cu > Bi > Cd > Pb > Zn > Ni > Co > Fe > Mg \qquad (6\text{-}14)$$

Important is that the adsorption of collectors to mineral surfaces depends very much on the solubility of the mineral itself and shall be larger than the compound generated by the chemical reaction of the same mineral with the collector. In consequence of this, the knowledge of mercury sulfide species is essential for the explanation of the flotation experiments performed in this thesis.

6.3 MERCURY SULFIDE SPECIES IN AQUATIC SYSTEMS

The occurrence of a variety of mercury species is depending very much on the pH and the solubility, but also whether the aquatic system is operated under oxic or anoxic conditions. This is significant for the understanding not only for the sufficient application of flotation technologies on high mercury wastes and for the stabilization/solidification process applied to such wastes, but also for the methylization process taking place in mercury-contaminated soils in general.

Fig. 6-3 is showing various dissolved mercury species in the system: **Hg : S : Cl = 0.5 : 1 : 1**. This system is applicable very good for soils from former chlorine-alkali electrolysis plants, owing to the existence of chlorine ions from process residues introduced to the ground by incidents or leakage.

On the other hand soil (rubble anyway) of former chlorine plants is in the majority of all remediation cases in the low alkaline range, mostly caused by Sodium (Na^+) or Potassium ions (K^+), but also by their hydroxides.

Owing to this the 'preferable pH range' for processing such materials should be:

$$7 \le \mathrm{pH} \le 9; \mathrm{pH} = -\log_{10}(a_{H^+}) \qquad (6\text{-}12)$$

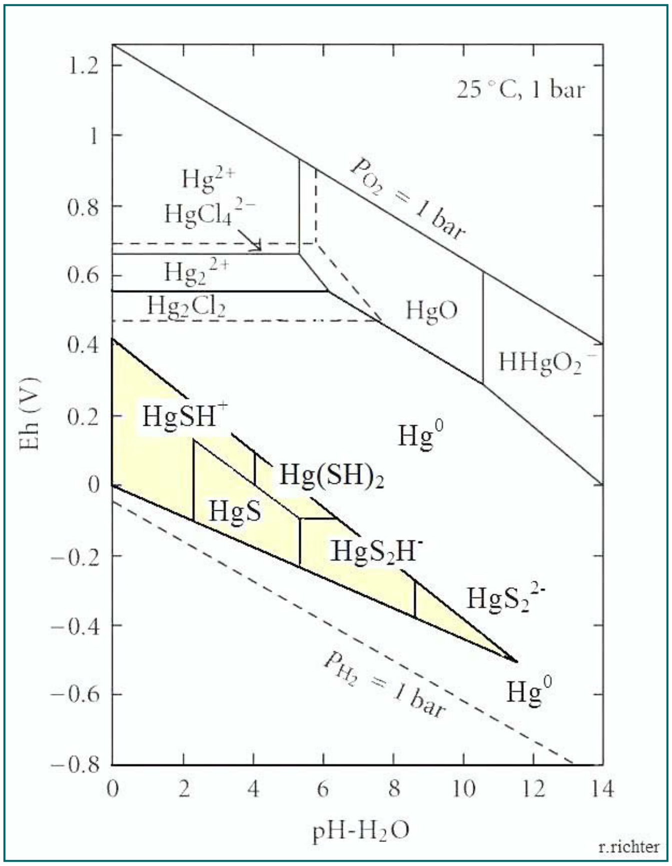


Figure 6-3: Eh-pH diagram (simplified) shows dissolved mercury species in the system **Hg : S : Cl = 0.5 : 1 : 1**

From the three known solid $HgS_{(s)}$ species such as red cinnabar, hexagonal hyper-cinnabar and black meta-cinnabar, in an aqueous system predominantly amorphous meta-cinnabar may be formed by the reaction of Hydrogen Sulfide on dissolved mercury compounds. The very important mercury sulfide compounds disappear completely in the system: **Hg : S : Cl = 5 : 1 : 1**[188], considering metallic mercury as the dominating species.

6.3.1 The solubility of some metal sulfide species

As far as metal salts are concerned, the solubility of ionic compounds in water results out of the solubility product:

$$K_{sp} = c_{eq}^{m}(A^{+}) \cdot c_{eq}^{n}(B^{-}); \left[\left(\mathrm{mol}/_{1} \right)^{3} \right] \qquad (6\text{-}13)$$

The solubility of ionic compounds such as metal salts A_mB_n dissolved in water (followed by dissociation) is related to the solubility product as follows:

$$S = \frac{c_{eq}(A^{+})}{m} = \frac{c_{eq}(B^{-})}{n} = \sqrt[n+m]{\frac{K_{sp}}{n^{n}\cdot m^{m}}};\left[{}^{mol}\!/\!{}_{l}\right];\left[{}^{g}\!/\!{}_{l}\right] \qquad (6\text{-}14)$$

Table 6-2: Solubility products of common solid mercury species[189]

Mercury species	**K_{sp} Solubility product $[(mol/l)^3]$**	**$\log K_{sp}$**	**At temperature [°C]**
Mercury(II) sulfide HgS (black)	2.0×10^{-53}	-52.699	25
Mercury(II) sulfide HgS (red)	2.0×10^{-54}	-53.699	25
Mercury(I) sulfate Hg_2SO_4	6.5×10^{-7}	-6.187	25
Mercury(I) chloride Hg_2Cl_2	1.43×10^{-18}	-17.845	25
Mercury(II) hydroxide HgO**	3.6×10^{-26}	-25.444	25
Mercury(I) thiocyanate $Hg_2(SCN)_2$	3.2×10^{-20}	-19.495	25
Mercury(I) picrate $[C_6H_2(NO_2)_3]_2Hg$ [190]	$6{,}12\pm0.05\times10^{-11}$	-10.213	25

(**) $HgO + H_2O \rightleftharpoons Hg^{2+} + 2\,OH^{-}$

In case of cinnabar as the dominant solid phase, $HgS_{(s)}$ dissolves in water, which is related to the above solubility product:

$$HgS_{(s)} \Leftrightarrow Hg^{2+}_{(aq)} + S^{2-}_{(aq)} \qquad (6\text{-}15)$$

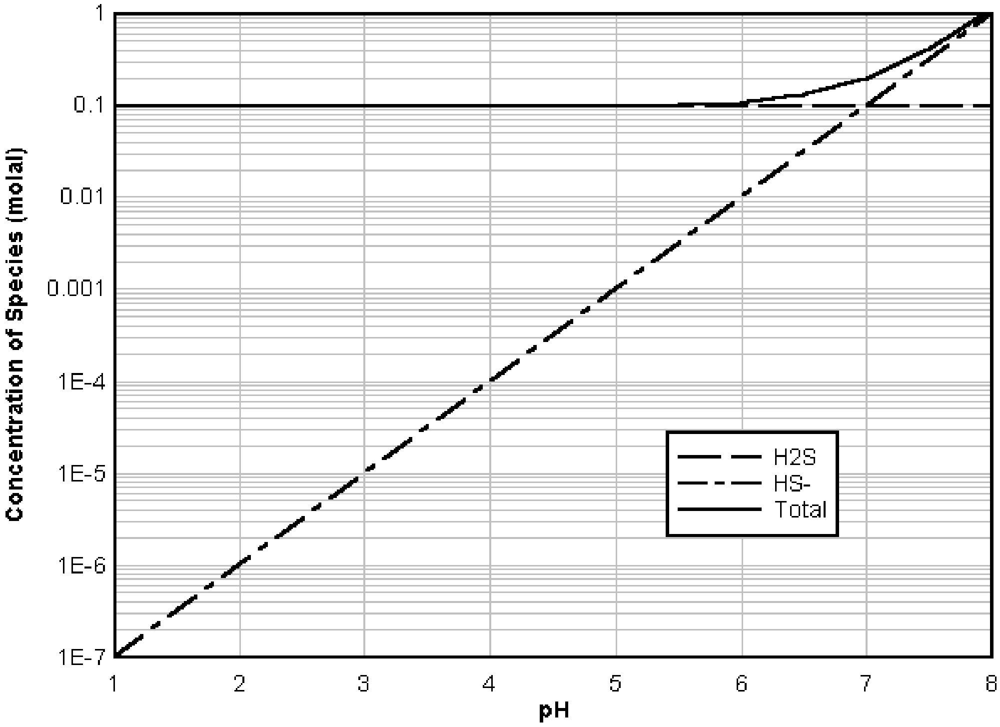


Fig. 6-4: Effect of pH on the solubility of Hydrogen Sulfide[191]

The solubility of $HS^{-}_{(aq)}$ in water raises linear with the pH and reaches the maximum at pH 8.

$$H_2S_{(aq)} \Leftrightarrow HS^-_{(aq)} + H^+_{(aq)} \qquad (6\text{-}16)$$

In the above shown simplified Eh-pH diagram, which represents our aquatic system, aqueous hydrogen sulfide $HS^-_{(aq)}$ becomes at pH 8 the predominant sulfide species. The dissolution of cinnabar in an aquatic system in the presence of hydrogen sulfide takes place as follows:

$$HgS_{(s)} + H^+_{(aq)} \Leftrightarrow Hg^{2+}_{(aq)} + HS^-_{(aq)} \qquad (6\text{-}17)$$

The complete solubility product of this reaction is already considerably higher than as per equation 6-15 ($\lfloor \log K_{sp1} = -36.70 \rfloor >> \lfloor \log K_{sp2} = -52.699 \rfloor$).

Besides this even more soluble mercury-sulfide species can be generated within the above shown aquatic system (fig. 6-4) under anoxic conditions. Tab. 6-3 shows the solubility (at 20^o C) of these sulfur-mercury complexes in greater detail. The sulfur mercuric ion $HgS_2{}^{2-}$ as the only soluble sulfurate mercury species is of great significance for the success of currently applied mercury technologies.

Table 6-3: Solubility products of solid mercury sulfide species in accordance with fig. 6-4[192, 193]

Mercury-sulfide species/ reaction	**logS**	**K_{sp} Solubility product $[(mol/l)^3]$**	**$logK_{sp}$**	**Equilibrium constant log K_f [mol/l]**	**pH range**
$HgS_{(S)} + H_2S \Leftrightarrow HgS_2H_2$	-5.97	4.928×10^{-18}	-17.31	37.5	4.0 – 6.2
$HgS_{(S)} + HS^-_{(aq)} \Leftrightarrow HgS_2H^-$	-5.28	5.78×10^{-16}	-15.24	32.0	5.5 – 8.5
$HgS_{(S)} + S^{2-} \Leftrightarrow HgS_2{}^{2-}$	+0.57	205.15	+2.31	23.5	8.5 – 11.8

Compared to cinnabar (tab. 6-2) as the controlling solid phase the advantage for flotation of the higher soluble mercury sulfide species is obvious. The concentration of (Hg^{2+}) = (S^{2-}) in the aqueous system is only $\sqrt{\left(Hg^{2+}\right)^2} = \sqrt{2 \times 10^{-53}} = 4.5 \times 20^{-27} \left[{}^{mol}\!/\!_{l}\right]$. The reaction of hydrogen sulfide with cinnabar results in a concentration of mercury such as:

$$S = \frac{\left(HgSH^-\right)}{\left(HS^-\right) \times \left(HgS\right)} = 10^{-5.28} \left[{}^{mol}\!/\!_{l}\right] \qquad (6\text{-}18)$$

Considering, that the activity of a solid is 1 and that at a pH of 8 (HS^-) = 1 [mol/l] (fig. 6-5) the concentration of ($HgSH^-$) is equal to the solubility 10 $^{-5.28}$ [mol/l].

6.3.2 The solubility and structure of some important class b metal xanthates

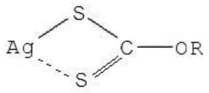
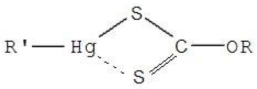
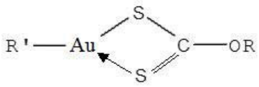
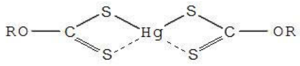
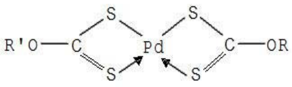
The xanthates of class b and borderline metals such as mercury, silver, copper and lead are more or less insoluble in water. In particular xanthates form very strong complexes with class b metals such as with mercury. The xanthates of the class a metals such as zinc, iron and manganese are already moderately soluble. Different solubility properties of heavy-metal xanthates reflect to a certain degree the chemisorption on the mineral surface, and explain the effect of selective collection of xanthates. Besides this also the length of the alkyl group has a considerable influence on the solubility (see tab 6-4 below):

Table 6-4: Solubility product of various class b and border line metal xanthates compared to their sulfides[194, 195]

Metal name	**Metal xanthate**	**Solubility product [(mole/l)^3]**	**Metal sulfide**	**Solubility product [(mole/l)^3]**
Copper	Copper ethyl xanthate	5.2×10^{-20}	Copper(II) sulfide	8×10^{-37}
Lead	Lead ethyl xanthate	2.1 up to 6.8×10^{-17}	Lead(II) sulfide PbS	3×10^{-28}
	Lead amyl xanthate	1.0×10^{-24}		
Zink	Zink ethyl xanthate	4.9 up to 5.3×10^{-9}	Zinc sulfide (alpha)	2×10^{-25}
	Zink amyl xanthate	1.6×10^{-12}	Zinc sulfide (beta)	3×10^{-23}
	Zink octyl xanthate	1.5×10^{-16}		
Silver	Argentous xanthates	5.2×10^{-19}	Silver sulfide Ag_2S	2×10^{-47}

Aurous xanthates in particular gold alkyl xanthates were synthesized by DENKO AND ANDERSON in 1945 and described as insoluble in water[196]. About mercuric xanthate is not very much published in the more recent literature. I.A. KOTEN's in the year 1924 published research results on alkyl and aryl mercuric hydroxides is still one of the most important articles dealing with alkyl mercuric xanthates $R'HgS(S)C^{\cdot}OR$[xlvii] even today. The reaction is being catalyzed by sodium hydroxides, preventing the formation of mercaptans[197].

Table 6-5: Structures of various class b metal xanthates forming square planar complexes

Metal	**Valens**	**Metal alkyl xanthate/ thiolates**	Formula	**Structure formula**
Asymmetric square planar structures				
Silver	I	Silver alkyl xanthates	$AgS\ (S)\ C^{\cdot}OR$	
Mercury	II	Alkyl mercuric xanthates (organo mercury type)	$R'HgS\ (S)\ C^{\cdot}OR$	
Gold	III	Aurous alkyl xanthates	$R'\ AuS\ (S)\ C^{\cdot}OR$	
Quasi symmetric square planar structures				
Mercury	II	Mercury(II) bis xanthates	$Hg(S_2COR)_2$	
Palladium	IV	Palladous alkyl xanthates	$R'O^{\cdot}C\ (S)\ S\ Pd\ S\ (S)\ C^{\cdot}\ OR$	 *.)

*.) Structural formula of palladous alkyl xanthate after Gaudin

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[xlvii] The nomenclature for xanthates is following the real conditions of the structure formula

The structures of some class b metal xanthates/thiolates involving chelating of the metals and the sulfur atom are shown in tab. 6-5 above. The quasi symmetric square planar mercury structures of mercury(II) bis xanthates $Hg(S_2COR)_2$[198].

CASAS ET AL. performed recently a research on the crystal structure of methyl mercury MeHgS (S) C·OR[199]. The more interesting interpretation of the results is that xanthates are able to immobilize highly soluble and extremely toxic methyl mercury compounds into insoluble mercurous xanthates, which qualifies xanthates as the preferable collector for the treatment of solid wastes from chlorine alkali electrolysis and acetaldehyde factories.

More recently preformed investigations on the X-ray structure of [Pd(Me-Xanthate)$_2$] showed the 4-coordinated geometry in solution and the square planar structure in the solid state[200] as per tab. 6-5.

6.3.3 The influence of frothing agents

One of the main requirements on froth flotation is the generation of long-standing foam, stable enough to hold the floated ore particles on the surface for a sufficient period of time.

Frothing agents for flotation purposes are generally organic substances with a molecular structure containing, analogous to the previously described collectors, a non-polar and a polar group. The polar constituents interacting with water molecules whilst the non-polar part rises from the water phase in the air bubble.

The polar group includes predominantly oxygen containing radicals particularly the hydroxyl-group (OH). Typical examples are amyl alcohol $C_6H_{11}OH$, cresol $CH_3C_6H_4OH$ and alkyl poly glycol ether $H\text{-}(OR)_n\text{-}OH$.

Alcohol frothers are very commonly used in ore flotation in particular in combination with alkyl-xanthates. In the preliminary experimental part of this thesis Flotanol D-14 was used as a frothing agents for lead and zinc flotation tests. Mercury flotation tests were successfully performed with Flotanol D-12. Both frothing agents, as brand names of the German vendor HOECHST, are basically ‘alkyl polyglycol ethers’. Polyglycol ethers $H\text{-}(OR)_n\text{-}OH$, because of their alcoholic OH-group are also capable for flotation in an alkaline range and besides this polyglycol ethers do not act as collectors.

6.4 TECHNICAL TERMS AND PRESENTATION OF FLOTATION RESULTS

The following technical terms are commonly used for the presentation of flotation results:

- Mass recovery in the concentrate R_M is defined as the concentrate mass m_C, recovered from the froth product in relation to the feed mass m_F:

$$R_M = \frac{m_C}{m_F} \times 100;[\%] \qquad (6\text{-}19)$$

- The mass of treated soil m_S is the difference of the feed mass m_F minus the concentrate mass m_C:

$$m_S = m_F - m_C \qquad (6\text{-}20)$$

- The recovery of the contaminant R_C is indicating which portion of the feed contamination could to be recovered in the concentrate:

$$R_C = \frac{m_C \times c_C}{m_F \times c_F} \times 100;[\%] \qquad (6\text{-}21)$$

The (metal) concentration in the effluent (concentrate) c_C but also the concentration of the contaminant in the feed c_F commonly expressed in [mg/kg].

- The mass recovery with regard to decontaminated soil R_S is defined as follows:

$$R_S = (1 - R_M) \times 100;[\%] \qquad (6\text{-}22)$$

- The 'Enrichment Factor ε describes the efficiency of the flotation process as the ratio of the concentration in the concentrate c_C to the contaminant in the original (feed) c_F :

$$\varepsilon = \frac{c_C}{c_F} \times 100;[\%] \qquad (6\text{-}23)$$

- The 'Treatment Efficiency Factor' is defined as a the ratio of concentrations of final to the original:

$$\eta = \frac{(c_F - c_S)}{c_F} \times 100;[\%] \qquad (6\text{-}24)$$

Treatment efficiency is commonly used to describe the effectiveness of treatment processes and also applicable to describe the efficiency of mercury removal due to separation processes, whereupon c_S is the remaining contamination in the soil after treatment (MOUSSAVI AND JAVIDNEJAD, 2006)[175].

- The Selectivity Index SI was introduced by Douglas (1962)[201] and combines the above described target variables to only one significant parameter:

$$SI = \frac{(R_C - R_M)}{(1 - R_M)} \times \frac{(c_c - c_F)}{(c_{max} - c_F)};0 \le SI \le 1 \qquad (6\text{-}25)$$

c_{max} characterizes the maximal possible (metal) concentration in the concentrate. In the ore processing industry c_{max} commonly is based on the chemical composition with regard to stoichiometric pure metals. In case of metal-contaminated soils this routine is not easily applicable. As a compromise applied for previously performed flotation tests with lead and zinc-contaminated soils, c_{max} was identified with the maximal achieved concentration in the effluent, providing scaling for a uniform interpretation of test results (STAPELFELDT AND RICHTER, 2002)[173].

7 EXPERIMENTAL

As an essential part of this thesis various experiments concerning soil washing with original excavated soil from decommissioned chlorine plants and acetaldehyde factories but also with artificially mercury-contaminated soil were performed accordingly using the following tests, analysis and extraction methods:

Table 7-1: Tests, analysis and extraction methods

<table>
<tr><th>Parameter/Procedure</th><th>Method</th><th>Description of selected Test (Analysis) Method</th></tr>
<tr><td>Froth flotation analysis tests</td><td>corresponding to DIN 22017[xlviii]</td><td>Nomenclature used and froth flotation analysis tests were performed in accordance with to DIN 22017</td></tr>
<tr><td rowspan="3">Particle size analyses using wet sieving</td><td>DIN 18123[xlix] and DIN 66165, part 1 and part 2;</td><td>Test sieves with woven wire cloth as per DIN ISO 3310-1 (corresponding to ASTM E 11 # below); sieves used:
(4), 25, 63, (75), 125, 200, 400, 1000, 4000 and 8000 µm</td></tr>
<tr><td>ASTM C136 – 06</td><td>Standard Test Method for sieve analysis of fine and coarse aggregates (see above); sieves used:
<table>
<tr><td>#</td><td>4</td><td>1</td><td>6</td><td>30</td><td>50</td><td>100</td><td>200</td></tr>
<tr><td>mm</td><td>4.75</td><td>2</td><td>1.18</td><td>0.6</td><td>0.3</td><td>0.15</td><td>0.075</td></tr>
</table></td></tr>
<tr><td>Method as above</td><td>TYLER Screen Scale (deviating slightly from ASTM)</td></tr>
<tr><td>Determination of silt</td><td>EN ISO 14688, formerly DIN 4022</td><td>
<table>
<tr><td rowspan="3">Silt (U)</td><td>Coarse silt (gU)</td><td>0.02 up to 0.063 [mm]</td></tr>
<tr><td>Middle silt (mU)</td><td>0.0063 up to 0.02 [mm]</td></tr>
<tr><td>Fine silt (fU)</td><td>0.002 up to 0.0063 [mm]</td></tr>
</table></td></tr>
<tr><td rowspan="2">Leaching procedures for solid waste</td><td>DEV S4 test after DIN 38414, part 4[l]</td><td>A suspension with a solid/water ratio of 1:10 at pH 7 is shaken overhead at 1 rpm in 1000 ml plastic bottles for 24 hours. As extraction reagents $KMnO_4$ and $Na_2S_2O_8$ are allowed.</td></tr>
<tr><td>TCLP test (metals only)</td><td>Test Method 1311 in “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,” EPA Publication SW–846 and EPA, 40 CFR, Part 261</td></tr>
<tr><td>Determination of water content in soil</td><td>DIN 18121, part 1</td><td>Oven drying method (modified for mercury: $t < 46\ ^{o}C$; or slowly dried in the fume cabinet at room temperature)</td></tr>
<tr><td>Density separation with heavy liquids (float/sink analysis)</td><td>Not applicable</td><td>Heavy liquid density fractionation test using sodium polytungstate aka SPT ($3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$) was performed separately for the particle size group 63 up to 200 µm and 200 up to 500 µm</td></tr>
<tr><td>Standard disintegration procedure for metal analysis in particular for mercury</td><td>DIN 38414, part 7</td><td>Chemical pulping with nitro-hydrochloric acid (aqua regis):
$HNO_3 + 3HCl \rightarrow NOCl + 2Cl_{nascent} + 2H_2O$</td></tr>
<tr><td>Determination of mercury and its inorganic compounds</td><td>DIN EN 1483</td><td>AAS cold vapour method (flame less) after DIN EN 1483 – E12 (DIN 38406, part 12). For the most recent performed analysis of sulphidisation/flotation tests AAS type Varian AA 240 was used.</td></tr>
<tr><td>Determination of total Carbon (org. and inorg.)</td><td>DIN 51721</td><td>Method after Rademacher and Hoverath by combustion and absorption on NaOH</td></tr>
</table>

[xlviii] DIN 22017: Investigations of the raw material in hard-coal-mining – Froth-flotation-analysis, March 2008

[xlix] DIN 18123: Determination of particle size distribution of soil, November 1996 (kombinierte Sieb- und Schlämm-analyse)

[l] Recently a newer leaching test for solid materials was established with DIN 19529 (2009-01) superseding DIN 19529 (2007-07). The test considers a solid/water ratio of 1:2 and allows a particle size up to 32 mm.

7.1 CATEGORIZATION OF SOILS FROM DIFFERENT PROJECT SOURCES

Wet sieving tests in combination with the chemical analysis of the contamination of the specific grain size fractions is the most essential part of all soil washing tests. In the course of this thesis various 'wet sieving analyses' were performed, or referred to, within a wide range of different soils from chlorine-alkali electrolysis plants and acetaldehyde factories[li], worldwide.

For a successful application of 'flotation' or any other physical/chemical treatment of metal-contaminated soil and in particular mercury-contaminated soil the knowledge where and how to make the 'separating cut' with regard to the highest contaminated particle size range in the original substance and with regard to leaching characteristics is very important.

7.1.1 Soil categorization based on wet sieving tests and chemical analysis of the particle size groups

Since the contaminated soils investigated in this thesis basically are all from the same industrial process and characterized by the same main contaminant (metallic) mercury, the following simplified categorization in type I, type II and type III can be made (see also Appendix A):

Table 7-2: Categorization of mercury-contaminated soils

Name	**Criteria I (Hg max.)**	**Criteria II (Leach. max.)**	Typical source	**Content of fines**
Type I	Max. Hg conc. is in the fine sand and/or silt/clay fraction	The max. Hg leaching is congruent to Hg max.	CAPs such as Buna H54, I56 and L66, Waldshut/T., Chien-Chen	Max. 20%
Type II	Max. Hg conc. is in the coarse sand fraction	The max. Hg leaching is congruent to Hg max.	CAPs[lii] such as Yarraville and Ústí n.L.	30 up to 80%
Type III	Max. Hg conc. is in the fine sand and/or silt/clay fraction	The max. Hg leaching is **not** congruent to Hg max.	Acetaldehyde factories such as Buna F44, Temirtau or the CFM[liii]	Max. 20%

Type I soil is understood as a wide stepped sandy soil with an almost ideal grain size distribution (Fuller parabola) and a concentration of fines (fig. 7-3) in a maximum range of 20% (referring to the entire soil range), were consequently the mercury is accumulating in the fines and also generates the highest leachability in this particle size range.

The most likely reason for this phenomenon might be that metallic mercury cannot infiltrate easily very cohesive clayish or loamy soils in particular not, when the soil is soaked with water.

[li] In this thesis the Chemical Factory Marktredwitz (CFM) is also categorized under the same soil type as the acetaldehyde factories.

[lii] Type II is also applicable for acetaldehyde factories in cohesive soils.

[liii] The Chemical Factory Marktredwitz (CFM), as a special case, has a similar contamination profile as acetaldehyde factories (see fig. 7-5)

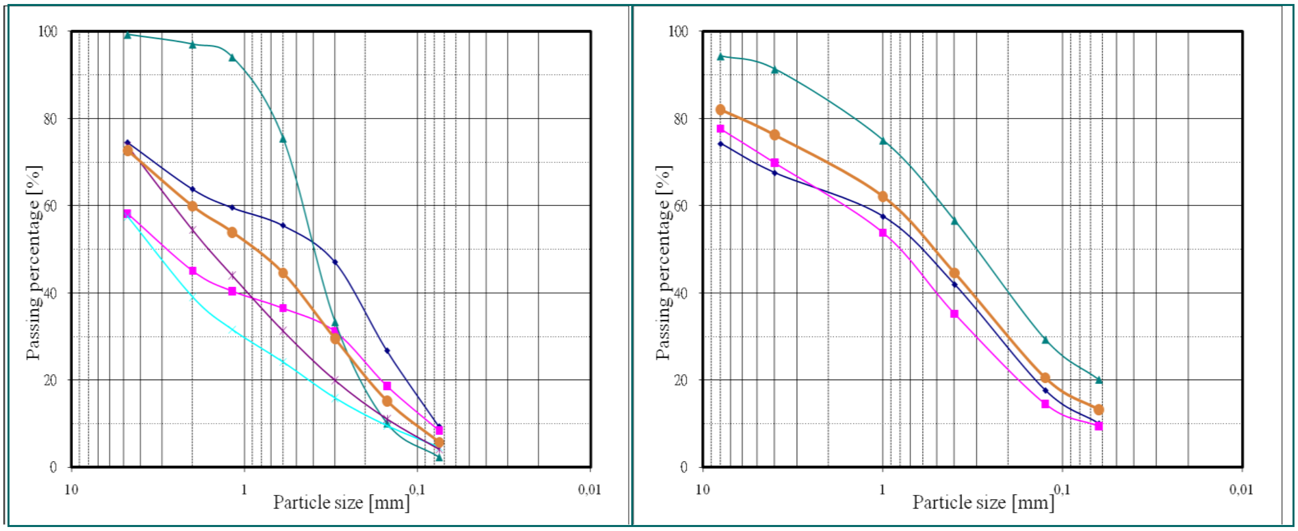


Figure 7-1: Particle size distribution of type I soil from Chien-Chen (Taiwan) and Buna Schkopau (Germany); the orange line presents the mean value (sources: based on orig. data from FIA Freiberg and Golder Associates)

Consequently in soil types with a considerably higher content of fines < 0.063 (0.075) mm the mercury concentration will be shifted to the coarser sand grains, where soil type II in table 7-2 stands for. Chlorine plants are often very closely located on the shore of nearby rivers. Therefore the soil is rich in clay minerals and fines such as from the Olin Saltville Plant in Virginia/USA, which contained a considerable amount of 56 Mass-% of fines < 0.063 mm.

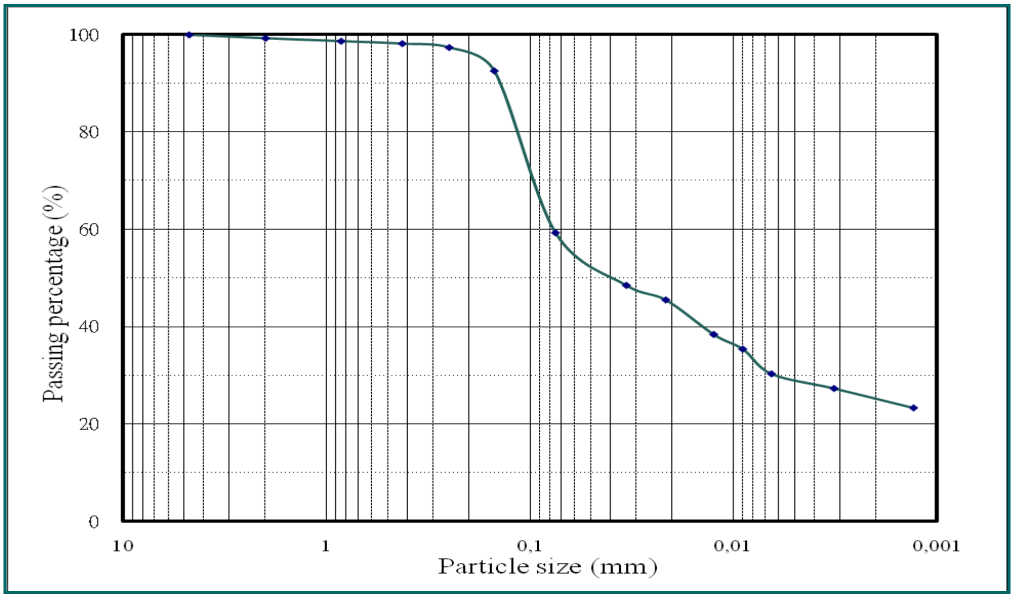


Figure 7-2: Particle size distribution of type II soil from the Olin Saltville Plant in Virginia/USA (based on orig. data collected by Golder Associates)

These ideal conditions may be disturbed in case that soluble mercury compounds exists such as in soil from acetaldehyde factories. Water soluble mercury compounds possibly can access clay minerals and may even be chemisorbed or absorbed due to amalgamation, which is reducing the leachability in the particle ranges with the highest concentration such as in case of soil type III.

7.1.1.1 Characterization of 'type I' soil

Sieve analyses with Buna soil from chlorine-alkali electrolysis H56 and L66 were performed with the test sieve sizes from 0.063 mm up to 8 mm. The mercury content was analysed for each particle group in both the original substance and in the leachate (DEV S4 test).

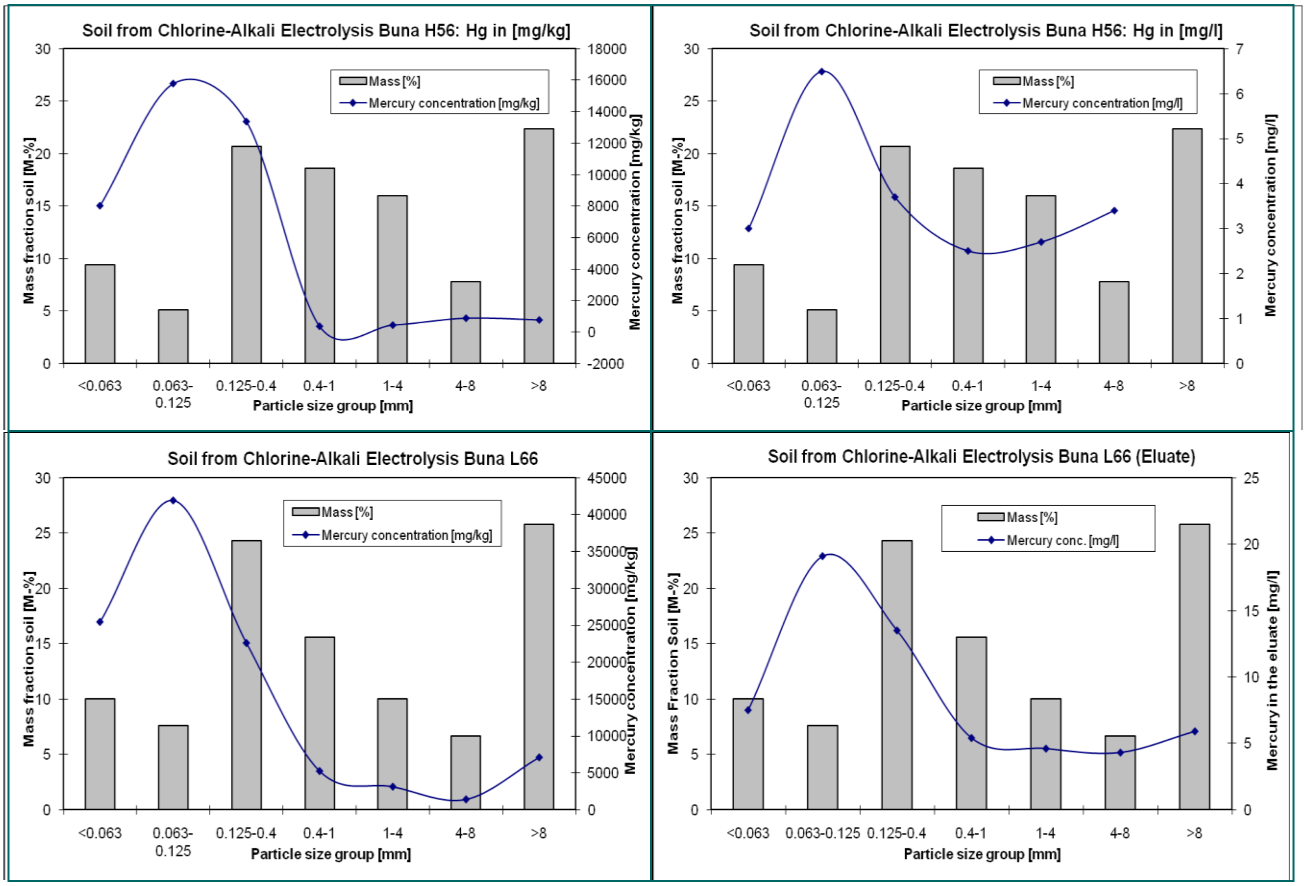


Figure 7-3: Mercury content and distribution vs. particle size in soil from Buna Chlorine Plants H56 and L66 based on orig. data from FIA Freiberg

Fig. 7-3 shows the sieve results as bars and the mercury analyses results as blue graphs. Particularly the right column shows the results analyzed from the original substance in [mg/kg] and the right side shows the mercury analyzed from the leaching test in [mg/l]. It can be shown that the highest mercury concentration was determined in the particle size group 63/125 μm and that the highest concentration corresponds to the highest leachability (solubility of in water).

Sandy soils from other remediation sites also show the highest mercury-concentration in the fine grain fraction such as from the old Lonza Works in Waldshut-Tiengen, which is a very sandy soil with a wide range of grain sizes. The comparison shows that even soils with a different mineralogical and physical characteristics showing the same pattern with regard to the concentration of mercury.

7.1.1.2 Characterization of 'type II' soil

Further wet sieve analyses with soil samples, was characterized by a high silt and clay content from the Yarraville chlorine-alkali electrolysis in Melbourne/Australia were performed with test sieve sizes from 0.075 mm up to 6.3 mm. The mercury content was analysed for each particle group in both, the original substance and in the leachate applying US EPA TCLP test (first row of fig. 7-4).

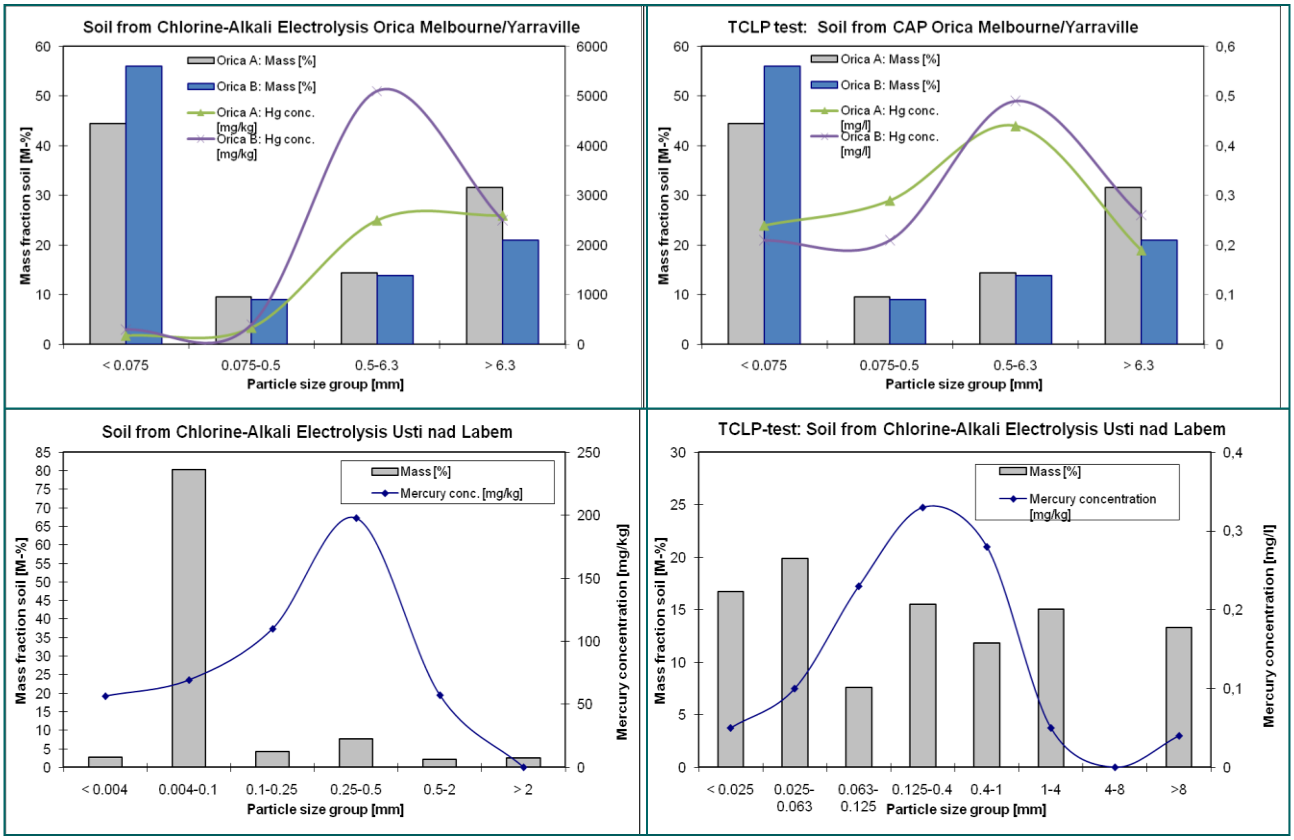


Figure 7-4: Mercury content and distribution vs. particle size in soil from Yarraville/Melbourne and Ústí nad Labem

Another type II soil sample from a chlorine-alkali electrolysis plant in Ústí nad Labem (Aussig a. d. Elbe, Czech Republic), was subject of investigation. As previously mentioned (DERMONT ET AL., 2007)[117] an on-site pilot soil washing test was performed in Ústí by the Czech company KAP, spol. s.r.o. in the year 2000 with soil material directly from the electrolysis area (next to sample bore hole J-12). The on-site investigation embraced a wet gravity separation test including a hydro cyclone and a centrifuge simulating gravitational separation[202]. Subject of these tests was also a survey with regard to sieving and mercury analysis data, where the left figure in the second row (fig. 7-4) is based on.

Another soil sample collected from a storage area associated to a treatment plant established on the site in Ústí was collected by the author in 2009. Wet sieving and TCLP tests performed concurring to the type II soil pattern are shown in fig. 7-4.

Petrographic investigations performed by KAP[166] conducted with soil from Ústí nad Labem shows that quartz (45 %) is the prevailing mineral species in the silt and fine sand range between 0.004 and 0.1 mm associated with the clay minerals montmorillonite (15%) and kaolinite (10%), but also with plagioclase feldspars, mica and calcite. In the clay particle size range montmorillonite is with 60% the dominant mineral.

7.1.1.3 Characterization of 'type III' soil

Figure 7-5 is showing a wet sieving analysis and the mercury concentration in both in the original substance and in the eluate performed with soil from the acetaldehyde factory F44 in Buna Schkopau:

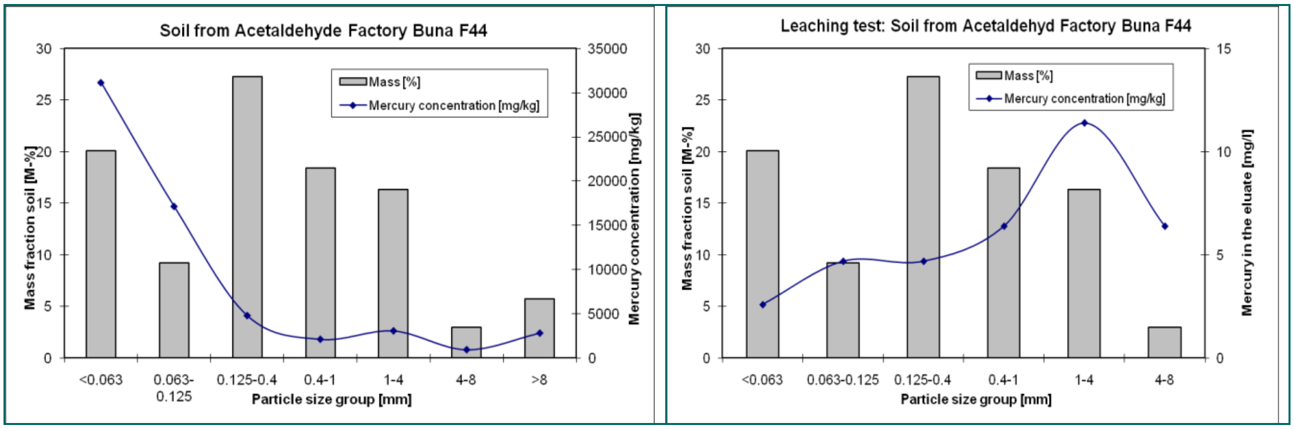


Figure 7-5: Mercury content and distribution vs. particle size in a soil sample from Buna Acetaldehyde Factory F44 (based on data from FIA Freiberg)

The contamination profile (fig. 7-5) of the wet sieving analysis deviates considerably from those of the chlorine plants from the same chemical site (fig. 7-3). The highest mercury concentration is obviously in the clay and silt particles size fraction < 63 µm. The peak with the highest solubility as performed by leaching test DEV S4 is not congruent with the particle size group of the highest concentration such as shown before for type I and type II mercury-contaminated soil.

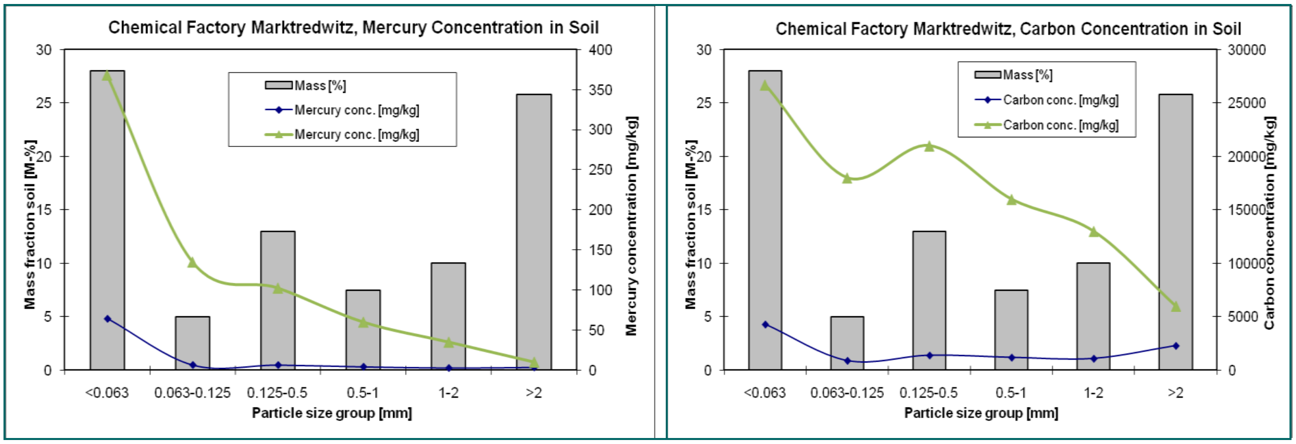


Figure 7-6: Mercury and carbon content vs. particle size distribution in a soil sample from the Chemical Factory Marktredwitz based on screening analyses performed by P. ZARBOK, 1999[203].

Fig. 7-6 is showing the results of soil investigations performed by P. ZARBOK, 1999 with material sampled from the Chemical Factory Marktredwitz[203]. The left side diagram shows mercury concentrations related to the grain size in good correlation to the sample from the acetaldehyde factory F44 Buna (fig. 7-5). Results of eluate or leaching tests from the CFM are not available. The right side diagram illustrates the concentration of carbon in the soil showing a certain correlation to the mercury concentration.

Owing to the contamination profiles all three soil types are capable for froth flotation. As a result of practical experience made in the past with some types of flotation apparatus, there is a technical restriction to a maximum grain size of 2 mm.

7.2 THE INFLUENCE OF ATTRITION AND DENSITY SEPARATION

In order to make soils more suitable for a treatment by froth flotation it is necessary to create the right separation cut, for example by hydro cyclones and/or to shift the maximum mercury concentration to a smaller particle size range via agitation/attrition, depending very much on the soil type (see above). Due to the high specific weight of mercury and with regard to an excessive content of coal detected in the soil, density separation had shown to be beneficial for Buna soil in preliminary tests (App. B-2).

7.2.1 Disintegration characteristics and effect of attrition (agitating mill)

Agitation as a method for processing minerals was first described in German language by O. Witt, 1906[204]. Schmidt and Rosenkranz introduced just recently a new washing drum as a more efficient disintegration device in an existing soil treatment plant[205].

7.2.1.1 Application of attrition in the Marktredwitz Plant

Attrition was also the main principle for the wet mechanical pretreatment in the Marktredwitz Plant. For the remediation of the CFM wastes, the worldwide first large-scale treatment facility for mercury-containing wastes had been erected outside of the Franconian district town Marktredwitz.

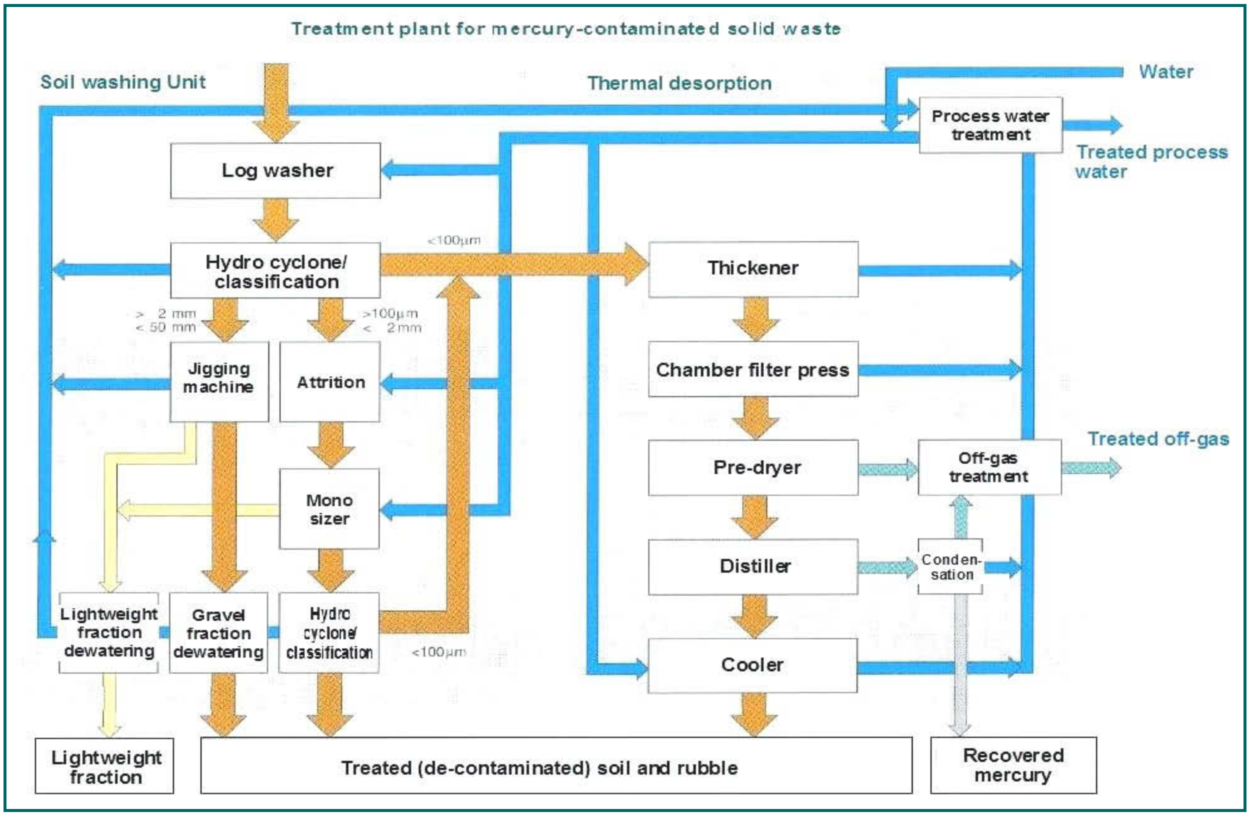


Figure 7-7: Process flow schematic of the soil treatment plant Marktredwitz (wet mechanical and thermal treatment)

This plant was a prototype, built for the first time on an industrial scale in order to remediate the materials from the dismantling, demolition and excavation of contaminated soil at the site of the two hundred year old (1788 – 1985) chemical factory in Marktredwitz including soil washing as a preliminary step to the thermal treatment, in order to reduce the throughput in the vacuum distillation. Within 2 years of operation 70,000 metric tons (77,000 US short tons) of rubble and soil was treated and 25 metric tons of mercury could be recovered.

The permitted facility design (fig. 7-7) comprised a cleaning stage for the sand and gravel fraction according to the Harbauer soil washing process, whereas attrition cells were used in order to transfer the contamination maximum to the finer particle size range. After undergoing repeatedly a hydro cyclone treatment, the overflow < 100 µm was subjected to the vacuum distillation. This consisted of a three-step rotary system, where solely the distiller and the cooling unit are operated under vacuum.

7.2.1.2 The influence of attrition on mercury-contaminated soils (type I and type III)

Investigations with regard to the effect of attrition on mercury-contaminated soil were also demonstrated with Marktredwitz soil by ZARBOK in1999[206]. Because the tests were performed with a 'type III' soil as shown in fig. 7-6, a further enrichment in the fines could not succeed. In the opposite it was observed, that after 25 min of attrition the mercury concentration in the dominant fine fraction 0.04 mm up to 0.125 mm was reducing from 223 [mg/kg] to 123 [mg/kg] and in the particle range smaller than 0.04 mm from 608 [mg/kg] to 422 [mg/kg].

This observation supports the accurateness of the soil categorization system as introduced in the previous section 7.1, but also questions the correct design with regard to attrition of the Marktredwitz soil treatment plant.

Another soil sample from the old Lonza Works in Waldshut-Tiengen (type I soil) was treated in an open agitating mill (see table 7.3) and showed a considerable enrichment of mercury in the finer particle size ranges. A significant enrichment in the fraction < 0.025 mm was perceived. After 30 minutes of attrition, 94% of the mercury which amount to around 20,000 mg/kg could be concentrated in the particle size group < 0.025 mm.

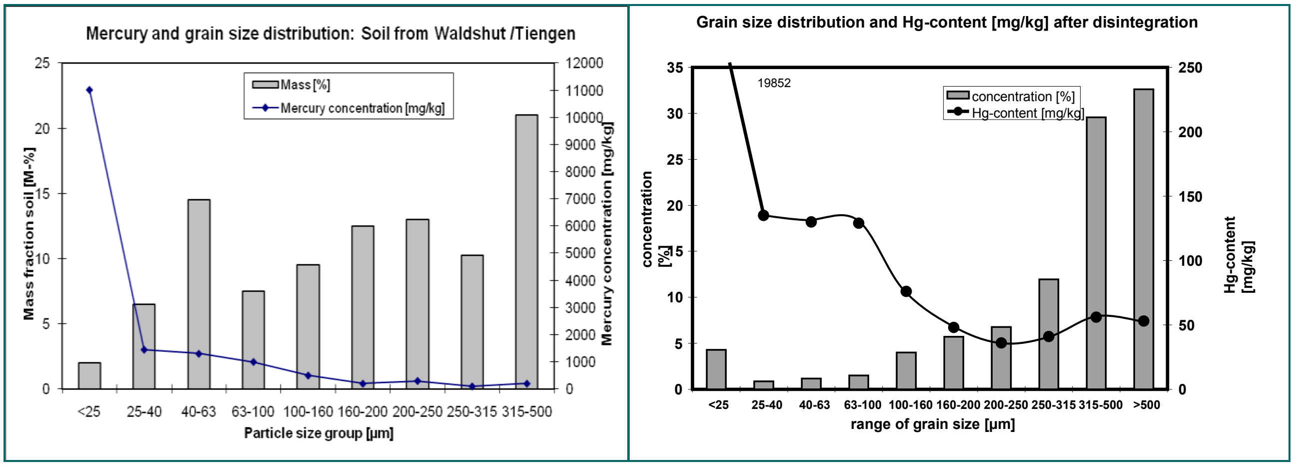


Figure 7-8: Grain size distribution and mercury concentration after a 30 minutes treatment in an agitation cell

After disintegration and proper sizing by hydro cyclone the enriched soil fraction ideally could be processed either by thermal desorption or by froth flotation. Results were recently published (RICHTER ET AL, 2008)[152].

7.2.2 Effect of Density Separation on mercury-contaminated soils

Particularly contaminated soils from chlorine alkali electrolysis facilities built before WWII contain regularly considerably high concentrations of carbon such as graphite from the electrodes and supplementary also carbon from other sources. Previously in fig. 7-6 the good correlation between Hg and carbon in the soil sampled from the CFM site already was shown.

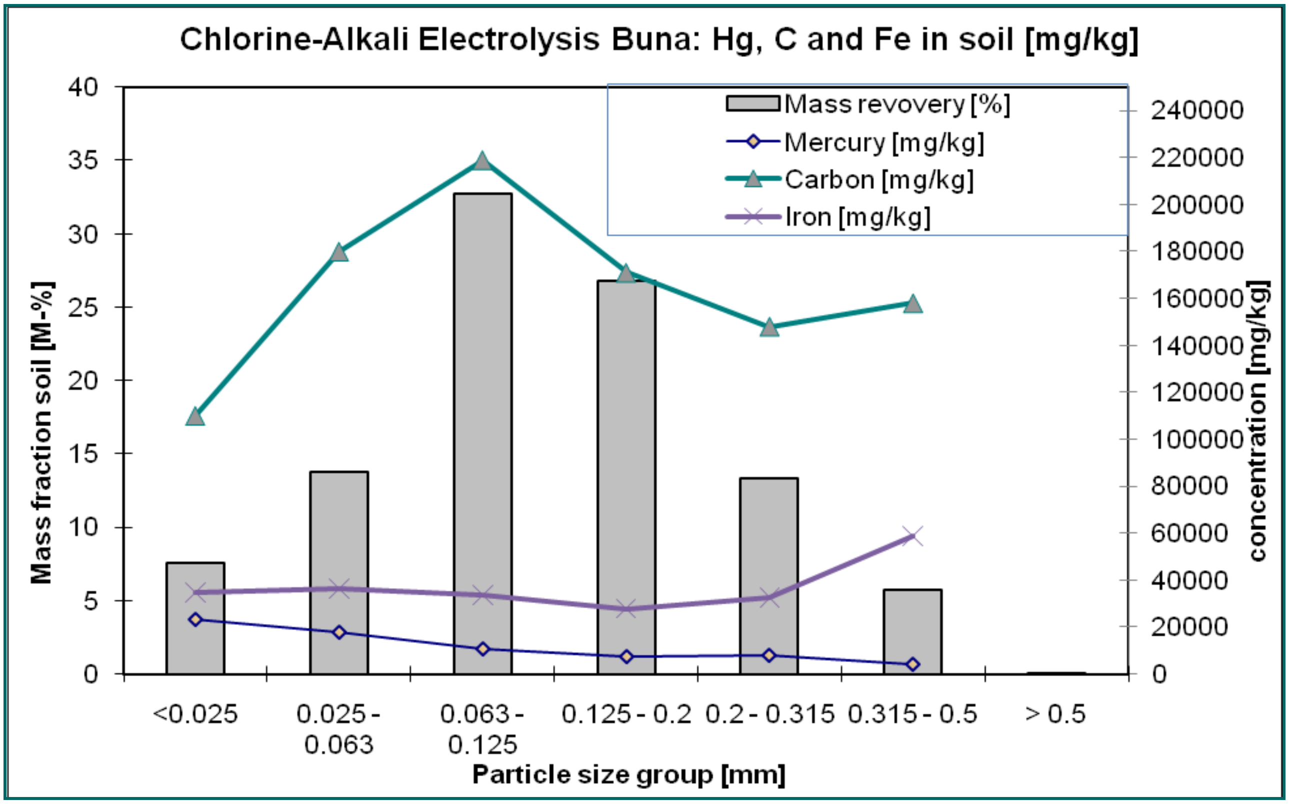


Figure 7-9: Concentration of Hg, C and Fe vs. particle size in Buna soil based on data analyzed at the TU Berlin

Pertaining to the relationship between carbon and mercury, Buna soil (fig. 7-9 above) shows a significantly weaker correlation than the CFM soil (fig. 7-6; right), which could be explained by the fact, that graphite is a less efficient adsorbent than coalified wood. Iron in soil can occur in various corrosion products such as in particular as hydroxides (Goetheite), oxides and carbonate and is also a possible adsorbent for mercury.

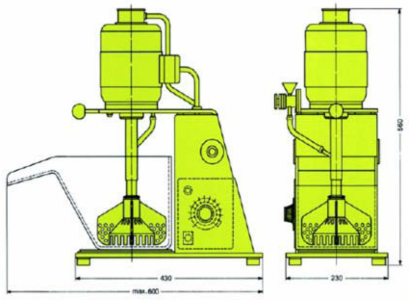
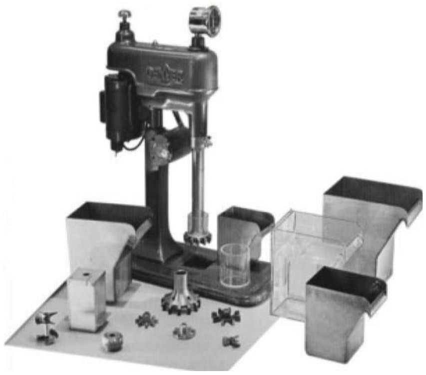
With the soil sample from Buna Schkopau as per fig. 7-9 a heavy liquid density fractionation test using sodium polytungstate aka SPT ($3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$) was performed for the particle size groups 63 up to 200 μm and 200 up to 500 μm. Almost 70 Mass-% of the entire mercury was found either in the highest (> 2.8 g/cm^3) or in the lowest density class (< 2.2 g/cm^3) representing beaded mercury partially adsorbed to iron and mercury due to adsorption to the carbon particles (App. B-2)[207].

Consequently the separation of the carbon is supposed to be a necessary process requirement in order to reduce the mercury concentration in soils and other solid wastes from chlorine alkali electrolysis plants and from acetaldehyde factories accordingly.

7.3 FLOTATION TESTS PERFORMED

For performing flotation and agitation tests the following shown machinery from different vendors was used:

Table 7-3: Flotation machinery used and conditions of experiments

Experiment/conditions	Technical date/specification	Sketch/drawing/photo of accessories
Preliminary flotation tests: Grain size range: 25-400 µm Hg = 1,000 mg/kg DM Pulp density: 200 g/l Variation of KAX (0 – 1,000 mg/kg) Variation: 6 ≤ pH ≤ 12	**KHD Humbold Wedag MN 935/5** • Year of fabrcation: 1987 • Agitator speed: n = 2,300-2,500 1/min • Volume of air: 190 l/h • Agitator measurements: Diameter 50 mm, height 8 mm Distance to the bottom 20 mm • Cell volume: 2 l • Electric power: 160 W	
Sulphidisation/flotation tests: Grain size range: 25-400 µm Hg = 800 mg/kg DM Hg = 1,000 mg/kg DM Hg = 1,200 mg/kg DM pH = 8 (const.) Pulp density: 200 g/l KAX = 400 mg/kg (const.)	**Denver D 12** • Year of fabrcation: 1987 • Agitator speed: n = 1,600 1/min • Volume of air: 190 l/h • Agitator measurements: Diameter 50 mm, height 8 mm Distance to the bottom 20 mm • Cell volume: 2 l • Electric power: 160 W	
Attrition (disintegration): Duration: 30 minutes Pulp density: 500 g/l	**Agitation mill with open vertical mineral barrel** • Agitatormotor: Bauknecht • Year of fabrcation: 1986 • Agitator speed: U = 900 1/min • Agitator measurements: Diameter 187 mm, height 284 mm Distance to the bottom 10 mm • Mineral barrel measurements: Diameter 248 mm, depht 445 mm	

7.3.1 Preliminary Flotation Tests with metal-contaminated Soils

Only a few investigations have been reported concerning flotation of heavy metal contaminated soils. The results were mostly insufficient for a further technical application (LANGEN, HOHBERG AND HAMACHER, 1996)[208].

7.3.1.1 Flotation Tests performed with lead and zinc-contaminated soil

Investigations were undertaken at the Technical University of Berlin into the flotation of heavy metal-contaminated soils using material originating from a former steel works and rolling mills plant in the inner city of Berlin, which was polluted with oxidized lead and zinc compounds (STAPELFELDT AND RICHTER, 1997 AND 2002)[118, 173].

Flotation could proceed successfully only after sulphidisation with potassium amyl xanthate (KAX), also often referred to as PAX as collecting agent. Lead recovery shows an optimum in the pH range between 9 and 11 and sodium sulfide concentration of 0.5 to 1.0 g/kg. The highest recovery of 73 % was reached at a pH value of 10 and a sodium sulfide concentration of 0.5 g/kg. The recovery and concentration of zinc decreased slightly with increasing pH as shown in App. C-1. The highest recovery of 44 % was achieved at pH 6 and sodium sulfide concentration of 0.5 g/kg.

7.3.1.2 Preliminary Flotation Tests performed with mercury-contaminated soil

Based on the experience gained with lead and zinc-contaminated soil flotation tests (see App. C1) pre-flotation tests were performed with an artificially mercury-contaminated soil of total Hg = 1000 mg/kg.

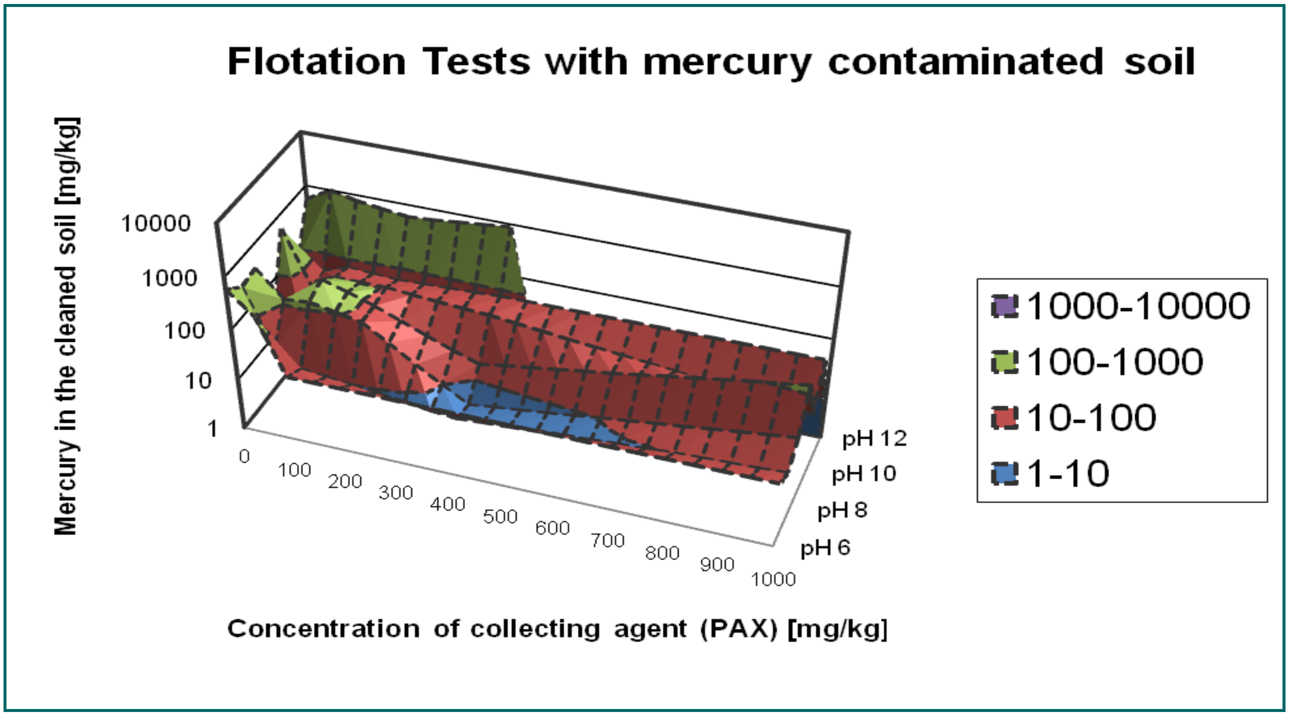


Figure 7-10: Preliminary flotation tests performed with a variation of collector (Potassium Amyl Xanthate) and pH

Without any sulphidisation the best decontamination results were achieved at pH 8 up to 9 and a collector dosage of KAX in a range of 400 ± 100 [mg/kg] (see fig. 7-10). Since the results are not easily transferable to all types of chlorine plant soils a flotation method based on sulphidisation will be developed as the main emphasis of this thesis.

7.3.2 Soil preparation for flotation tests and flotation program

In order to further facilitate comparable results the following flotation test soils were prepared artificially, containing 800 mg/kg, 1,000 mg/kg and 1,200 mg/kg of elemental mercury, simulating a type I mercury-contaminated soil. A minor amount of calomel Hg_2Cl_2 in a range of 50 mg/kg was also added to simulate a chlorine plant soil and to get closer to the solubility conditions in fig. 6-4.

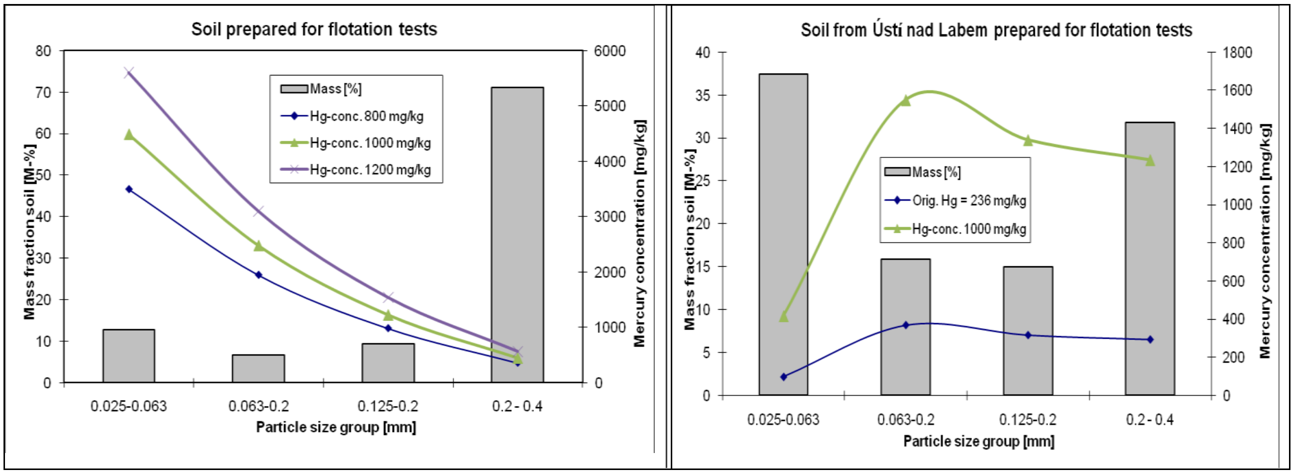


Figure 7-11: Test soil with 3 different degrees of Hg-contamination and test soil from Ústí nad Labem

Table 7-4: Test soils prepared for flotation tests containing 800 mg/kg, 1,000 mg/kg and 1,200 mg/kg mercury

Particle size [mm]	Weight pass [g]	Weight pass [%]	Art. Hg-cont. 800 [mg/kg]	Art. Hg-cont. 1000 [mg/kg]	Art. Hg-cont. 1200 [mg/kg]
0.025 – 0.063	15.76	12,85	3500	4490	5600
0.063 – 0.125	8.20	6,69	1950	2482	3100
0.125 – 0.200	11.50	9,38	985	1230	1540
0.200 – 0.400	87.20	71,09	360	450	565
total	**122.66**	**100**	**800**	**1000**	**1200**

Table 7-5: Soil from Ústí nad Labem prepared for flotation tests

Particle size [mm]	Weight pass [g]	Weight pass [%]	Orig. Hg-cont. [mg/kg]	Art. Hg-cont. [mg/kg]
0.025 – 0.063	52.20	37.40	98	415
0.063 – 0.125	22.20	15.88	368	1550
0.125 – 0.200	21.00	15.02	316	1340
0.200 – 0.400	44.40	31.76	293	1235
total	**139.80**	**100.06**	**236**	**1000**

In parallel also soil from a currently ongoing mercury remediation project, which was sampled by the author on the location in Ústí nad Labem was prepared considering the original contamination and some supplementary mercury was added in order to reach a comparable level to the purely artificially generated test soil (see Fig. 7-

11, right and tab. 7-5).

The flotation tests were performed within a standard Denver D 12 laboratory flotation machine at a constant rotation speed of 1,600 [1/min] in a 2 liter glass cell. The only varying parameter is the sulphidisation agent. Based on preliminary tests, 'Sodium-Dimethyldithiocarbamate' (SDDC aka Na-DMDTC), which was added in concentrations between 0.5 g/kg and 8 g/kg was found most suitable.

Table 7-6: Flotation program (Course scheme of the flotation tests)

Step/activity performed	**Description/used reagent**	**Duration [s]**
Dispersing	400 g of soil of a grain size range 25-500 µm is dispersed in a 2 l flotation cell (pulp density 200 g/l)	120
Sulphidisation	Na-DMDTC[liv] is added in concentrations between 0.5 g/kg and 8 g/kg (pH neutral)	900
Addition of collector	KAX = 400 mg/kg (const.)	120
pH adjustment	adjusted in a range of pH = 8	-
Addition of frother	Flotanol D 12 was added drop wise (appr. 0.1 g/kg)	20 approx.
Flotation	Flotation started, when froth developed	300
Dewatering effluent	Effluent containing Hg sulphide was dewatered in a suction strainer supported by a water-jet vacuum pump using a standard laboratory round filter	-
Drying of tailings after screen dewatering	Pre-drying occurred under the fume cabinet slowly over night. Afterwards for 1 h in the drying oven at 42 °C.	12 h
Weighing and packing of samples	Weighing was performed on a Mettler laboratory high precision scale and samples packed for analysis afterwards	-

A photo documentation showing the above described activities is attached to this thesis in Appendix C-2.

[liv] Brands of DMDTC used: EPOFLOC L1 and Metalclean-B

7.3.3 Results of flotation tests and discussion

The results of the flotation tests are listed in Appendix C-1. Already during the performance of the tests mercury sulfide could be detected visually as black amorphous particles (see Appendix C-3: fig. C3-2 and fig. C3-3) given already an impression whether the tests were successful or not.

The best test result with regard to mercury in the original substance could be achieved with a DMDTC sulphidisation dosage of 2 g/kg (B1BEP2)[lv]. Here the mercury concentration in the mercury-contaminated soil sample could be reduced **from Hg = 1000 mg/kg to Hg = 4 mg/kg**, only.

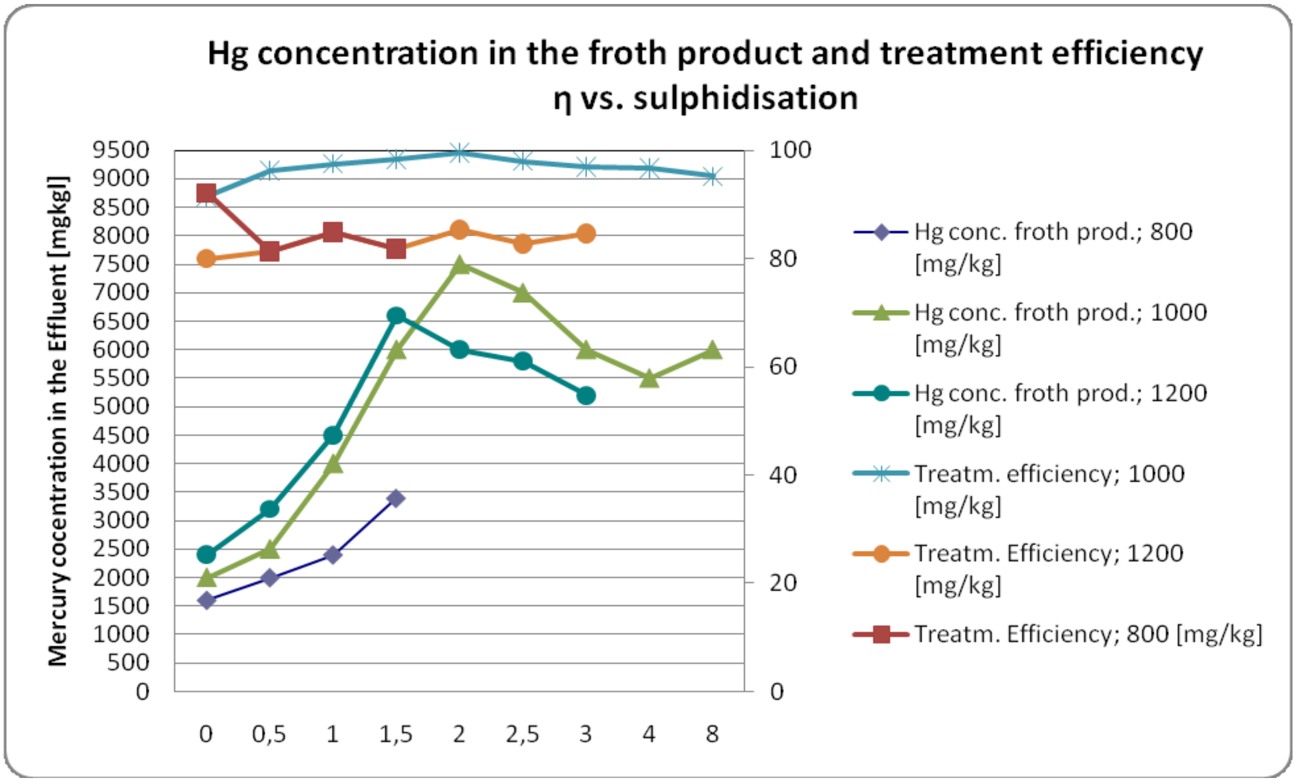


Figure 7-12: Mercury concentration in the froth product and treatment efficiency vs. sulphidisation

The highest treatment efficiency with **η = 99.6 %**, as shown in fig. 7-12 (above), could be reached within the test row B '**Hg = 1000 mg/kg'** with a DMDTC sulphidisation dosage of 2 g/kg, accordingly. Here also the highest concentration of mercury in the froth product could be achieved. The maximum is also matching with the TCLP test results in fig. 7-13.

Other results of the same test row show values merely above the threshold value Z2 as per German LAGA (10 mg/kg). The treatment efficiency of the higher contaminated test row D 'Hg = 1200 mg/kg' is in all points considerably lower. Since the laboratory flotation was performed only in one single cell, it is most likely that a common cell to cell flotation in a row, implemented in a soil washing plant with 6 or more cells, would lead to a higher degree of decontamination and therefore to better results.

It also could be demonstrated along with the test row C 'Hg = 800 mg/kg', that different brands of DMDTC agents also show different sulphidisation characteristics.

[lv] Based on the content of solids in the pulp

7.3.3.1 Interpretation of TCLP test results

To verify the applicability of the ‘new flotation process’ presented in this thesis the tailings of all tests rows were undergoing a Toxicity Characteristic Leaching Procedure (TCLP) as per EPA Test Method 1311.

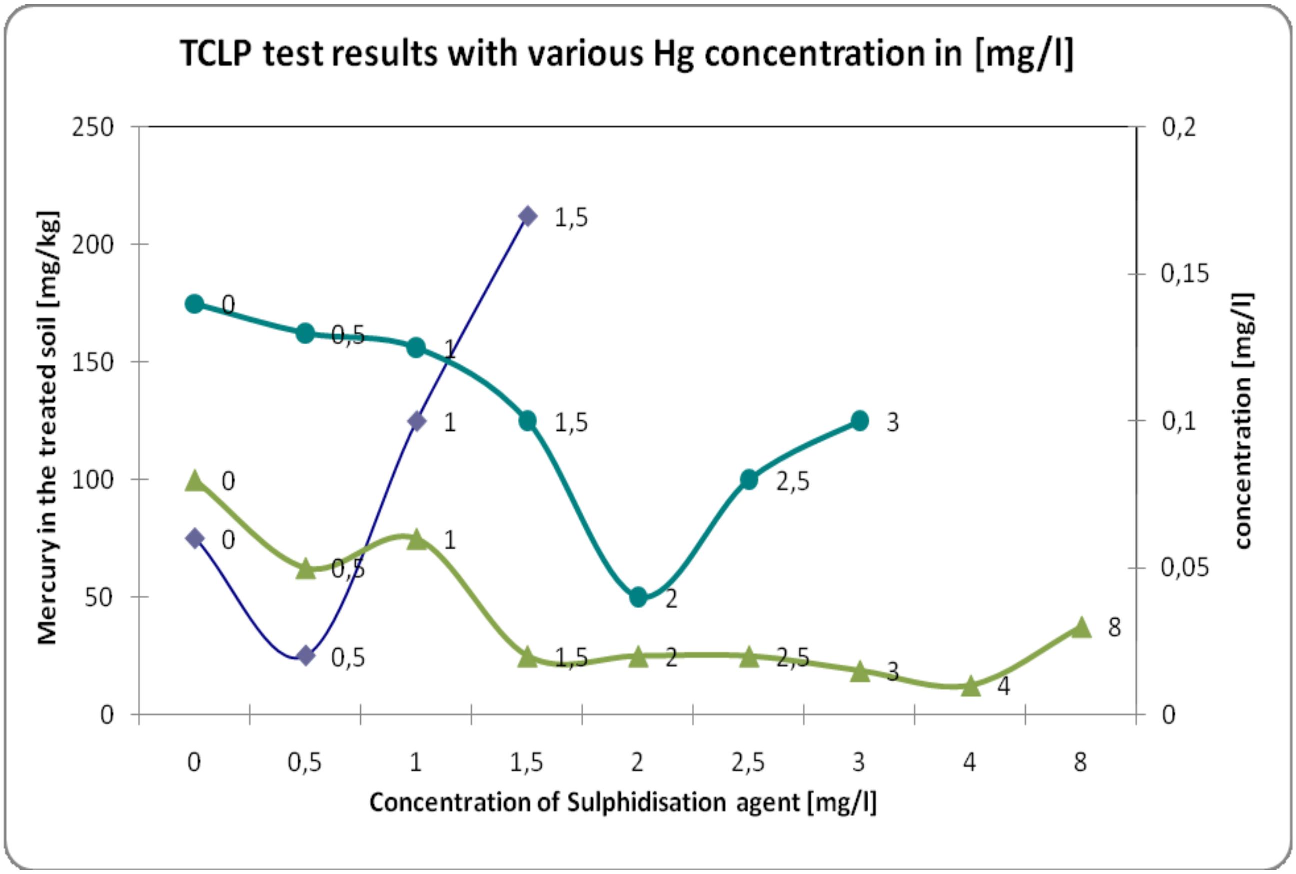


Figure 7-13: TCLP test results performed with the treated soil (tailings) of all three test rows performed (green; test row B: 1000 mg/kg; purple; test row C: 800 mg/kg and turquoise; test row D: 1200 mg/kg)

Referring to fig. 7-13 it can be demonstrated, that the flotation tests performed are entirely successful, because of not exceeding the associated D-list parameter for mercury (Hg = 0.2 mg/l) in any single result[lvi].

It has to be noted, that the slightly deviating graph of test row C (purple line), presenting an original contamination of Hg = 800 mg/kg, was performed with another sulphidisation agent than tests rows B and D.

[lvi] Since the TCLP test is characterizing hazardous waste via toxicity, hazardous waste could be transformed successfully in non-hazardous waste

7.3.3.2 Interpretation of flotation test performed with soil from Ústí nad Labem

The test soil from Ústí nad Labem, with a content of fines (silt and clay) in a range of almost 40 M-% (see table 7-5), which was chosen to demonstrate a practical application is under normal conditions not capable for a treatment in a soil washing process. That is the reason why currently a thermal treatment is used on the site. With the original contaminated soil a decontamination effect from originally Hg = 236 mg/kg to 26 mg/kg could be achieved, which is just below the site treatment limit of 30 mg/kg.

The flotation test with the artificially increased mercury concentration (see fig. 7-11, green curve right side) could not fully succeed, since the decontamination effect from 1000 mg/kg to 126 mg/kg is not efficient compared to a threshold value of 30 mg/kg as demanded by the contract and the environmental authorities. On the other hand the same sample passed the TCLP test accordingly. Consequently the result would be sufficient in most all projects where a final disposal as per US EPA rules is allowed.

7.3.3.3 Technical verification of the sulphidisation/flotation process for high mercury waste

In consequence of the reasoning described in sections 3 and 6 above, one of the most important premises for the successful flotation of mercury and its compounds, in particular their sulfides is, that the mineral itself shall be more soluble than the metal xanthate generated during the flotation process itself. It is understood that the larger the difference in solubility is, the more efficient the flotation process will proceed.

Fact is that the metal xanthates shown in the tab. 6-4 are entirely less soluble than their associated sulfides. The application of flotation of these metal sulfides by using xanthates requires necessarily oxidation or in cases of sulphidisation the generation of soluble metal sulfide species such as shown especially for mercury in tab. 6-3 and in fig. 6-4.

Since the sulfur mercuric ion HgS_2^{2-} with a solubility product in a range of about 200 [$(mol/l)^3$] seems to be the most promising candidate, sulphidisation but also the use of xanthate as collecting agent is most efficient in a pH range of around 8, because the solubility of bisulfide (HS^-) reaches its maximum value also here. Consequently during the sulphidisation/flotation process more mercury is going into solution than in other common flotation processes.

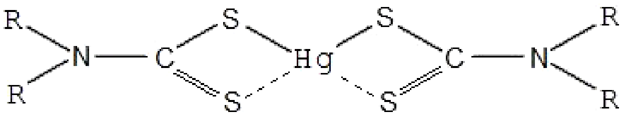
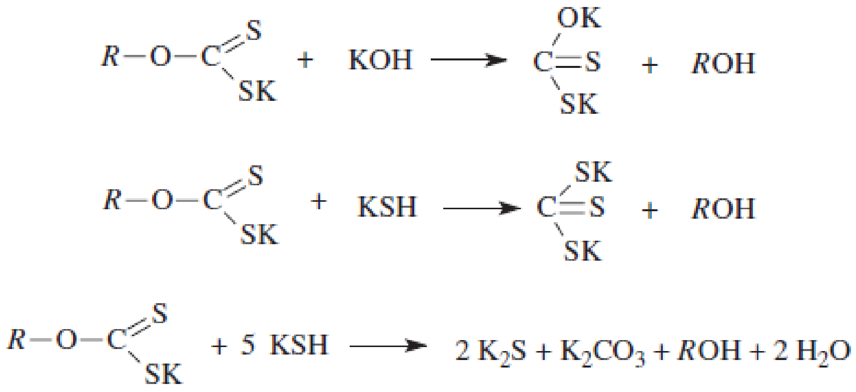


Figure 7-14: mercury(II) bis dithiocarbamate complex $Hg(S_2CNR_2)_2$ (after Tieking)

For the sulphidisation Sodium-Dimethyldithiocarbamate (SDDC) aka DMDTC was added in varying concentrations starting at a neutral pH of around 7, where already a dissociation of the entirely water soluble SDDC molecule $NaS_2CN(CH_3)_2$ occurs.

Dissociation products such as carbon disulfide CS_2, sodium sulfide Na_2S[lvii] and thiourea $SC(NH_2)_2$[209] are able to react strongly with the mercury. Considering a raise of the pH up to a range of 8 may allow the formation soluble sulfur mercuric ions as already postulated.

[lvii] The dissolution of SDDC is attended by an increase of the pH. The final pH adjustment was done by addition of caustic soda. So the formation of sodium sulfide Na_2S is definitely possible.



(7-1)

In case of a direct reaction of the Sodium-Dimethyldithiocarbamate with mercuric ions square planar mercury (II) bis dithiocarbamate complexes of the general formular $Hg(S_2CNR_2)_2$ with a similar quasi symmetric structure as the class b metal xanthates shown in tab. 6-5 maybe formed as well.

Whilst the sulphidisation agent is relatively stable at higher values of the pH, the collecting agent Potassium Amyl Xanthate at higher pH values (in alkaline solution) xanthates dissociate by splitting of an alcohol[210].

This example shows why the application of alcoholic frothers is very much compatible to xanthates even in higher pH ranges. On the other hand the necessary formation of water insoluble square planar class b metal xanthate complexes may not be easily possible. For that reason the pH for the mercury flotation process introduced in this thesis shall be restricted to a range between 8 and 9.

The advantages and benefits of the of the sulphidisation/flotation process for high mercury waste are:

- Efficient decontamination of high mercury solid wastes in a contamination range up to 1000 mg/kg
- Transformation of even highly toxic organic mercury compounds into leach-stable insoluble mercury xanthate complexes capable for disposal or a downstream solidification/stabilization
- Sulphidisation of all mercury compounds in the sand fraction and in the froth product occurs, forming materials with low solubility characteristics
- Technology is applicable for a required particle size range of 500 µm in accordance with the selection of the flotation cell type
- In certain ranges the froth product mercury(II) xanthate may even be capable for a further treatment by solidification

8 IMPLEMENTATION OF FLOTATION IN SOIL WASHING PLANTS

Some of the existing soil washing facilities in Germany had been upgraded during the past 15 years with the intention to treat much more complex and more highly contaminated wastes in accordance with technical and economic requirements of the market.

Table 8-1: Summary of the processing targets of soil washing plants and the plant components[lviii]

Plant Component	Processing target
1. log washer 2. wash drum 3. agitation reactor 4. attrition cell	Disintegration, de-agglomeration and removal of surface-adhering contaminants from soil particles by means of multi-stage energy introduction
5. hydro cyclone 6. classification screen 7. centrifuge (decanter/tricanter) 8. spiral classifier	Separation of contaminated fractions by classification processing steps
9. jigging machine 10. upstream sorter (mono sizer) 11. froth flotation (agitator cells) 12. pneumatic flotation 13. sorting drum 14. spiral separator 15. (shaking table)	Systematic selective separation of contaminants by sorting processes
16. rinsing by water spray nozzles 17. counter-stream hydro cyclones 18. mono sizer	Displacement of contaminated interstitial water surrounding the soil particles by rinsing and draining procedures
19. thickener 20. coagulator 21. lamella separator	Solid/liquid separation
22. chamber filter press 23. belt press 24. vacuum drum filter	Dewatering of contaminated ultra-fine particle fraction
25. precipitation 26. sand filter 27. activated carbon filter	Water purification for the removal of contaminants dissolved in the process water

As it was already highlighted in section 5 above, none of the currently existing soil washing plants is permanently reliable for high mercury wastes (soil/rubble) in a range up to 1,000 mg/kg.

The results presented in section 7 have been proven, that flotation as a treatment option in particular with simultaneous sulphidisation is capable to provide a solution in a particle size range up to 0.5 mm.

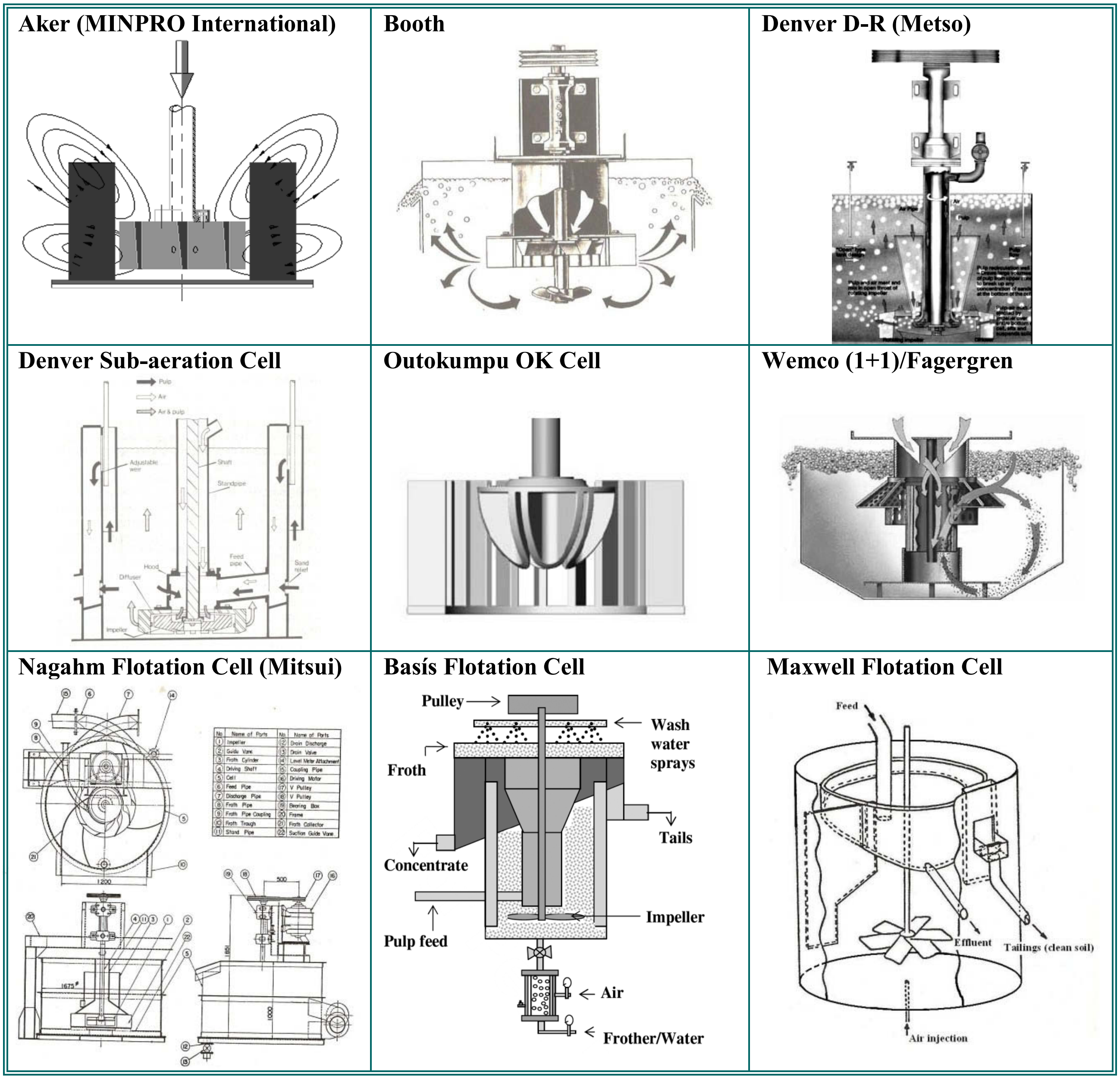
[lviii] Table 8-2 is a continuation of a table first established by W. Gröschel (Harbauer GmbH & Co. KG) in 1993

8.1 FLOTATION CELL SELECTION

This section reviews various types of commercial flotation machines and their working principles. In general all currently used flotation apparatus can be divided in two main groups: mechanical and pneumatic machines.

8.1.1 Mechanical Flotation Cells

Mechanical flotation apparatus are mostly equipped with an agitator. Various designs are available provided by a number of vendors using either the 'forced air' or the 'self aspirating' principle.



Aker (MINPRO International)

Booth

Denver D-R (Metso)

Denver Sub-aeration Cell

Outokumpu OK Cell

Wemco (1+1)/Fagergren

Nagahm Flotation Cell (Mitsui)

No	Name of Parts	No.	Name of Parts
①	Impeller	⑫	Drain Discharge
②	Guide Vane	⑬	Drain Valve
③	Froth Cylinder	⑭	Level Meter Attachment
④	Driving Shaft	⑮	Coupling Pipe
⑤	Cell	⑯	Driving Motor
⑥	Feed Pipe	⑰	V Pulley
⑦	Discharge Pipe	⑱	V Pulley
⑧	Froth Pipe	⑲	Bearing Box
⑨	Froth Pipe Coupling	⑳	Frame
⑩	Froth Trough	㉑	Froth Collector
⑪	Stand Pipe	㉒	Suction Guide Vane

Basís Flotation Cell

Maxwell Flotation Cell

Figure 8-1: Overview of currently used mechanical flotation cell designs (POLING[211], WILLS[212] and PARGA ET AL.[213])

The main function of the agitator (impeller) in all the different designs is:

- To generate bubbles in sufficient amount and size
- To provide a turbulent zone required for the collision and the attachment of the bubbles to the particles
- To disperse the particles in the pulp and to keep them in suspension
- To avoid sanding-up, in particular in the corners of rectangular cells

In some of the in fig. 8-1 shown mechanical flotation machines the impeller is also providing:

- The self-aeration by creating a vacuum and induce air via the standpipe into the pulp
- The cell to cell transport of the pulp (Denver sub-aeration type)
- A certain attrition effect which is considerably high provided by the centrifugal pump type Denver impellers

In the past 30 years the market for mineral processing equipment was undergoing a consolidation and various equipment suppliers merged together, were taken over by competitors or the production of certain machinery was suspended. Because of this many good and proven cell designs have been disappeared from the market. Therefore well known brands such as Sala flotation machines, using a shallow, relatively large turbine-type impeller and providing the air via the standpipe already as bubbles, Galigher's Agitaire cell and the Humboldt Wedag cell are not included in fig. 8-1.

The flotation cell shape itself was also subject of various modifications over the decades started from originally rectangular cells such as Aker, Galigher-Agitaire, Booth, Denver, Sala and Wemco, via the U-bottom shaped Outokumpo cell to cylindrical cells and finally to tank cells[214]. The size was also subject of permanent modification. In particular in the mid 1975s a trend to large-capacity cells was predominant[215, 216].

8.1.2 Pneumatic Flotation Cells

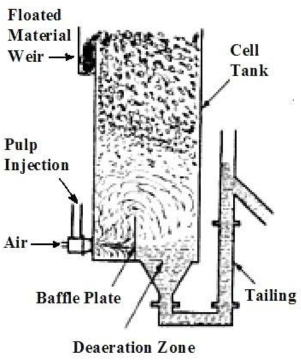
Even considering the 'Callow cell' or the 'Forrester air-lift machine' as a forerunner, most authors claim, that the first application of a pneumatic cell was performed by William DAVIS at Conzinc Rio Tinto of Australia Limited (CRA). This new flotation equipment was called therefore 'DAV-CRA' cell (see fig. 8-2) and was first applied in a zinc mine of the Australian Broken Hill Mining District in the 1960s[217]. The difference to earlier developed technologies was that not only the air, but also the pulp was injected into the cell under pressure by means of a nozzle at the bottom. The injected pulp was separated from the de-aeration zone and the release of the tailings by a straight vertical baffle plate in the middle of the cell tank (fig. 8-2).

In Germany the invention and the development of pneumatic flotation cells are intimately connected with the names of WOLFGANG SIMONIS[lix], ALBERT BAHR[lx] and RAINER IMHOFF. The original objective was to find a more efficient flotation technology for very fine coal and ore particles, which could not be treated successfully by common agitator cells. A patent was applied by SIMONIS and his coworkers in association with KHD for his 'free jet flotation' (Freistrahlflotation) in 1981[218] and in the same year by BAHR for the 'Bahr cell'[219].

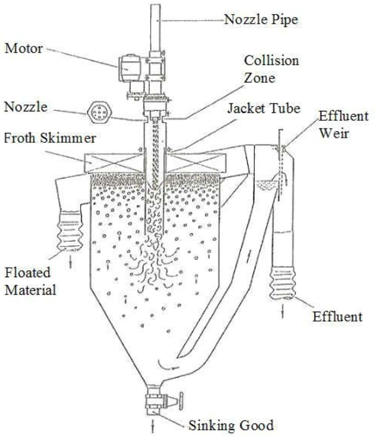
[lix] **Prof. Dr.rer.nat. Wolfang Simonis** (1927-2009), Chair of mineral processing and refinement (Aufbereitung und Veredlung) at the Technical University Berlin until 1992

[lx] **Prof. Dr.-Ing. Albert Bahr** (†),Chair of mineral processing at the Technical University Clausthal

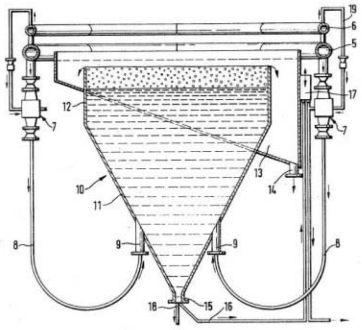
Davcra Cell (Rio Tinto) – 1966[212]



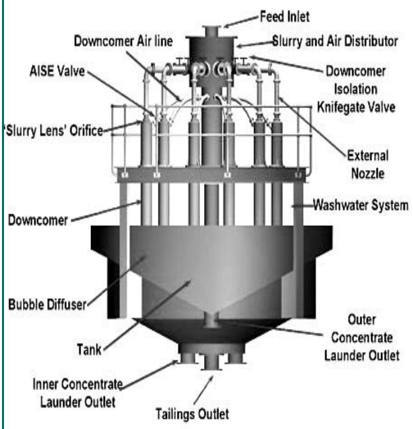
Free Jet Cell (Simonis/KHD) 1981[218]



Bahr Cell – 1981[219]

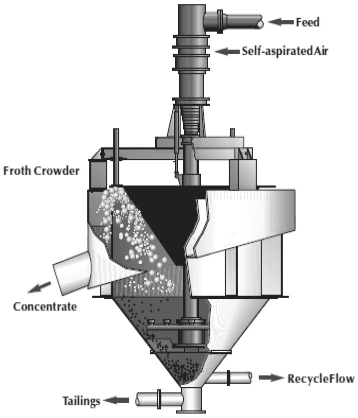


Jameson Cell – 1989



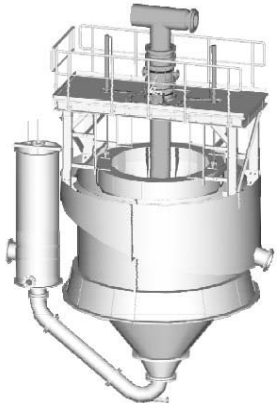
Source: JamessonCell.com

Imhoflot V-cell – 1996[223]

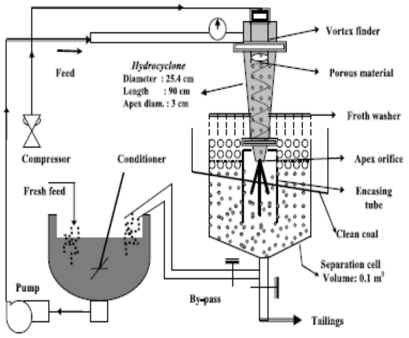


Imhoflot G-cell – 2006[222]

Pneuflot (Humboldt Wedag)[226]



LM Cell (Cheng Xinghua) – 1997[227]



ULF Flotation Cell (Suša) – 1997
(Source: Dr. Janez Suša[229])

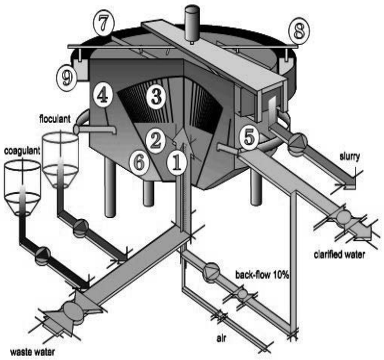


Figure 8-2: Overview of currently used and recently developed pneumatic flotation cell types

IMHOF as a former pupil of Prof. Bahr at the Technical University of Clausthal/Germany continued developing the pneumatic flotation technology and had notable influence on the design of the cells of EKOF, KHD and Allmineral. In a close cooperation with the mining industry in Chili he created his own trademark 'IMHOFLOT'[220, 221] and in 2006 a US patent was granted to him for the G Cell[222], currently commercially distributed by Maelgwyn Mineral Services, UK[223].

Figure 8-2 doesn't claim to be complete and includes mainly the cell types mentioned in the text before. Besides this, it also shows the 'Jameson Cell', developed by Prof. GRAEME JAMESON at the University of Newcastle/NSW (Australia) and the Mt. Isa Zinc Mines (now Xstrata Queensland Ltd.)[224, 225] but also the 'Pneuflot' flotation cell of Humboldt Wedag, which is a derivate of the Bahr cell, as it was first built by EKOF in Bochum. The entire line of business was later transferred from EKOF to KHD, holding also the patent of the free jet flotation with Prof. Simonis. Here the cell was undergoing individual improvements leading to the 'Pneuflot' flotation cell, today dealt with by Humboldt Wedag[226]. Fig. 8-2 shows that all recently designed cells have a 'central downcomer', as it was first introduced by Prof. W. SIMONIS.

Under the strong influence of the new development of pneumatic flotation cells in Germany in the late 1980s, in particular the Harbauer soil washing plants in Berlin and Vienna, where equipped in an early stage with pneumatic cells and not with mechanical cells such as the Dutch plants, already mentioned before. The experience with pneumatic cells in soil washing plants has demonstrated that pneumatic cells as a stand-alone device are:

- Not capable for the treatment of coarse sand particles because of the permanent risk of sanding and
- sensitive for frequently occurring changes in pulp density and in the concentration of contaminants.

An interesting development in the recent years is the LM Cell invented by CHENG XINGHUA in 1997. The idea is to release the pulp directly via hydro cyclone underflow in the pneumatic cell. This technology recently was applied to ultra fine coal[227]. Most probably this design could be easily adapted for an application in soil washing plants as well.

Not listed in the systematic of fig. 8-2 are flotation water treatment devices such as dissolved air flotation cells, aka DAFs, since they are not easily applicable for pulps with a high content of solids.

An exception was made in this thesis for the newly developed ARCANOE® uniform laminar flow flotation (ULF) using an inductive dispersing nozzle (IDN), invented by JANEZ SUŠA, which is already patented in Europe in 1997 and in the US in 2000[228]. Since most of the mechanical and pneumatic cells are designed more or less empirically with regard to flow conditions inside the cell, the ULF flotation apparatus is calculated for a constant laminar flow not exceeding a Reynolds number (Re) of 2000. The flotation plant for waste water treatment comprises an intake installation (1), a flocculation section (2), a lamination section (3), a separating section (4), a water discharge installation (5), a sedimentation section (6), a slurry collecting section (7), a slurry scraper (8), a trough for the slurry and pushers for conveying the same (9).

Compared to DAF type water treatment systems the costs for installation, energy and maintenance are claimed to be by 50% lower. Since the ULF cell is proving a certain flow in order to keep particles in suspension the device could be beneficial for an application in soil washing plants for example as a cleaner device in combination with other cell types[229].

8.2 TECHNICAL IMPLEMENTATION AND SIZING

In Central Europe the market for the erection of ‘new soil washing plants’ is currently restricted, owing to the competition between the soil washing centers and the low-cost landfill operating companies and cheap pseudo soil washing plants is stopping at present any beneficial expansion. Only plants where the period for amortization of investment is already finished are able to compete on the market. Therefore most of the previously described plants in Austria and Germany have reached an age of about 20 years and more. Two scenarios for the implementation of the described mercury treatment process are feasible:

- Upgrading of existing soil washing plants to increase the applicability for metals (mercury)
- Design of a ‘specific mobile soil washing plant’ applicable for on-site treatment of mercury waste

8.2.1 Implementation of a flotation in a soil washing plant in Berlin

As already described above, in Austria and Germany new soil washing plants are not going to be built very soon. So ‘upgrading’ is the more likely option such it was already performed in the soil washing centre Berlin-Gradestrasse for PAH-contaminated soil from tar and roofing felt factories by RICHTER, SCHMIDT ET AL., 1997[lxi, 165].

The successful implementation of a PAH flotation was based on the following design requirements:

- Mineral content in the pulp: approx. $250 < \kappa < 300$ [g/l]
- Particle size max. 2 [mm][lxii]
- Feeding directly from hydrocyclone underflow into the flotation unit
- Cell-to-cell transport required by self aspirating impeller type
- Entire throughput (mass flow) of solids: $\dot{m}_s \leq 15$ [t/h]
- Attrition effect desired owing to adherence of contaminants on the mineral grain
- Contamination: Polycyclic aromatic hydrocarbons in a range of PAH (EPA) ≤ 20,000 [mg/kg]
- Synchronized discharge of the treated sand from the last cell (squeeze valve)

The maximum required pulp volume flow $\dot{V}$ based on the mineral content κ is:

$$\dot{V} = \frac{\dot{m}_s}{\kappa} = \frac{15[t/h]}{0,3[t/m^3]} = 50[m^3/h] \tag{8-1}$$

Based on this requirement the cell size was calculated as follows:

Discharge of the treated sand:	$35[m^3/h]$	(8-2)
<u>Effluent (froth product):</u>	$\underline{6[m^3/h]}$	
Required entire cell volume:	$9[m^3/h]$	

[lxi] The implementation of mechanical flotation cells in the soil washing plant Berlin-Gradestrasse with regard to necessary PAH-treatment requirements was entirely planned and supervised by the author.

[lxii] Because of adherence of the contaminant to the grain it was necessary to treat the entire sand fraction by flotation.

<u>Selection:</u> A row including 6 cells of 1.5 [m^3] each, considering a residence time of 1 hour.

To fulfill also the requirements of necessary attrition and cell-to-cell transport a Denver type sub-aeration cell was selected which was available on the market in a size of 1500 liters from the vendor SKET (fig. 8-3).

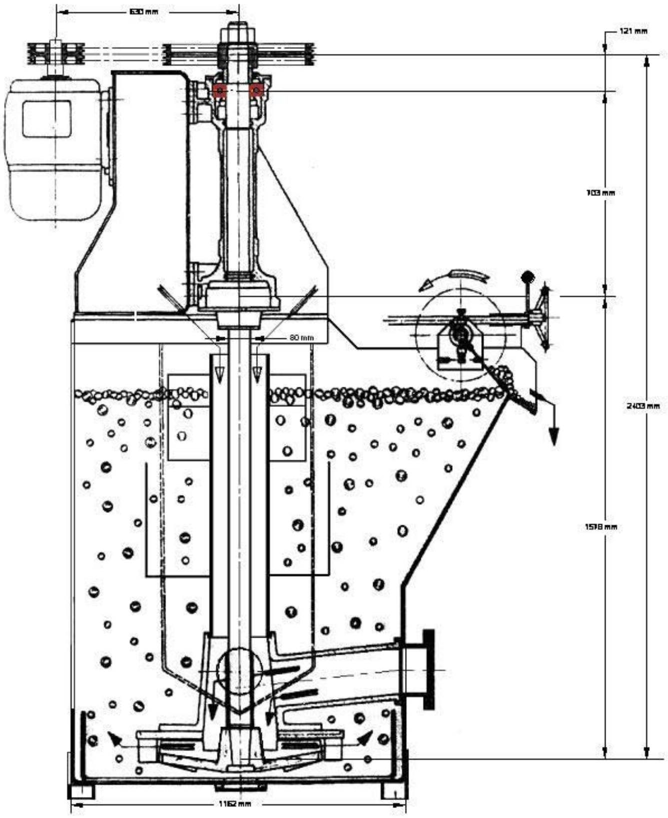


Figure 8-3: Modified 1,500 liter Denver type sub-aeration machine of the German vendor SKET used successfully as a PAH flotation device in the soil washing plant Berlin-Gradestrasse

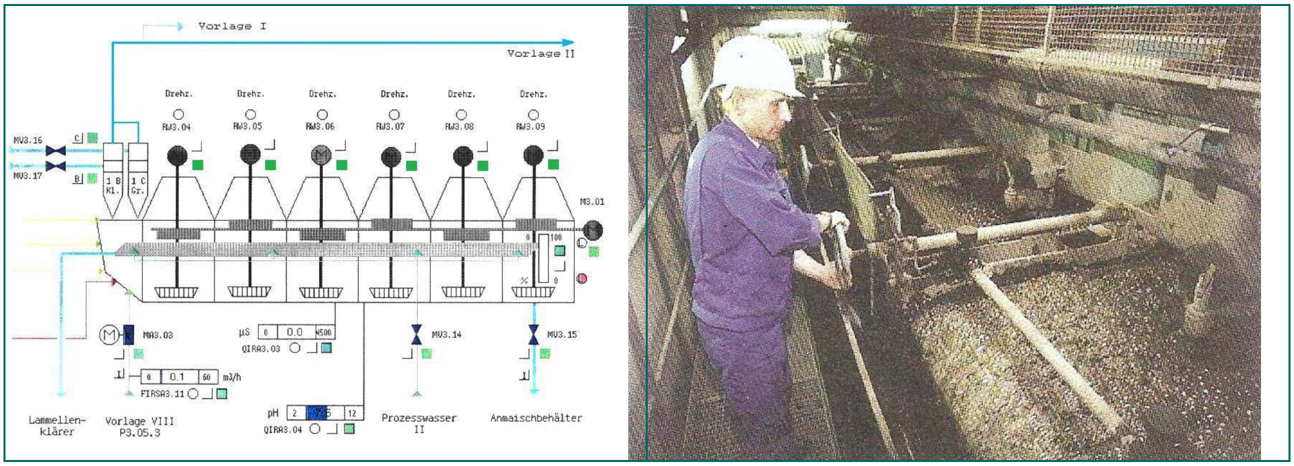


Figure 8-4: HMI graphic of the installed froth flotation and photograph showing the plant section head Dipl.-Berging. A. J. Schmidt adjusting the cell-to-cell flows manually (source: Harbauer/GBAV)

8.2.2 Specific requirements for an implementation of a mercury flotation Unit

Owing to the soil type classification, as per section 7.1.1, basically all three mercury-contaminated soil types can be treated by mechanical flotation apparatus. In particular for 'type I' mercury-contaminated soil attrition has shown to be beneficial. For 'type III' unnecessary attrition is not recommended, because of uninvited transfer of mercury to the coarser grain size fractions and avoidable destruction of coal grains.

As far as contaminated coal particles (including weathered graphite) are concerned, decarbonisation via mono sizer (upstream sorter) is recommended. In case of the previously described PAH-flotation it has been proven to be advantageous to locate the mono sizer downstream of the flotation, because after contact with the collection agent (Montanol) it was observed, that the degree of separation improved notably.

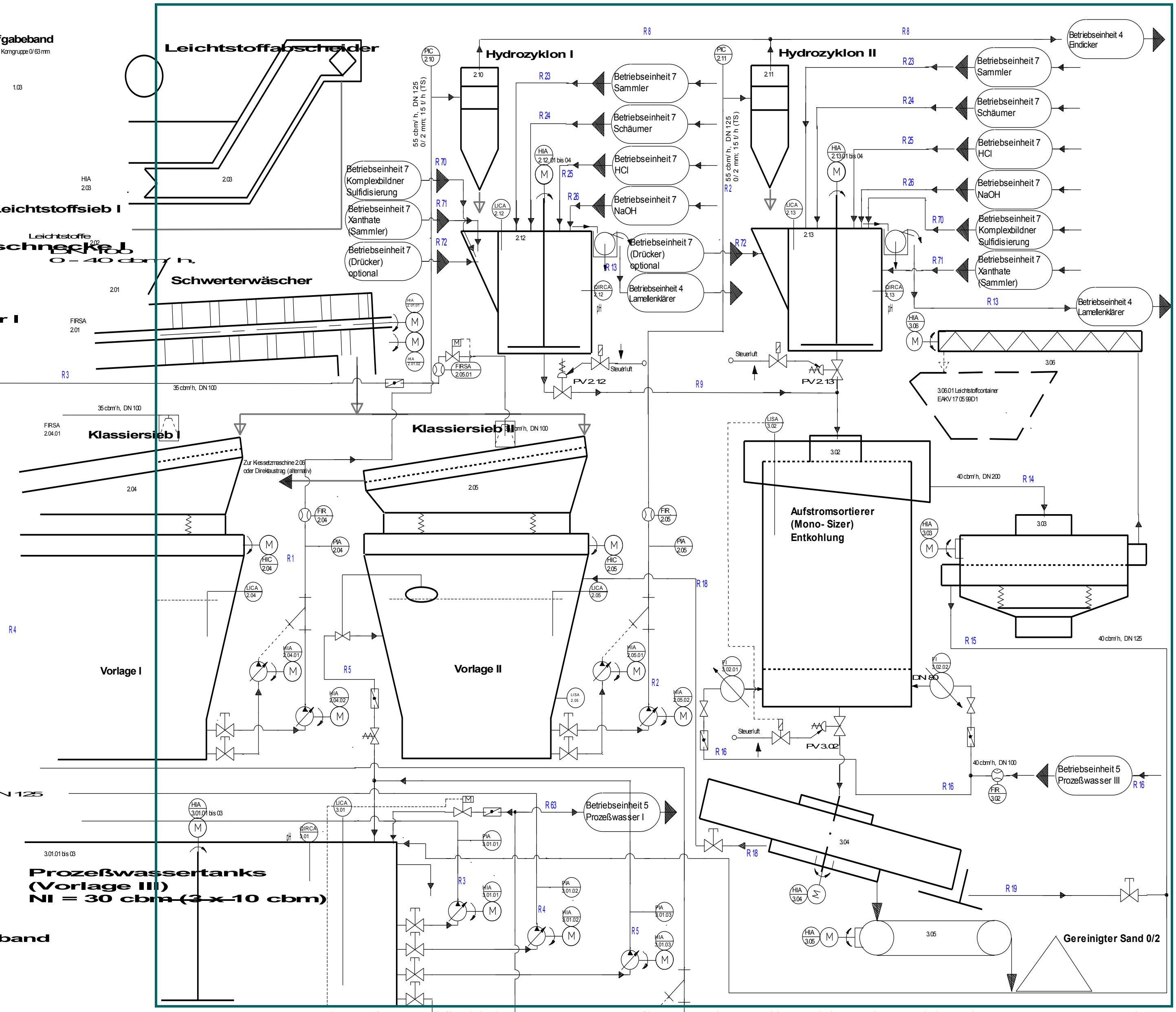


Figure 8-5: Integration of a specific high mercury waste flotation in a soil washing plant with a downstream mono sizer

By using xanthates the covering of coal grains with the collector would not have an influence on the degree of separation in the mono sizer, but since xanthates form insoluble complexes with mercury adsorbed[lxiii] on the coal, a downstream arrangement of the sorter would reduce the leachability of mercury from the separated coal considerably.

Owing to the above said the preferable sequence for the arrangement of equipment is recommended as follows:

Disintegration => Screening => Hydrocycloning => (Attrition) => 'FLOTATION' => Decarbonization

In this regard fig. 8-1 is showing as an example a 'cut-out' of a PID (the complete PID is shown in Appendix D-2) designed in the more recent years by the author in order to establish a soil treatment plant with a strong emphasis on heavy metal decontamination in the so-called supplier park between the Buna factory premises in Schkopau/Germany and the 'Hochhalde Schkopau'[lxiv]. The plant design is applicable for implementation but also for a mobile on-site plant technology and is considering an acceptance level for mercury up to 3,700 mg/kg based on two rows of cells with respect to a cell-to-cell flow.

The 'cell-to-cell design' using sub-aeration cells arranged in rows (as shown in figure 8-4) is most beneficial for soil washing plants because of:

- High flexibility with regard to the degree of contamination (involving more cells provide an increase of the degree of decontamination, if required).
- High flexibility pertaining to required throughput rates (involving more than one row in parallel)[lxv].
- Providing necessary attrition, if required, also controllable by the number of cells to be involved; allowing to a certain degree also a mild treatment concerning unwanted destruction of coal grains.
- Possibility to arrange the cells compliant to structural requirements of the plant, which is more relevant in case of upgrading existing soil washing plants.
- Almost insensitive against blocking due to build-up of sand and/or silt (sanding-up)
- Technology is applicable for a required particle size range of 500 µm (up to 2 mm possible) because it is almost insensitive against blocking due to build-up of sand and/or silt

The above list of advantages can barely be fulfilled by any pneumatic cell, but since the minimization of fines is one of the most cost relevant factors of operation it is recommended to treat the froth product by pneumatic flotation either with or without pre-treatment in a lamella separator.

Since the flotation process developed in this thesis is working with soluble mercuric sulfates, a chemical treatment plant for the removal of Hg form the process water is a vital requirement in parallel to the normally existing thickener and plate separator general water treatment stream. In most of the previously described soil washing plants such a physical/chemical process water treatment units are included in the current design anyway.

[lxiii] In case of soluble mercury compounds such as typical for 'type III' soils are involved even absorption is embroiled.

[lxiv] A pile type disposal area above track level, established 70 years ago for process residues from the 'Buna works'. The plant should help to provide some of the required capping material for the necessary closure of the dump and help to create jobs for about 30 people in an economically weak region.

[lxv] Being flexible regarding optimization of throughput rates is an essential tool concerning run down prices for medium contaminated wastes.

By using sulfide precipitation, for example with sodium sulfide, combined with a downstream flocculation and a separation of solid matter separation rates of 99.9 % can be achieved with mercury input concentration of Hg > 10 mg/l. The remaining concentration is at the best 10-100 µg Hg/l. The pH-value should be within the neutral range[230, 231].

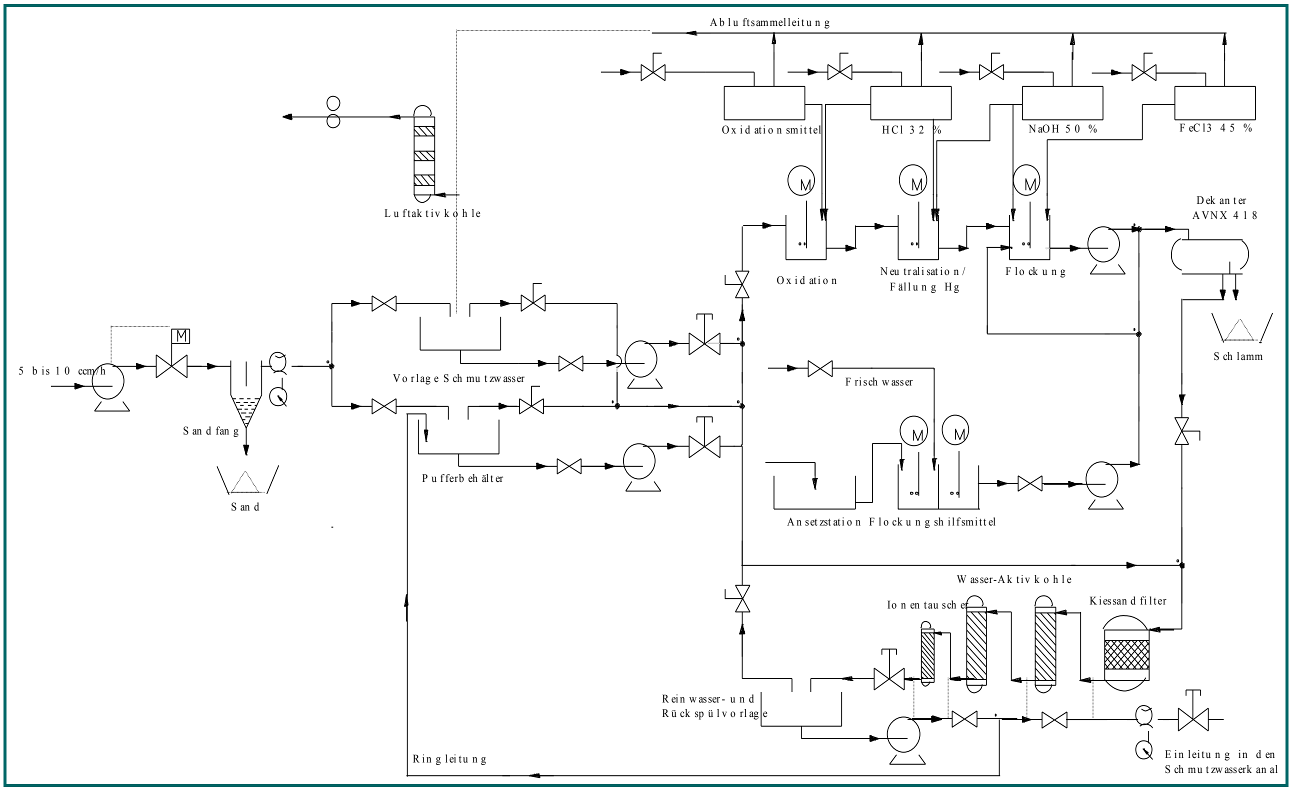


Figure 8-6: Specific waste water treatment plant designed for mercury and its water soluble compounds (R. Richter)

Within the process displayed in fig. 8-6 organic mercury compounds as may be found on former acetaldehyde sites are in a first step oxidized in an oxidation vessel connected upstream of the filters. Subsequently, an embedding or co-precipitation of mercury is conducted using flocculants and auxiliary flocculants followed by a sludge separation.

The use of appropriate activated carbon and consideration of the pH-value may lead to dissociative decontamination rates of more than 99 %. Ion exchangers, with for example sulfidized acceptor groups (mercaptan-typ), are often used for waters with a high chlorine concentration or as a subsequent cleaning step for soluble mercury. This technology is currently applied for the water treatment of an acetaldehyde facility in Kazakhstan and was also applied in the treatment plant Marktredwitz.

8.2.3 Cost estimation for a mobile plant using the example of Chian-Jhen site/Taiwan

On CPDC's Chian-Jhen site aka. Chien-Chen site in Kaohsiung in South Taiwan 70,000 metric tons of mercury contaminated soil shall be treated on location in a semi mobile washing plant. This figure is based on just recently made soil investigations and mass estimations:

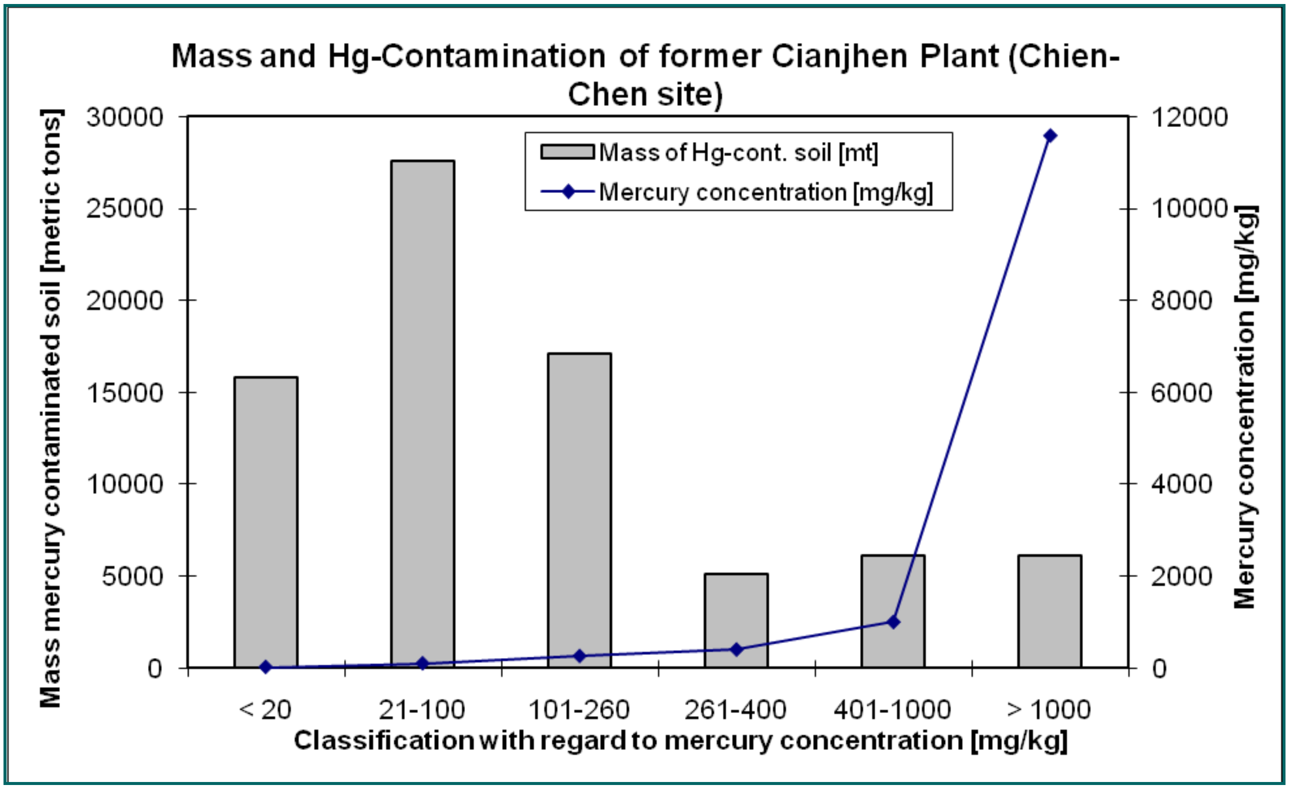


Figure 8-7: Mass estimation with regard to contamination classes used as a basis for a cost calculation

The effective operational capacity of this plant is about 15 metric tons/hour. Based on these assumptions, a rough cost estimate can be made. Fig. 8-7 also is showing that only a minor quantity of soil from former chlorine plants is contaminated higher than 1,000 mg/kg. The average mercury contamination is slightly higher than 1,000 mg/kg. So soil washing is an ideal alternative to thermal desorption for this particular project, which was estimated in a range between 320 up to 380 US$/metric ton.

This cost estimate is only for operating costs of the plant including loading works to the hopper of the plant and discharge from plant. – It is not including transports on the site and excavation. – It also has to be mentioned, that the plant (steel surfaces) will be contaminated at the end of the soil treatment operation. So decontamination by high pressure water jet injection sprayers or equal is necessary. Regarding to this the water-treatment should be independent from the plant.

The soil washing plant book value is estimated with 11 Mio. US$, after upgrading with flotation.– Full amortization of the book value of the plant in 14 month as a worst case calculation will be considered.

This model also was practiced in Marktredwitz and is the main difference between permanently established soil treatment centers, such as the ABW in Vienna or the soil washing plant Berlin-Gradestrasse, and mobile plants only used for one project directly on the remediation site.

The plant intended to be established, based on 70,000 tons will be used at the site for approximately 14 months (including time for assembling, commissioning, treatment, decontamination):

Assembling and Commissioning	150,000 US$
Disassembling and Decontamination	50,000 US$
The amortization costs for14 month:	11.000,000 US$
Tent and exhaust air treatment (14 month)	200,000 US$
Vehicle (wheel) washing facility etc. (14 month)	30,000 US$
Transport costs for the plant etc.	120,000 US$
Spare parts for 14 month:	100,000 US$
Black & white container (incl. HSE) for14 month:	50,000 US$
10 Operators (incl. PPE) for 14 month:	840,000 US$
Loading to hopper (shovel) for 14 month:	80,000 US$
Water treatment for 14 month:	50,000 US$
Engineering and management costs	100,000 US$
Laboratory	50,000 US$
Treatment of fines	2.100,000 US$
Others	30,000 US$
Sum	15.250,000 US$

Price would be **218 US$/metric ton**, based on **70,000 metric tons**, which is only slightly higher than for a comparable treatment in a soil washing centre (150 up to 180 US$/metric ton).

Next to the amortization for the plant the costs for the treatment of fines is the second highest item. By combination of flotation technologies the out-put of contaminated fines can be reduced drastically and help to reduce costs accordingly.

9 SUMMARY AND CONCLUSION

Professor W. SIMONIS called the important relationship between the ‘raw material to be treated’, ‘the reactor where the treatment shall occur’ and the ‘operating conditions’, ‘the holy trinity of mineral processing’. This doctoral thesis is following basically this structure. Therefore an overview is given about all former and currently ongoing mercury remediation and treatment projects with regard to abandoned chlorine alkali electrolysis plants, former acetaldehyde facilities and chemical factories (in particular the Chemical Factory Marktredwitz), where the author was directly or indirectly involved in the past twenty years.

As one of the results of this thesis a categorization of the soils of these projects was made. It was found, that based on the mercury contamination of the particle size groups with regard to direct analyzed results based on the dry mass and in the leachate (DEV S4 and TCLP test) a obliging classification in three types of soil could be prepared, which can be used to make the right decision for a necessary treatment especially as far as soil washing/physico-chemical treatment is concerned.

Owing to presently applied ‘state of the art’ soil/solid waste treatment technologies it could be shown, that currently no soil washing plant in the USA or in Europe is capable to treat high mercury waste in a range of about 1,000 mg/kg. Currently such wastes are treated ‘more or less unnecessarily’ by thermal desorption following basically the recommendation of US EPA 55 FR 22569 for RMERC with regard to high ‘Mercury-Inorganic Subcategory Waste’ with a total Hg content ≥ 260 mg/kg.

Therefore as a main emphasis of this thesis ‘a new mercury waste flotation method’ based on a sulphidisation with sodium-dimethyldithiocarbamate, using organic sulphidisation agents and xanthates in the same process step, was developed and successfully tested for different mercury contamination levels such as for 800 mg/kg, 1,000 mg/kg and for 1,200 mg/kg. The method involves the different solubility of various mercuric sulphide species in aqueous systems such as in particular the sulfur mercuric ion HgS_2^{2-}, which is generated under pH conditions of around 8, only. Whilst in preliminary tests performed with mercury-contaminated soil in a range of 1,000 mg/kg the removal of mercury from the soil was proven to be possible for a particle size range of 25-500 µm, the maximum grain size could be extended to 500 µm, makes the process more applicable for a practical application in soil washing plants.

The positive effect of attrition, applicable for soil washing plants could be confirmed, basically for soil, classified in this thesis as ‘type I’. The removal of coal from all soil types was fond beneficial for all tested soil types, because of the strong affinity between mercury and coal particles in soil.

All TCLP-tests performed with treated soil in laboratory scale were passing the leaching criteria for Hg < 0.2 mg/l. In the dry substance the target value “Zuordnungswert 2 (Z2)” of the German LAGA: Hg ≤ 10 mg/kg DW could be reached.

As already pointed out in section 7.3.3.3 the advantages and benefits of the sulphidisation/flotation process for high mercury waste are:

- Efficient decontamination of high mercury solid wastes in a contamination range up to 1000 mg/kg
- Transformation of even highly toxic organic mercury compounds into leach-stable insoluble mercury xanthate complexes capable for disposal or a downstream solidification/stabilization
- Sulphidisation of all mercury compounds in the sand fraction and in the froth product occurs, forming materials with low solubility characteristics
- Technology is applicable for a required particle size range of 500 µm in accordance with the selection of the flotation cell type

- In certain ranges the froth product mercury(II) xanthate may even be capable for a further treatment by solidification

Practical experience with the implementation of a flotation unit in an existing soil washing plant was already gained by the author during the implementation of a PAH flotation in a soil washing plant in Berlin in 1997. Based on this experience a description is given how to implement the flotation process in an existing or in a newly designed soil washing plant.

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Appendix File
associated to:

Processing of mercury-contaminated industrial waste

Rüdiger B. Richter

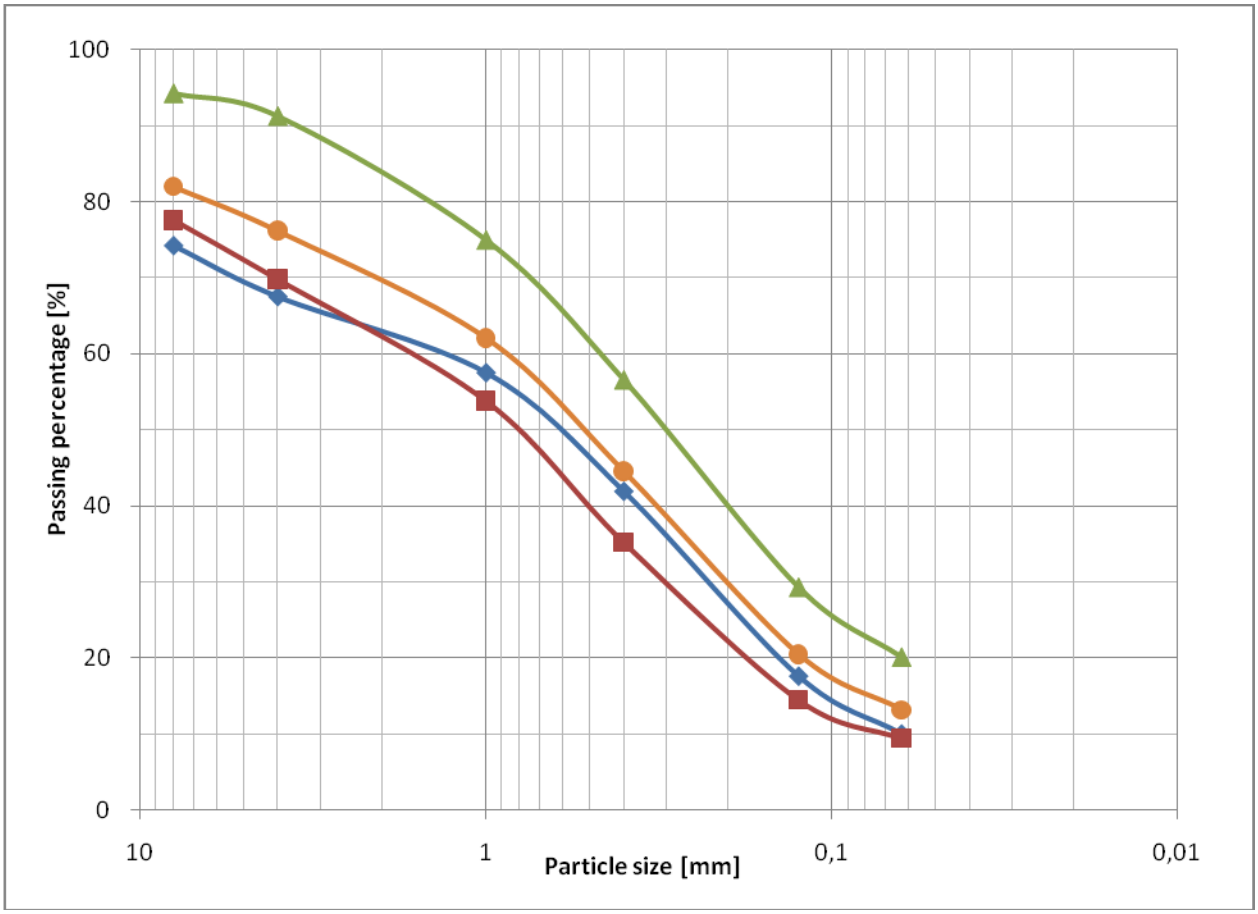
APPENDIX A:

Grain size distribution of mercury-contaminated soils from former chlorine-alkali electrolysis plants

Appendix A-1:

Grain size distribution from the former chlorine alkali electrolysis plants L66 and H56 and from the acetaldehyde factory in Buna Schkopau

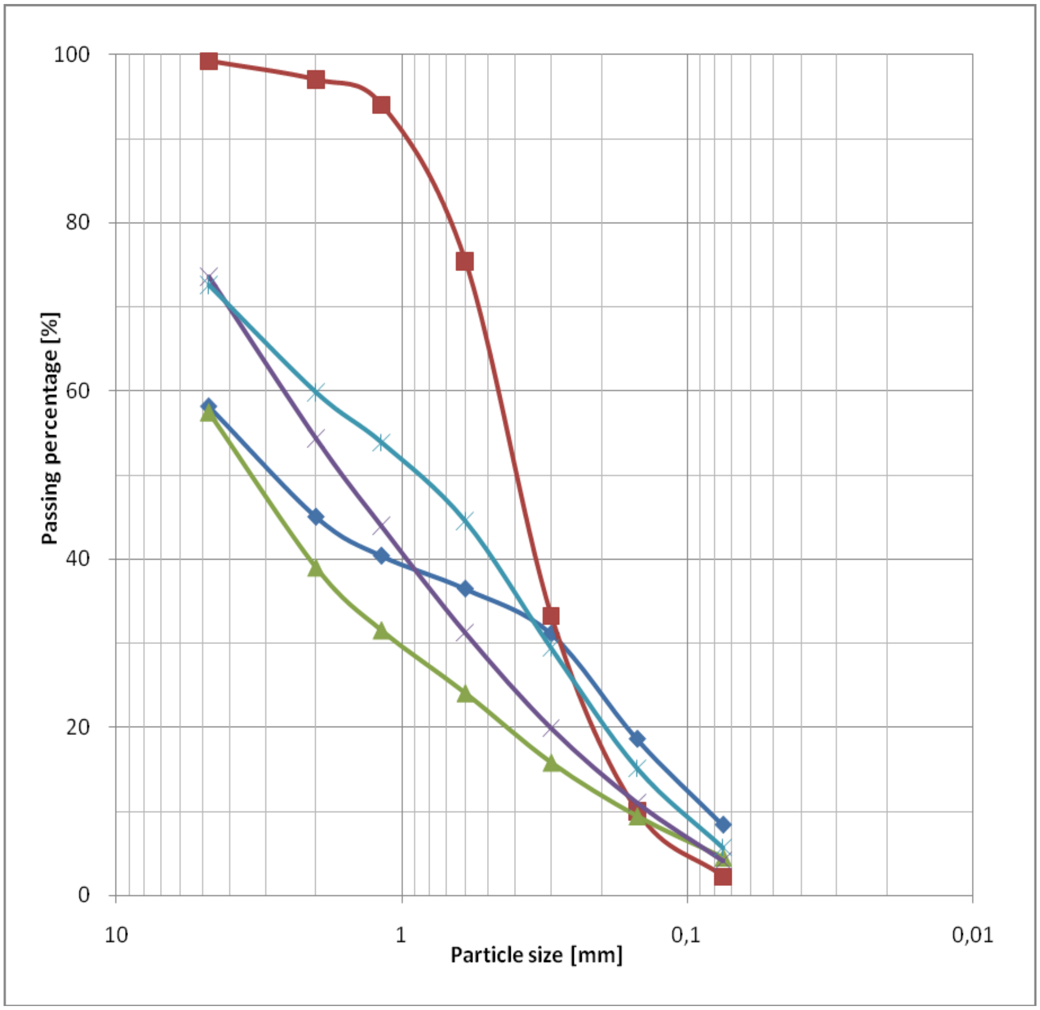
Buna Works Schkopau				
screen [mm]	L66 pass [%]	H56 pass [%]	F44 pass [%]	average [%]
8	74,20	77,60	94,30	82,03
4	67,50	69,80	91,30	76,20
1	57,50	53,80	75,00	62,10
0,4	41,90	35,20	56,60	44,57
0,125	17,60	14,50	29,30	20,47
0,063	10,00	9,40	20,10	13,17
0	0,00	0,00	0,00	0,00



(Based on orig. data from FIA Freiberg)

Appendix A-2: Grain size distribution from the former Formosa Chien-chen Plant in Kaohsiung, Taiwan

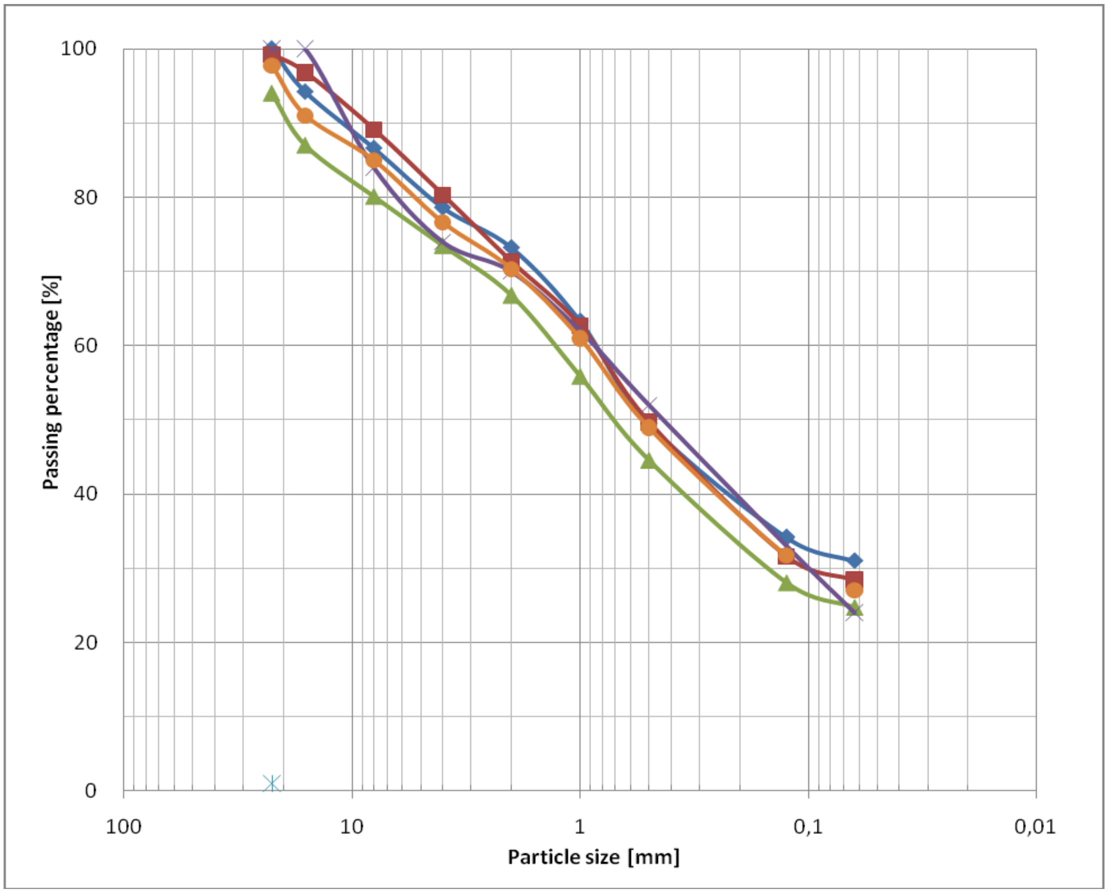
Chien-chen Taiwan						
screen number	**C01 pass [%]**	**C02 pass [%]**	**C03 pass [%]**	**C04 pass [%]**	**C05 pass [%]**	**average [%]**
#4	74,50	58,11	99,23	57,43	73,63	72,58
#10	63,78	45,00	97,00	39,00	54,38	59,83
#16	59,55	40,37	94,03	31,54	43,95	53,89
#30	55,45	36,45	75,44	24,09	31,26	44,54
#50	47,03	31,12	33,27	15,83	19,91	29,43
#100	26,68	18,60	10,00	9,46	11,05	15,16
#200	9,25	8,40	2,23	4,55	4,14	5,71
Total	0,00	0,00	0,00	0,00	0,00	0,00



(Based on orig. data from Golder Associates, 2011)

Appendix A-3: Grain size distribution from the former chlorine alkali electrolysis plant in Ústí nad Labem (Aussig a.d. Elbe)

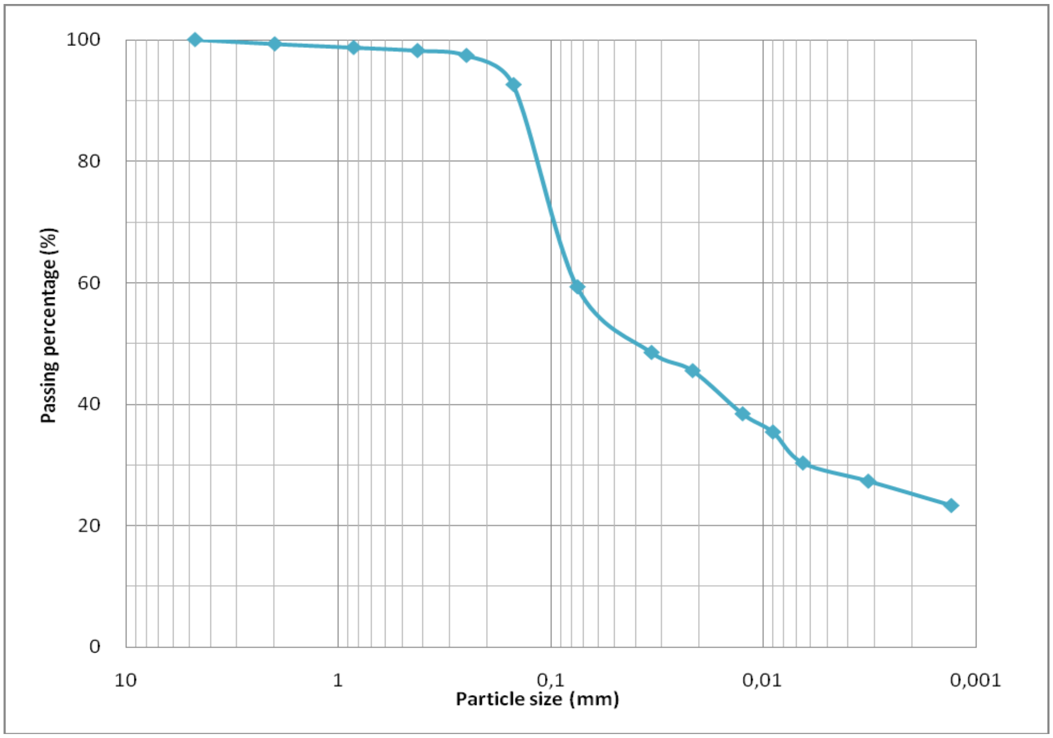
Ústí nad Labem					
screen [mm]	**K13 pass [%]**	**K14 pass [%]**	**K17 pass [%]**	**RR pass [%]**	**average [%]**
22,4	100,00	99,20	94,00	100	97,73
16	94,20	96,80	87,00	100	91,00
8	86,60	89,10	80,10	84	84,95
4	78,60	80,30	73,50	74	76,60
2	73,20	71,30	66,80	70	70,33
1	63,30	62,70	55,90	62	60,98
0,5	49,50	49,70	44,60	52	48,95
0,125	34,20	31,60	28,10	33	31,73
0,063	31,00	28,40	24,80	24	27,05
0	0,00	0,00	0,00	0,00	0,00



Screening analysis performed by: Banske Projekty Teplice A.S. (K13/K14) and Ergo Umweltinstitut (K17), 2006

Appendix A-4: **Grain size distribution Olin Saltville chlorine alkali electrolysis plant**

Olin Saltville Plant				
sieve size [#/ET min]	screen [mm]	weight [g]	stay [%]	pass [%]
#4	4,75	205,0	13,00	100,00
#10	2	203,6	12,00	99,30
#20	0,85	203,9	12,00	98,70
#40	0,425	204,2	12,00	98,20
#60	0,25	204,6	12,00	97,40
#100	0,15	207,0	13,00	92,60
#200	0,075	223,4	14,00	59,30
2.00	0,0336	24,0	1,00	48,50
5.00	0,0215	22,5	1,00	45,50
15.00	0,0125	19,0	1,00	38,40
30.00	0,009	17,5	1,00	35,40
60.00	0,0065	15,0	0,00	30,30
250.00	0,0032	13,5	0,00	27,30
1440.00	0,0013	11,5	0,00	23,30
Total		1574,7	99,00	0,00

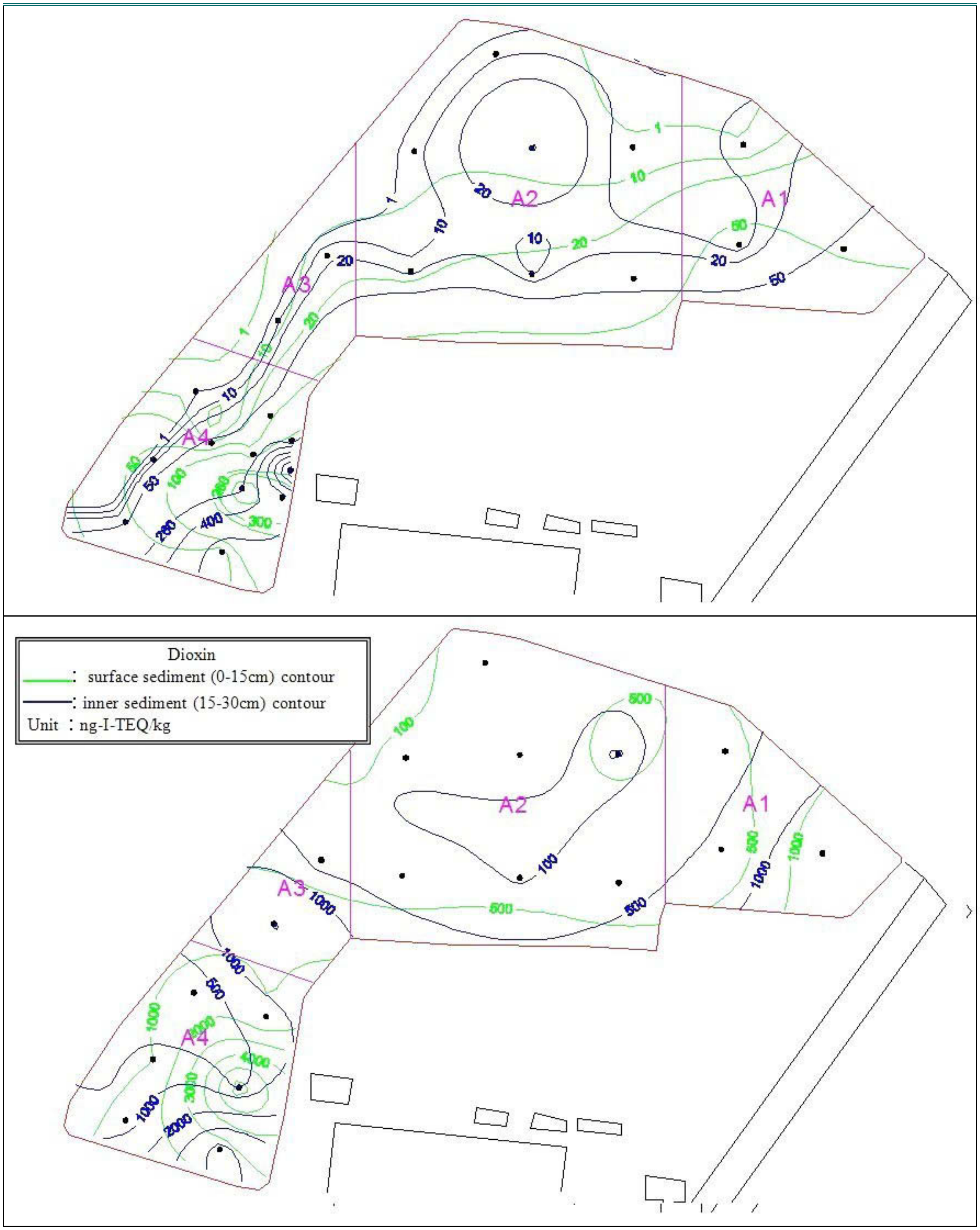


(Based on orig. data from Golder Associates, 1994)

APPENDIX B:

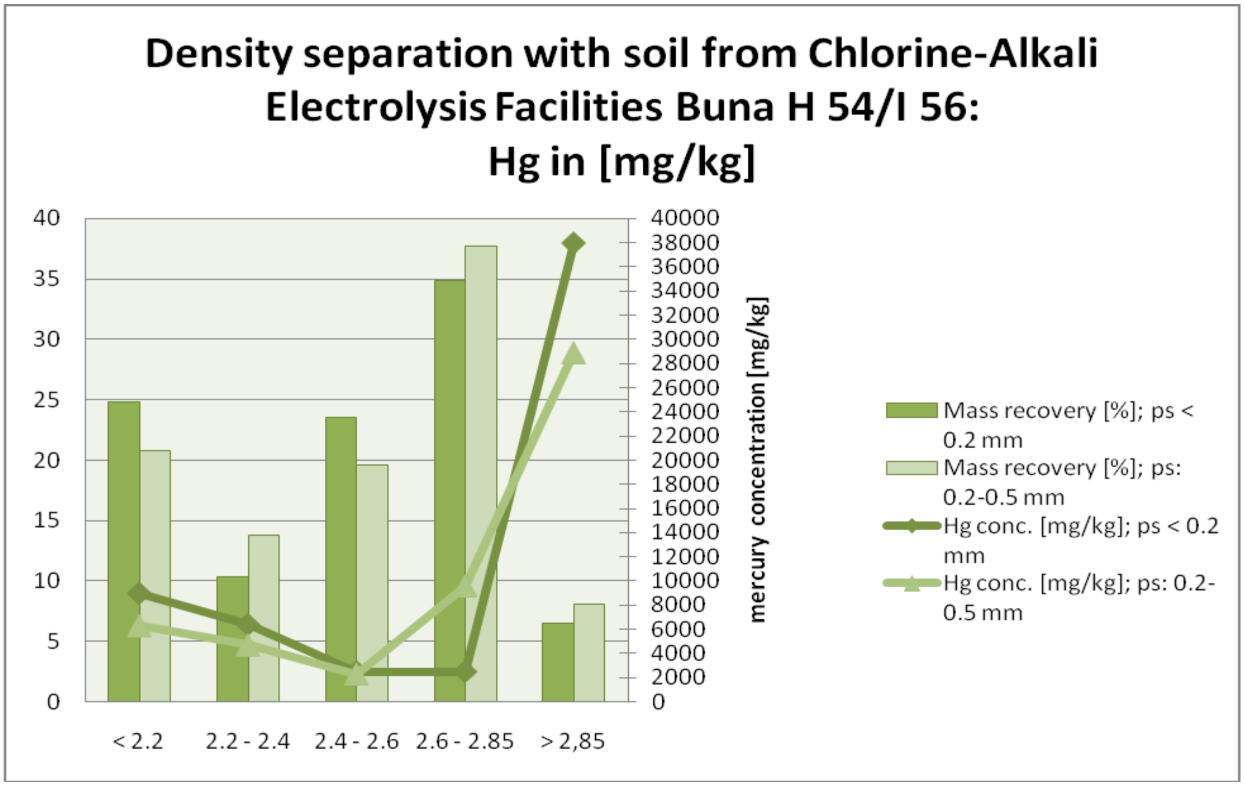
Contamination characteristics of soils from former chlorine-alkali electrolysis plants

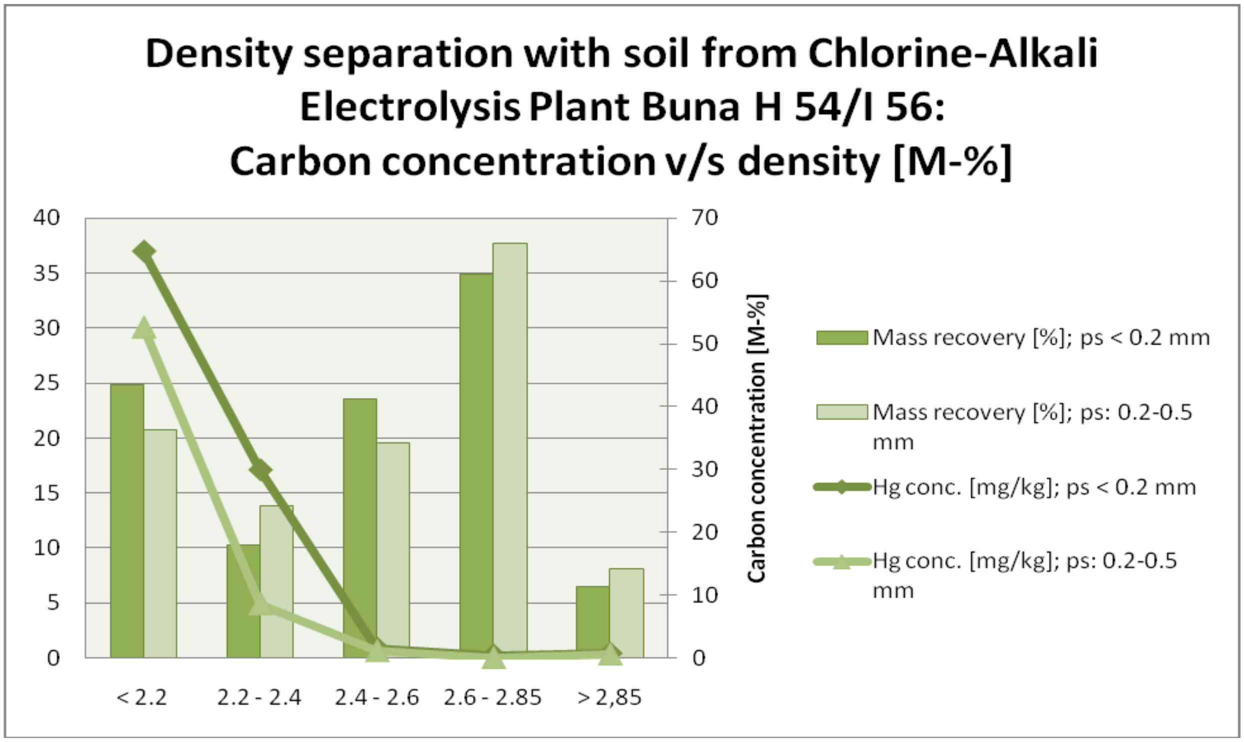
Appendix B-1: Mercury and dioxin concentrations overlapping in particular in the sea water pond sediments of the former cell plant at Anshun (安順)/Taiwan



Source: MWH

Appendix B-2: The correlation between mercury and carbon in Buna soil



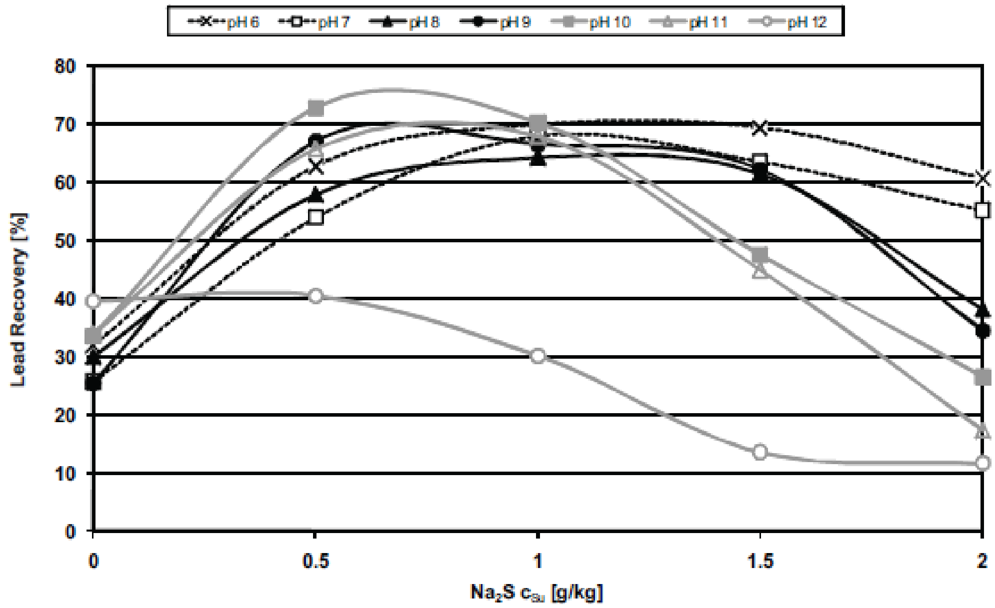


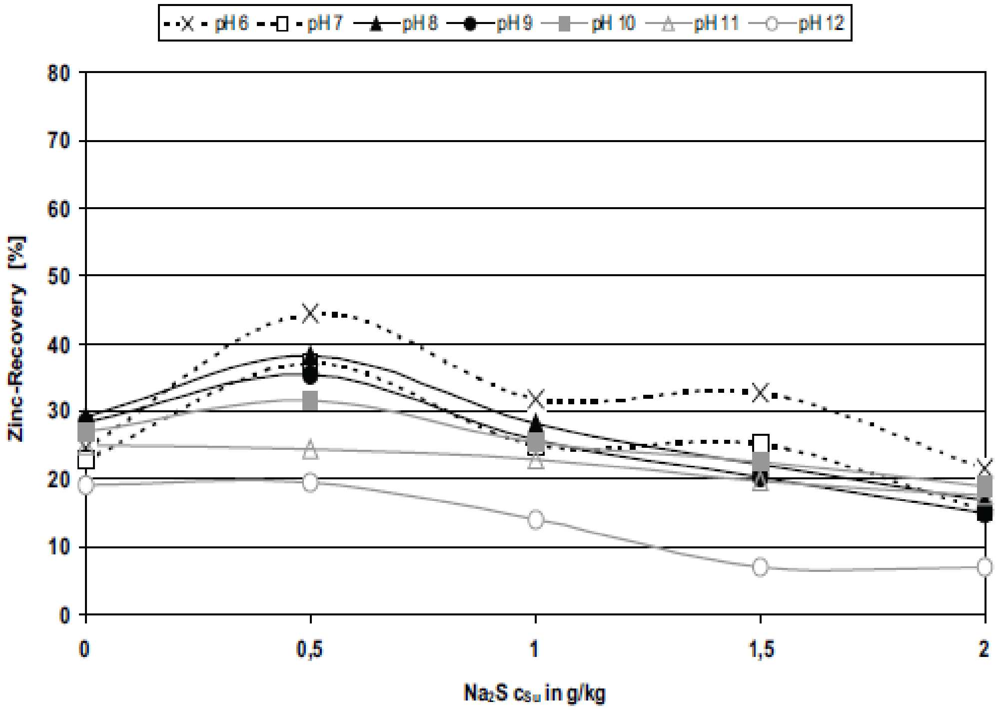
(Based on orig. data from Teichmann, TU Berlin, 1997)

APPENDIX C:

Flotation tests

Appendix C-1: Lead and zinc recovery performed with KAX after Sulphidisation





(STAPELFELDT AND RICHTER, 1997 AND 2002)[118, 173]

Appendix C-2: Flotation tests with Hg-contaminated soil performed after sulphidisation

Input [mg / kg]	Series name	B…. Tailings (treated fraction)			E…. Froth Product		mass recovery	treatment efficiency η	Contaminant Recovery
		mass [g]	TCLP; Hg [mg/l]	Hg [mg/kg]	mass [g]	Hg [mg/kg]	[%]	[%]	[%]
Hg = 1000 [mg / kg]	B1 _ EP 0	392.2g	0,06	86	1.8g	2000	0.45%	91.40	0.90%
	B1 _ EP 0.5	391.8g	0,03	37	1.2g	2500	0.30%	96.30	0.75%
	B1 _ EP 1	387.2g	0,06	25	3.4g	4000	0.85%	97.50	3.40%
	B1 _ EP 1.5	396.2g	0,02	16	2.03g	6000	0.51%	98.40	3.05%
	B1 _ EP 2	389.2g	0,02	4	4.05g	7500	1.01%	99.60	7.59%
	B1 _ EP 4	391.4g	0,01	33	2.39g	5500	0.60%	96.70	3.29%
	B1 _ EP 8	389.4g	0,03	48	1.65g	6000	0.41%	95.20	2.48%
Hg = 800 [mg / kg]	C1_EP 0	393.4g	0,06	63	0.69g	1600	0.17%	92.10	0.35%
	C1_EP 0.5	396.1g	0,02	150	1.36g	2000	0.34%	81.25	0.85%
	C1_EP 1	395.0g	0,10	121	0.70g	2402	0.18%	84.86	0.53%
	C1_EP 1.5	390.6g	0,17	146	1.69g	3400	0.42%	81.75	1.80%
Hg = 1200 [mg / kg]	D1_EP 0	395g	0,14	108	1.84g	2400	0.46%	91.00	0.92%
	D1_EP 1.5	401.3g	0,10	13	1.18g	6600	0.30%	98.92	1.62%
	D1_EP 2	395.5g	0,04	176	2.00g	6000	0.50%	85.33	2.50%
	D1_EP 2.5	399g	0,18	208	1.99g	5800	0.50%	82.67	2.40%
	D1_EP 3	398g	0,10	184	1.79g	5200	0.45%	84.67	1.94%

Appendix C-3: Photo documentation of flotation tests performed in the year 2010 (MU Leoben)

Figure C3-1: Flotation of Hg-contaminated soil, test rows performed with 800, 1000 and 1200 [mg/kg]

Figure C3-2: Hg-Sulfid floated to the surface (KAX as collecting agent)

Figure C3-3: Flotation occurs after adding Flotanol D12 as a frother – froth product collected in a tab.

Figure C3-4: Suction strainer supported by a water-jet vacuum pump for dewatering of the froth product

Figure C3-5: Laboratory equipment used for the tests performed

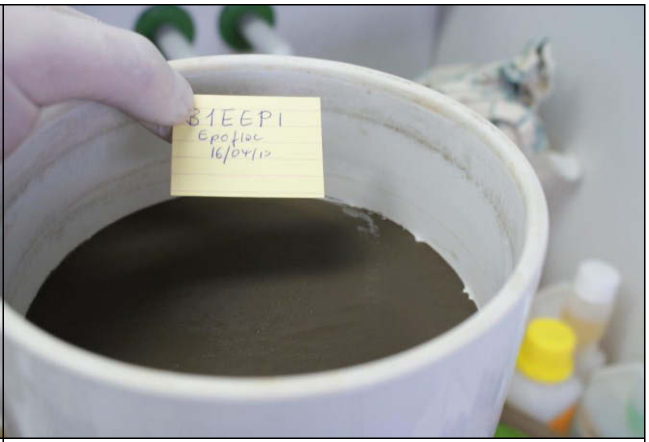
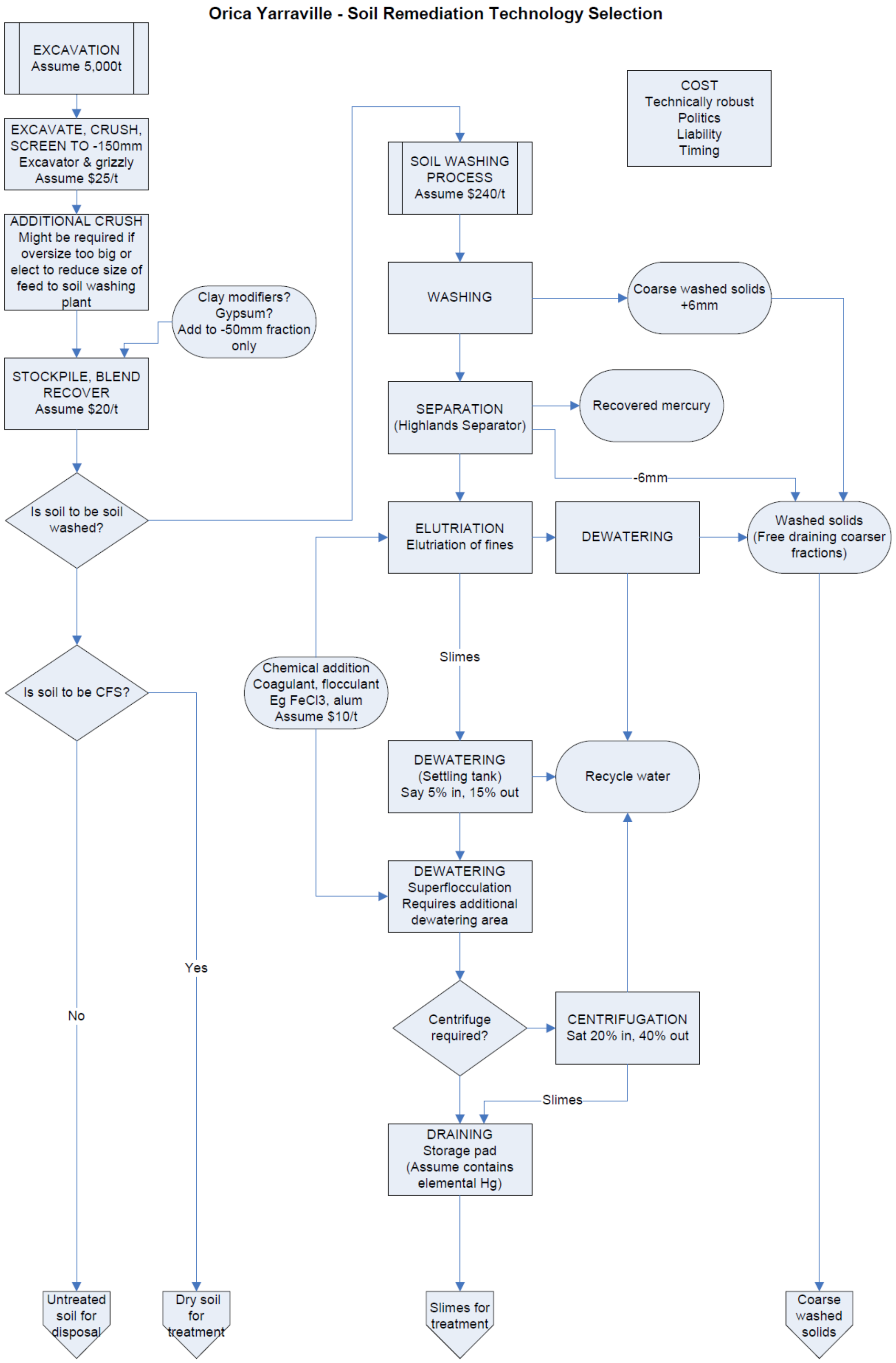


Figure C3-6: Dewatered flotation froth product B1EEP1 in the funnel of the suction showing a high concentration of mercury sulfide

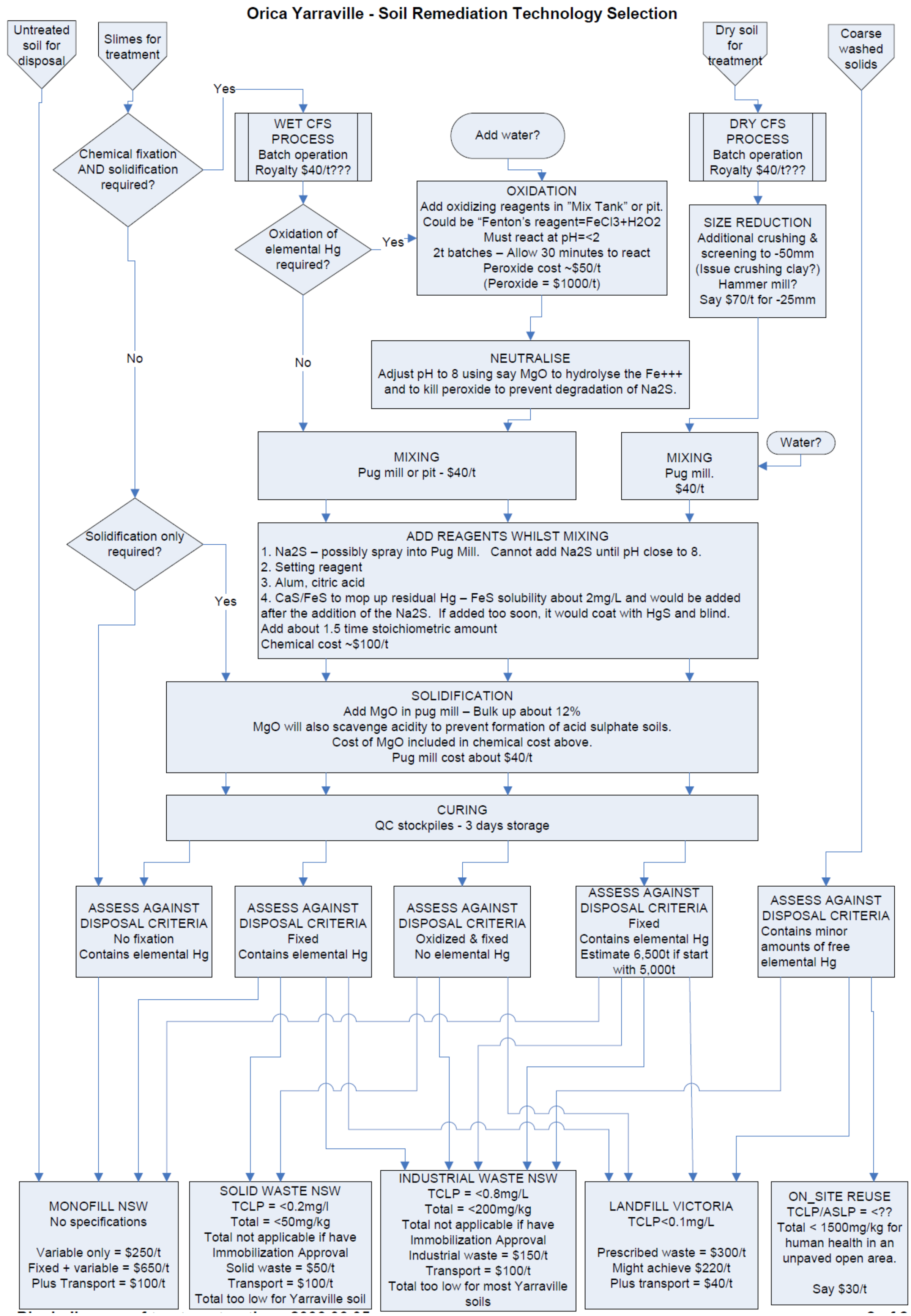
APPENDIX D:

Plant design: Soil washing facilities for high mercury solid waste

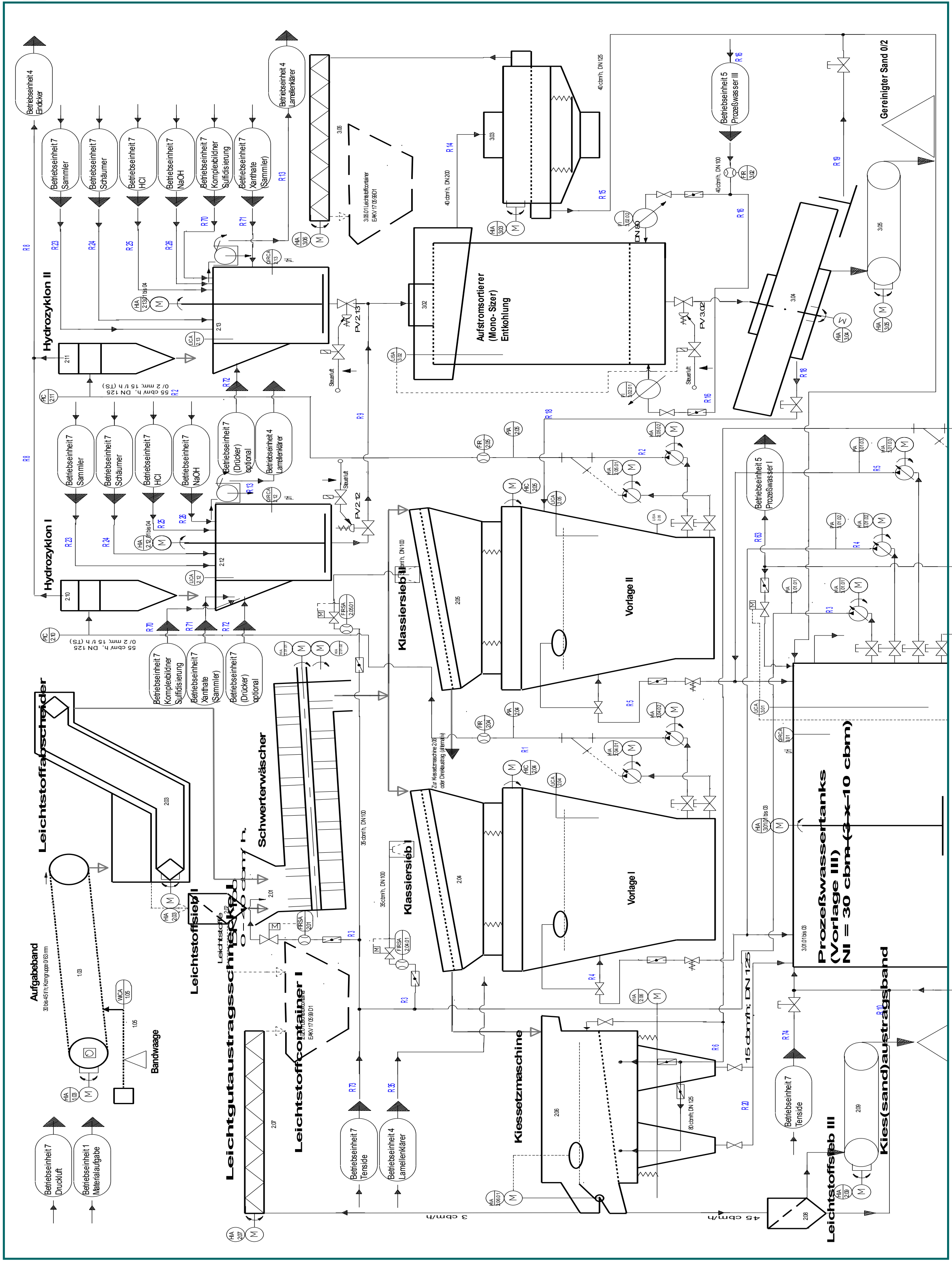
Appendix D-1: Soil Remediation Technology Selection – Yarraville Chlorine Plant Case



(Source: Golder Associates)


Orica Yarraville - Soil Remediation Technology Selection
Untreated soil for disposal
Slimes for treatment
Dry soil for treatment
Coarse washed solids
Chemical fixation AND solidification required?
Yes
No
WET CFS PROCESS Batch operation Royalty $40/t???
Add water?
DRY CFS PROCESS Batch operation Royalty $40/t???
Oxidation of elemental Hg required?
Yes
No
OXIDATION
Add oxidizing reagents in "Mix Tank" or pit.
Could be "Fenton's reagent=FeCl3+H2O2
Must react at pH=<2
2t batches – Allow 30 minutes to react
Peroxide cost ~$50/t
(Peroxide = $1000/t)
SIZE REDUCTION
Additional crushing & screening to -50mm
(Issue crushing clay?)
Hammer mill?
Say $70/t for -25mm
NEUTRALISE
Adjust pH to 8 using say MgO to hydrolyse the Fe+++ and to kill peroxide to prevent degradation of Na2S.
MIXING Pug mill or pit - $40/t
MIXING Pug mill. $40/t
Water?
Solidification only required?
Yes
ADD REAGENTS WHILST MIXING
1. Na2S – possibly spray into Pug Mill. Cannot add Na2S until pH close to 8.
2. Setting reagent
3. Alum, citric acid
4. CaS/FeS to mop up residual Hg – FeS solubility about 2mg/L and would be added after the addition of the Na2S. If added too soon, it would coat with HgS and blind. Add about 1.5 time stoichiometric amount
Chemical cost ~$100/t
SOLIDIFICATION
Add MgO in pug mill – Bulk up about 12%
MgO will also scavenge acidity to prevent formation of acid sulphate soils.
Cost of MgO included in chemical cost above.
Pug mill cost about $40/t
CURING
QC stockpiles - 3 days storage
ASSESS AGAINST DISPOSAL CRITERIA No fixation Contains elemental Hg
ASSESS AGAINST DISPOSAL CRITERIA Fixed Contains elemental Hg
ASSESS AGAINST DISPOSAL CRITERIA Oxidized & fixed No elemental Hg
ASSESS AGAINST DISPOSAL CRITERIA Fixed Contains elemental Hg Estimate 6,500t if start with 5,000t
ASSESS AGAINST DISPOSAL CRITERIA Contains minor amounts of free elemental Hg
MONOFILL NSW
No specifications
Variable only = $250/t
Fixed + variable = $650/t
Plus Transport = $100/t
SOLID WASTE NSW
TCLP = <0.2mg/l
Total = <50mg/kg
Total not applicable if have Immobilization Approval
Solid waste = $50/t
Transport = $100/t
Total too low for Yarraville soil
INDUSTRIAL WASTE NSW
TCLP = <0.8mg/L
Total = <200mg/kg
Total not applicable if have Immobilization Approval
Industrial waste = $150/t
Transport = $100/t
Total too low for most Yarraville soils
LANDFILL VICTORIA
TCLP<0.1mg/L
Prescribed waste = $300/t
Might achieve $220/t
Plus transport = $40/t
ON_SITE REUSE
TCLP/ASLP = <??
Total < 1500mg/kg for human health in an unpaved open area.
Say $30/t

Appendix D-2: Integration of sub aeration cells in a soil washing plant (PID; R.B. Richter)



APPENDIX E:

Thermal desorption tests

Appendix E-1: Thermal desorption tests performed with Buna and Marktredwitz material

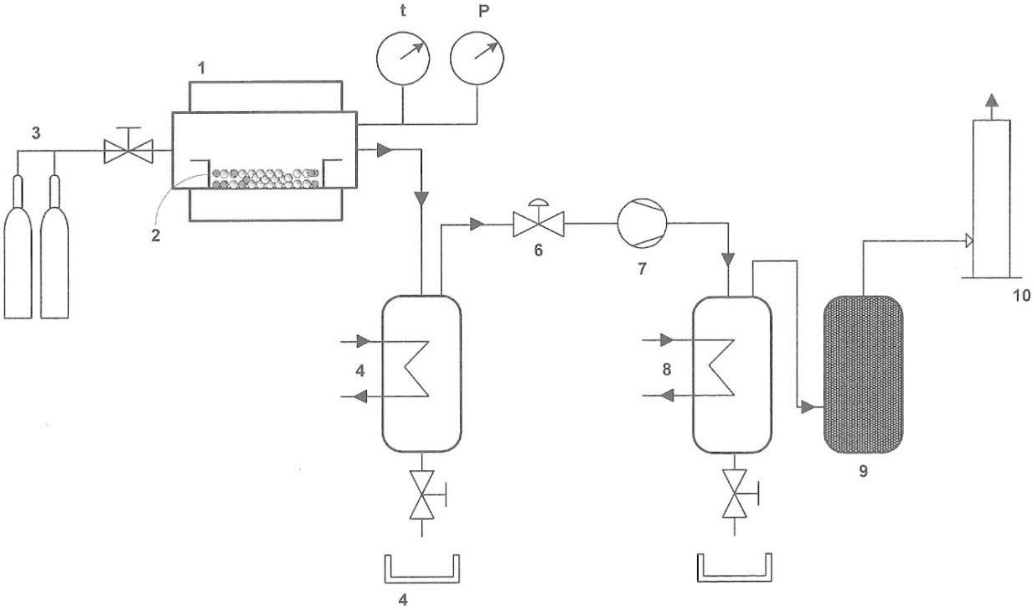


Figure E1-1: Dewatered Bench scale thermal desorption plant (1 = thermal desorption, 2 = sagger, 3 = carrier gas, 4 = condenser I, 6 = control valve, 7 = water ring vacuum pump, 8 = condenser II, 9 = char coal filter, 10 = stack (Richter and Schmidt, 2011)

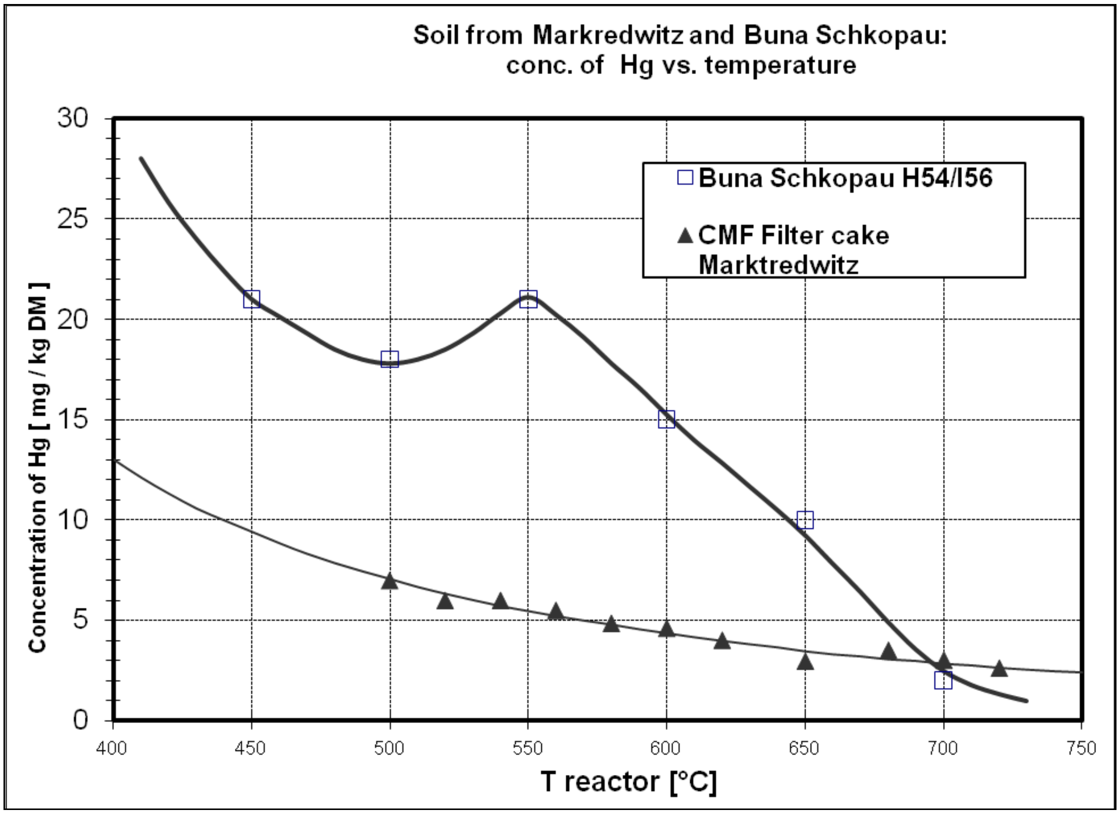


Figure E1-2: Comparison of thermal desorption tests performed with soil from Buna and pre-treated (Hg-enriched) filter cake from the soil treatment plant Marktredwitz (t = 40 min, p = 50 hPa); Richter and Schmidt, 2011

APPENDIX F:

Technical details of the Marktredwitz plant

Appendix F-1: Mechanical completion of the thermal desorption plant Marktredwitz in 1992

Appendix F-2: Detail photos from the technical equipment of the thermal desorption plant Marktredwitz such as distiller and vacuum sluices

APPENDIX G:

List of chlorine plants in Europe

Appendix G-1: Chlorine plants in Europe (Source: Eurochlor, October 2009)

Country	Company	Site	Process	Capacity [000 m. tons]
Austria	Donau Chemie	Brückl	M	70
Belgium	SolVin	Antwerp	Hg, M	474
	SolVin	Jemeppe	M	174
	Tessenderlo Chemie	Tessenderlo	Hg, M	400
Bulgaria	Polimeri	Devnya	D	124
Czech Rep.	Spolana	Neratovice	Hg	135
	Spolchemie	Usti	Hg	61
Finland	AkzoNobel	Oulu	Hg	43
	Finnish Chemicals	Joutseno	M	75
France	Perstorp	Pont de Claix	D	170
	Arkema	Fos	D, M	310
	Arkema	Jarrie	Hg	170
	Arkema	Lavera	Hg, D	350
	Arkema	Saint Aubin	M	20
	MSSA	Pomblières	Na	42
	PPChemicals	Thann	Hg	72
	Prod. Chim. d'Harbonnières	Harbonnières	Hg	23
	Solvay	Tavaux	Hg, M	375
	Tessenderlo Chemie	Loos	Hg	18
Germany	BASF	Ludwigshafen	Hg, M	385
	Bayer	Dormagen	M, HCl	480
	Bayer	Leverkusen	M, HCl	360
	Bayer	Uerdingen	Hg, M	240
	Bayer	Brunsbüttel	HCl	210
	Dow	Schkopau	M	250
	Vinnolit	Knapsack	Hg, M	250
	CABB	Gersthofen	M	40
	Dow	Stade	D, M	1585
	AkzoNobel	Ibbenbüren	Hg	125
	AkzoNobel	Bitterfeld	M	88
	Evonik Degussa	Lülsdorf	Hg	136
	INEOS ChlorVinyls	Wilhelmshaven	Hg	149
	AkzoNobel Industr. Chemicals	Frankfurt	Hg	167
	Solvay	Rheinberg	D, M	200
	VESTOLIT	Marl	M	260
	Vinnolit	Gendorf	Hg	172
	Wacker Chemie	Burghausen	M	50
Greece	Hellenic Petroleum	Thessaloniki	Hg	40
Hungary	BorsodChem	Kazincbarcika	Hg, M	299
Ireland	MicroBio	Fermoy	M	6
Italy	Altair Chimica	Volterra	M	27
	Solvay	Bussi	M	25

	Syndial	Assemini/ Cagliari	M	153
	Syndial	Porto Marghera	Hg	200
	Solvay	Rosignano	M	150
	Tessenderlo Chemie	Pieve Vergonte	Hg	42
Netherlands	AkzoNobel	Botlek	M	633
	AkzoNobel	Delfzijl	M	109
	SABIC GE Plastics	Bergen-op-Zoom	M	89
Norway	Borregaard	Sarpsborg	M	45
	Elkem	Bremanger	M	10
	INEOS ChlorVinyls	Rafnes	M	260
Poland	Rokita	Brzeg Dolny	Hg	125
	Zachem	Bydgoszcz	D	60
	Anwil	Wloclawek	M	214
Portugal	Solvay	Povoa	M	29
	CUF Quimicos Industriais	Estarreja	M	68
Romania	Oltchim	Ramnicu Valcea	Hg, M	260
	ChimComplex	Borzesti	M	107
Slovak Rep.	Novácke Chemické Závody	Novaky	Hg	76
Slovenia	TKI Hrastnik	Hrastnik	M	15
Spain	Ercros	Huelva	Hg	101
	Ercros	Sabinanigo	Hg	25
	Ercros	Vilaseca	Hg, M	190
	Electroquímica de Hernani	Hernani	M	15
	ELNOSA	Lourizan	Hg	34
	Ercros	Flix	Hg	150
	Química de Cinca	Monzon	Hg	31
	SolVin	Martorell	Hg	218
	Solvay	Torrelavega	Hg	63
Sweden	AkzoNobel	Skoghall	M	95
	INEOS ChlorVinyls	Stenungsund	Hg	120
Switzerland	SF-Chem	Pratteln	Hg	27
	Borregaard	Atisholtz	M	10
UK	INEOS ChlorVinyls	Runcorn	Hg, M	746
	Albion Chemicals	Thetford	M	7
Total				**13,127**

M = membrane; Hg = mercury; D = diaphragm

APPENDIX H:

Curriculum vitae of the author

Appendix H-1: Curriculum vitae of the author

Name: Rüdiger B. Richter
Profession: Manager for Mineral Processing Plants/ Waste Treatment (Soil Remediation) Plants/Sr. Mining, Civil and Process Engineer

Date of Birth: 3 June 1961
Nationality: German
Education: Dipl.-Ing., equal to MSc, Mining Engineering/Mineral Processing, Mining University Leoben/Austria and Technical University Berlin, 1991.
Pre-degrees in Mining Engineering and in Civil Engineering, equal to BSc, Mining University Leoben/Austria and Technical University Berlin, 1988.
Engineers Degree, not fully equal to BEng, in Civil Engineering, Technical College Graz/Austria, 1984; upgraded to 'Dipl.-HTL-Ing.' with a thesis about soil washing in 2008.

Awards/ Prizes: Nomination for the Wilhelm-Holzmann-Prize, 1994.
Friedrich v. Klinggräff Medal, 1993.
Dr.-Ing. E.h. Erhardt-Andreas Prize for the best thesis (TU Berlin), 1992.

Qualifications: Professional Engineer for civil and environmental engineering (Chamber of Civil Engineers Berlin), 1999.
European Engineer (EUR ING), certified by FEANI, Paris, 1995.
Approved expert for facilities using groundwater-endangering substances, 1995.

Affiliations: Chamber of Civil Engineers Berlin (Professional Engineer)

Specific Experience: Mr. Richter has more than 20 years of professional experience in planning, construction, commissioning, optimization and operation of large mineral (waste) processing facilities (flotation, pelletization, physical and chemical treatment, vacuum distillation of mercury, thermal desorption, incinerators and water treatment and in the closure and treatment of highly-contaminated industrial facilities in particular with heavy metals).
Currently in the position of Commissioning Manager for a refinery waste treatment plant including 8 different processes in the United Arab Emirates.
Previously he was employed for a number of years as a senior plant manager at a fully automated multi-step physical/chemical mineral waste processing plant in Berlin-Gradestrasse, which is one of the most up-to-date soil washing plants in Germany. Here he was responsible for operation, optimization and the technical modifications of the plant. The target was to double the throughput to and improve the degree of decontamination. Also he designed a flotation Unit for highly-contaminated organically contaminated soil and gained extensive experience of the treatment of the contaminant-enriched (heavy metals) process water. The results were published in several professional journals.
Also he was in charge as a Project Manager and Commissioning Manager for the largest thermal soil remediation plant in Europe (Marktredwitz/ Bavaria), using vacuum distillation/ thermal desorption based on rotary kilns and physical/chemical treatment for mercury-contaminated mineral wastes.
As a Government Consultant he was in charge for the closure of several chlorine plants and the acetaldehyde factory in Buna (200 million Euros).
Mr. Richter is recognized in Germany as an expert on the closure of chlorine plants (chlorine alkali electrolysis after the amalgam process with mercury). As a consultant and Project Manager he has been in charge on site for a large number of such projects. This experience includes plants in the United Arab Emirates, Australia, Sweden and Taiwan.
As an experienced Site Commissioning Manager and Plant Operation Manager Mr. Richter has good leadership qualities, based in part on his sound understanding of the required technical skills. Mr. Richter works effectively and diplomatically to achieve the project objectives. Mr. Richter supervised as a plant manager several master theses and was

holding guest lectures on a regular basis (once a semester) at the department of mineral processing at Technical University Berlin. Lectures also were given at the University of Applied Science in Wismar and at the Chamber of Crafts Berlin. Mr. Richter is author of several publications about treatment of mineral wastes and mineral processing. His mother-tongue is German. He has a very good spoken and written knowledge of English and is able to communicate on a basic level in Russian language

Experience:

2009 to date **Abu Dhabi Oil Refining Comp. TAKREER/ Ruwais, UAE**

Technical Advisor, Act. Section Head, BeAAT Department Manager

Responsible for the entire operation, waste management and waste flow approval of the Central Environment Facility 'BeAAT', including eight different treatment processes and a laboratory as described in greater detail below.

2004 to 2009 **Golder Associates GmbH Celle, Germany/ Abu Dhabi, UAE**

Associate, Project Director Middle East – Global Waste Expert (Sr. Civil, Mining & Process Eng.)

- Acquisition and supervision of projects in Middle East Refinery Industry especially in hazardous waste treatment plants and controlled dismantling/ demolition of industrial facilities.
- Commissioning Manager for the Central Environment Facilities (BeAAT/ treatment plant for refinery wastes) at Ruwais Refinery, Emirate Abu Dhabi from 2005 till now. Responsible for all pre-commission and Commissioning activities including all disciplines, such as Process & Chemical Engineering / Waste Management, Electrical Eng./ Instrumentation, Mechanical and Civil Engineering. The plant includes various treatment processes, such as incineration, thermal desorption, solidification, flotation, physical/chemical treatment, centrifugation, mercury distillation and landfills class I & class II.
- Technical evaluation of a mercury (dental) waste treatment plant in Germany.
- Environmental and process consultancy for a hazardous waste problem in a mineral processing plant for zinc ores near Belo Horizonte/ Brazil
- Consultant for a soil treatment project (mercury) near Melbourne/ Australia.
- Consultancy and site supervision for chlorine plant (mercury) decontamination, dismantling, controlled demolition and disposal (mono dump) at Abu Dhabi Refinery United Arab Emirates from Oct. 2004 till Oct. 2005.
- Consultant for the dismantling and decontamination concept for a chlorine plant in Sweden.
- Consultant for demolition and disposal of a mercury contaminated chemical plant in Kazakhstan.

1997 - 2004 **Consultant** **Berlin, Germany**

- Advising the German Federal Authorities (Treuhandanstalt) on contamination at chemical industry sites in central Germany (former GDR). Responsible for decommissioning, dismantling and demolition of mercury-contaminated chlorine plants in Buna from 1997 till 2001.
- Cost controller and technical expert for the erection of rolling mills in Hettstedt.
- Project manager for dismantling and decontamination of a mercury-contaminated chlorine plant (Chlor I) in Bitterfeld.
- Planning and project management for decommissioning, dismantling and re-erection in Buna of a multi-step mineral waste treatment plant (centrifuging, physical/chemical treatment, evaporation and solidification).

- Planning (process/ P&I design) and permitting-management (environmental assessment, process hazard analysis etc.) for a hydraulic (physical/chemical) soil remediation plant in Buna.
- Structural calculations for construction of a multi-storey steel chemical plant in Schönebeck.
- Demolition planning and structural calculations for dismantling of steelwork at the ice hockey and skating stadium in Berlin.
- Demolition planning, structural calculations and project management for dismantling and decontamination of a mercury-contaminated chlorine plant (Chlor III) in Bitterfeld.
- Project manager (landfill) for the disposal of heavy metal contaminated materials at Helbra (Theissen slurry).
- Planning (process/ P&I design) and permitting management for the handling of contaminated water on the former mining site in Helbra.
- Expert reports on flood-damaged buildings in central Germany.
- Project manager for the reduction of the flooding-related groundwater levels in Bitterfeld.
- Planning and permitting management of a treatment plant for contaminated groundwater in Bitterfeld - 40 m^3/h, including a stripping tower, flocculation and precipitation stages, and catalytic combustion of the exhaust air.
- Site management for treatment of soil at a former coal-storage area contaminated with radioactive thorium and cobalt at BASF Schwarzheide.
- Site management for treatment of soil heavily contaminated with dioxins and furans at a former copper smelter, Marsberg.

1993 - 1997 **Harbauer GmbH & Co. KG Berlin/ Marktredwitz, Germany**

Project Manager and later Senior Plant Manager

- Project manager/ commissioning manager for the largest thermal soil remediation plant in Europe for mercury-contaminated waste, in Marktredwitz/ Bavaria:
    - Fully automated plant including: crusher, mill and screening steps, physical/chemical treatment, dewatering units, three rotating kilns (thermal desorption, vacuum distillation and incineration), steam boilers, water treatment and solidification and immobilization of the output material.
    - Design review, P&I-diagram review, Process Hazard Analysis (PHA), permitting-management, site supervision, pre-commissioning (direction of movement check, safety chain check, program check etc.), commissioning/ monitoring test run procedures, investigating weak points of process and optimization of the plant.

- Senior plant manager for a soil washing plant in Berlin. Technical and financial control (also acquisition) of a fully-automated multi-step hydraulic remediation plant (the most modern in Germany) for highly contaminated mineral waste:
    - Technical modification of the plant to double the throughput and improve the degree of purification.
    - Development of a flotation process for soil heavily contaminated with heavy metals, PHC and PAH.
    - Improvement of the water treatment unit (50 m^3/ h) for the contaminant-enriched process water (heavy metals, cyanides and phenols). The unit included flotation, flocculation and precipitation stages, neutralization, slurry thickeners, separators and chamber filter presses.

1991 - 1993 **VierIng Verfahrenstechnik GmbH Berlin, Germany**

Project Manager

- Engineer in charge of a research project on the solidification and immobilisation of hazardous waste using a multi-step palletizing process:
  - Treatment of inorganic hazardous wastes containing soluble heavy metals to make them into a stable product suitable for a landfill for non-hazardous waste.
  - Hazardous waste was also mixed with fly-ash, then pelletized and encapsulated with a cement shell in order to form a solid product able to retain the contaminants.
- Contributions to the development of a vacuum distillation process for treating mercury-contaminated waste.

1989 - 1991 **Technical University**
Faculty of Process Engineering **Berlin, Germany**

Student Assistant at the Department of Mineral Processing (Prof. Simonis)

- Design and construction of experimental machinery.
- Computer-assisted experimental investigations of the behaviour of a model steel-ball mill.
- Team member in a research project on multi-step agglomeration (pelletizing) of iron ores

1986 - 1989 **Practical Training** **South Africa/UK/Germany**
(Mining and Mineral Processing)

- Operator: Mineral Processing Plant (Milling and Flotation/ Zinc, Lead and Copper) Rammelsberg/ Bollrich, Preussag Metall, Goslar/ Germany
- Miner: Open Cast Lignite Mine Alversdorf, BKB, Helmstedt/ Germany
- Junior Engineer: Platinum/ Chromium Mine, Impala Platinum South Africa
- Miner: Tin Mines, Cornwall/ UK
- Miner: Coal Mine Heinrich Robert, German Coal, Hamm, Germany
- Foreman: Tunnel Construction (Dornbuschtunnel), Walter Bau AG, Fulda, Germany

Experience abroad: Australia, United Kingdom, South Africa, Russia, United Arab Emirates and Uganda

Languages:
German: mother tongue
English: fluent
Russian: basic
Netherlands/Afrikaans: basic
Arabic: beginner