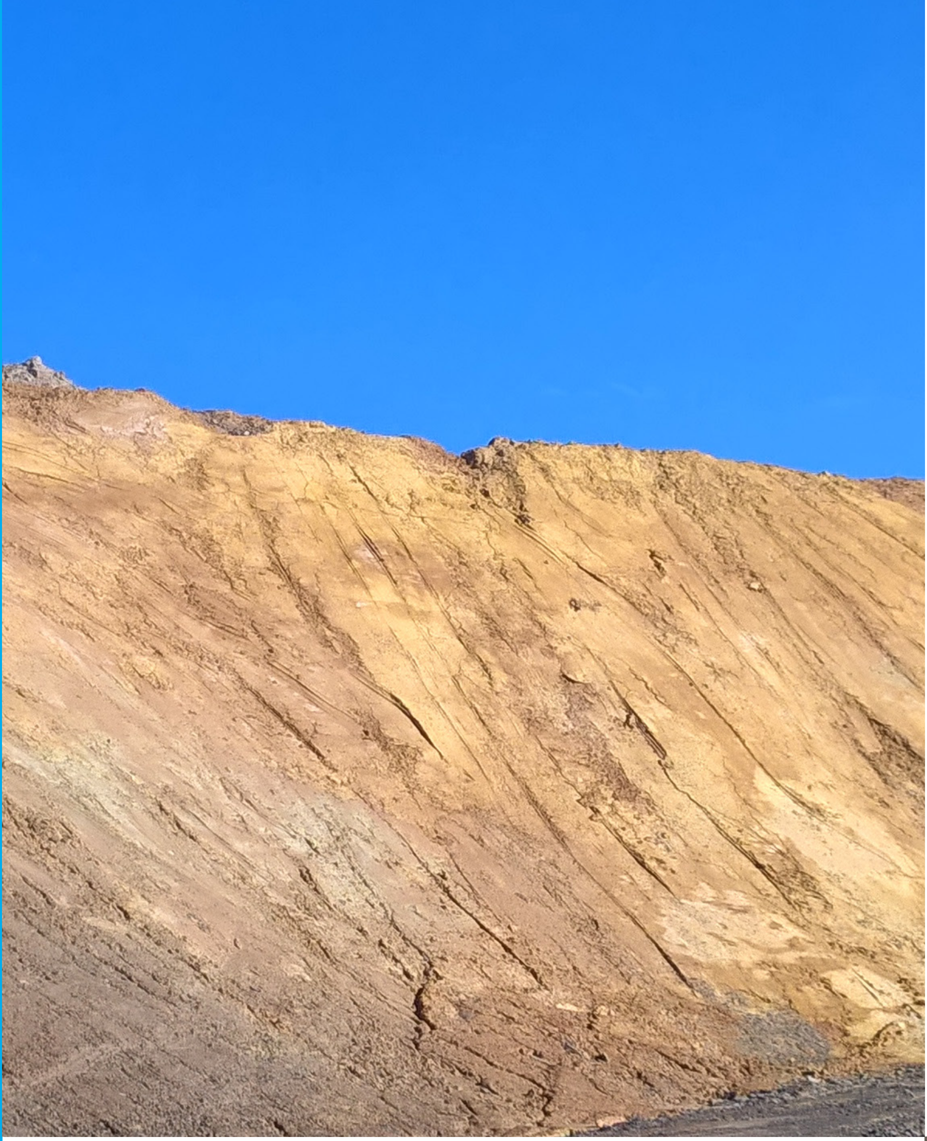
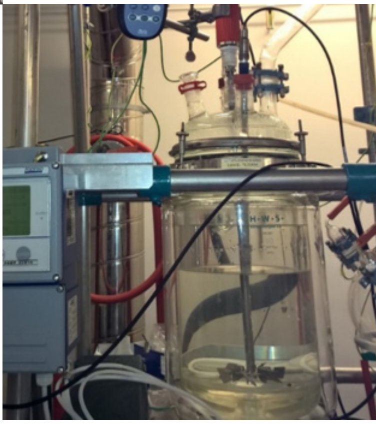


SCIENCE • TECHNOLOGY • RESEARCH HIGHLIGHTS • VISIONS
317



The Jarogain Process for Metals Recovery from Jarosite and Electric Arc Furnace Dust

Process Design and Economics

Petteri Kangas | Max Nyström | Inka Orko |
Pertti Koukkari | Pekka Saikkonen | Jussi Rastas

VTT TECHNOLOGY 317

The Jarogain Process for Metals Recovery from Jarosite and Electric Arc Furnace Dust

Process Design and Economics

Petteri Kangas, Max Nyström, Inka Orko and Pertti Koukkari

VTT Technical Research Centre of Finland Ltd

Pekka Saikkonen and Jussi Rastas

Promeca Consulting Oy

ISBN 978-951-38-8597-7 (Soft back ed.)
ISBN 978-951-38-8596-0 (URL: http://www.vttresearch.com/impact/publications)

VTT Technology 317

ISSN-L 2242-1211
ISSN 2242-1211 (Print)
ISSN 2242-122X (Online)
http://urn.fi/URN:ISBN:978-951-38-8596-0

JULKAISIJA – UTGIVARE – PUBLISHER

Teknologian tutkimuskeskus VTT Oy
PL 1000 (Tekniikantie 4 A, Espoo)
02044 VTT
Puh. 020 722 111, faksi 020 722 7001

Teknologiska forskningscentralen VTT Ab
PB 1000 (Teknikvägen 4 A, Esbo)
FI-02044 VTT
Tfn +358 20 722 111, telefax +358 20 722 7001

VTT Technical Research Centre of Finland Ltd
P.O. Box 1000 (Tekniikantie 4 A, Espoo)
FI-02044 VTT, Finland
Tel. +358 20 722 111, fax +358 20 722 7001

Cover image: Landfill site; Justin Salminen 2017

Juvenes Print, Tampere 2017

Jarogain Production Process Engineering Analysis

Hydrometallurgical process for utilising zinc-rich waste streams
Analysis based on Discounted Cash Flow Analysis, EBITDA basis. All values in 2016

Plant capacity: 400 000 t/a of jarosite
50 000 t of EAF-dust
Zn in concentrate: 26 000 t/a
Pb-concentrate production: 11 000 t/a
Ag (in Pb concentrate) production: 50 000 kg
In-Ga-Ge –concentrate production: In: 23 000 kg/a, Ga: 9 000 kg/a, Ge 15 000 kg/a
Mg-concentrate production: 137 000 t/a

Capital costs (ISBL)	
H_2SO_4 treatment	5 100 000 €
Leaching	3 900 000 €
Sulfidation and flotation	10 500 000 €
Hydroxide precipitation	2 100 000 €
Sulfide precipitation	3 000 000 €
Arsenic removal	2 400 000 €
Evaporation and cryst.	7 500 000 €
Evaporation and cryst.	4 000 000 €
Thermal treatment	14 800 000 €
Total	53 300 000 €
Added costs	111 900 000 €
(% of main units)	210 %
Total (ISBL)	**165 200 000 €**

Capital costs (OSBL)	
Storages, Handling, Of-	33 000 000 €
H_2SO_4 plant	45 600 000 €
H_2S plant	10 500 000 €
MgO preparation	400 000 €
Boiler	55 000 000 €
Waste water treatment	200 000 €
Total Investment Cost	**309 900 000€**
Design & Project manag.	31 000 000 €
(% of TIC)	10 %
Project contingencies	31 000 000 €
(% of TIC)	10 %
Other CAPEX	18 600 000 €
Total Plant Cost (TPC)	**390 500 000 €**
Lifetime of plant (years)	30
Construction time (years)	3
Pay-back time (years)	15
Discount rate (%)	9 %

Manufacturing costs (€/a)	
Fixed costs	19 600 000 €
H_2SO_4	7 700 000 €
SO_2	0 €
MgO	11 700 000 €
H_2S	1 500 000 €
NaHS	2 400 000 €
Coal	8 600 000 €
Other chemicals	2 400 000 €
Lime	700 000 €
Utilities	1 900 000 €
Electricity	8 520 000 €
Waste	7 600 000 €
Logistics	10 600 000 €
Total	83 200 000 €

Revenues (€/a) (@LCOP)	
Pb-concentrate	40 800 000 €
Zn-concentrate	42 700 000 €
In-, Ga-, Ge-concentrate	21 600 000 €
Fe-concentrate	6 400 000 €
Mg-concentrate	11 000 000 €
Treatment costs	9 000 000 €
H_2SO_4	8 400 000 €
Total	139 900 000 €
Net sales revenue (€/a)	131 400 000 €
Gross margin (€/a)	76 400 000 €
EBITDA (€/a)	56 800 000 €
Levelised Cost of Production of concentrates (of pure metal prices, Fe and Mg-concentrate)	**80 %**

Contents

Appendices

Abstract

List of symbols

BAT	Best Available Technology
CAPEX	Capital Expenditures
CEPCI	Chemical Engineering Plant Cost Index
CS	Carbon Steel
CSTR	Continuous Stirred Tank Reactor
DCF	Discounted Cash Flow
EAF	Electric Arc Furnace
EBITDA	Earnings Before Interest, Taxes, Depreciations and Amortizations
EXP	Experiment
FRP	Fibre Reinforced Plastic
ISBL	Inside Battery Limits
LCOP	Levelized Cost of Production
MGD	Million Gallons per Day
MVR	Mechanical Vapour Evaporator
NPV	Net Present Value
O&M	Operations & Maintenance
OPEX	Operational Expenditures
OSBL	Outside Battery Limits
p	Pressure
T	Temperature
TEA	Techno-Economic Analysis
TIC	Total Invested Capital

TCR	Total Capital Requirement
TPC	Total Plant Cost
RLE	Roast-Leach-Electrowinning
SS	Stainless Steel
V	Volume

1. Introduction

Currently, the main part (85 %) of the world's zinc is produced by the Roast-Leach-Electrowinning (RLE) process [1,2]. This approach was widely adopted after the 1970 and has been referred to as jarosite or goethite technology. Although the yield of zinc obtained increased from less than 90% to 97–98%, an adverse result of these new processes was their large amount of waste, appearing in the form of jarosite and goethite residues. For every tonne of zinc metal produced using the RLE process, typically 0.5 tonne of such residues is generated.

Zinc residues are classified as a hazardous waste due to their content of e.g. Cd, As and Pb. Traditionally, jarosite has been disposed of in problem waste facilities, or stored in on-site residue areas or tailings dams. During over 40 years of operation, significant volumes of such metal-containing waste has been stockpiled in both the EU and elsewhere.

With regard to uses of zinc metal, nearly 50 % of the currently produced zinc is applied in prevention of corrosion, as a result of which a major portion will be returned with steel waste into the electromelting-type processes of the steel industry. During this processing, zinc becomes evaporated and oxidized, and is carried away from the process with the formed dusts. The zinc oxide content of these dusts of steel factories varies from 20 up to 40%. The estimated production of steel melting electric arc furnace (EAF) dust globally is ca. 7.5 Mt/a, of which ca. 45% is recycled (within the EU the EAF the dust recycling rate exceeds 80 %).

The dusts are commonly processed using the Waelz process (see e.g. [3]), in which the EAF dust is fed to a rotary kiln and reduced to Zn-vapour that is then finally oxidized and recovered at baghouse filters. The recovered dust (Waelz oxide) includes well over 250 000 t/a of zinc in the EU. Trace amounts of halogens (chlorides and fluorides) remain in the Waelz kiln product and must be removed before the oxides can be fed to the electrolytic zinc process, as they would cause corrosion and fuming problems while also disturbing the electrolysis [4].

Due to environmental concerns, increasing restrictions on the construction and management of storage facilities for zinc residue have been applied. Governments are strengthening environmental legislation to force companies to find commercially and environmentally viable means to develop such process flowsheets that will allow either significant reduction of residue formation or their recirculation into useful products. It would also represent a considerable advantage if the zinc-containing dusts of the steel industry could be processed in a manner facilitating early removal of halogens, taking place in the close vicinity of the zinc manufacturer.

Three major lines for the treatment of jarosite waste have been proposed: stabilisation for use as a landfill or component in e.g. road construction, pyrometallurgical smelting to produce an inert slag and recover some of the metal contents, and finally various hydrometallurgical techniques for more complete recovery of the valuable components within the waste. Due to the aforementioned harmful constituents (As, Cd), the stabilisation developments have had only limited success. The stabilisation processes do not recover the contained metal values, and the cost of reagents required as part of the process can be high.

Pyrometallurgical treatments have been adapted e.g. in Korea and China, [1,5,6] and will offer a robust solution; they are however hampered by their required investment and unavoidable high energy consumption and carbon footprint. Thus, interest in reprocessing jarosite to recycled value-added products by hydrometallurgical means similar to those readily applied in the RLE process has also been increasing during recent years [7–12]. The challenge is in proofing the viability of hydrometallurgical treatment both in the recovery of the contained metals and in producing an inert material suitable for safe disposal of non-product elements.

Based on earlier studies [13,14], a novel hydrometallurgical Jarogain process, combining recycling treatment of jarosite with recovery of zinc from the EAF dust, has been developed [15]. In the Jarogain process, a holistic operation consisting of low-cost and energy-efficient techniques is targeted at the recovery of concentrates which will then bear the major value-added metal components, without generating problem waste.

This study outlines the process design and corresponding economics of the Jarogain process based on the experiments of Proof-of-Concept studies. Technical performance of the key process areas of the holistic recovery are presented. The variable production costs are estimated based on the technical evaluation. The assessment of investment costs is also conducted. Finally, the techno-economic potential of the new Jarogain concepts is assessed on the basis of the discounted cast flow (DCF) analysis.

1.1 Goal

The aim of this report is to illustrate the process design of the proposed Jarogain concept and to estimate the techno-economic feasibility of the process.

1.1 Methodology

Technical evaluation was based on the mass and energy balances. The key reactions within the different process areas were included and the main process parameters were obtained from the Proof-of-Concept part of this study or based on the previous knowledge of the project group. The process design follows the proposed

Jarogain concept and utilises the typical unit operations and flowsheets applied in the hydrometallurgical industry (e.g. RLE plants, metal recovery plants).

The investment estimates were given on the basis of the main process units (reactors, clarifiers, filters, pumps, furnaces) and related process parameters (T, p, pH, V, residence time). Here the literature was utilised for reference prices ([16],[17],[18]) which were later scaled to current capacity and the year 2016. Based on the costs of the main process units, other cost factors were obtained (installation, piping, electrical, instrumentation etc.). In addition, factors such as contingency and working capital were included and thus a total capital cost of the Jarogain process was obtained.

The economic feasibility of the proposed Jarogain process was assessed on the basis of the discounted cash flow (DCF). The lifetime of the plant was assumed to be 30 years, the payback time 15 years and the interest rate was 9%. The duration of plant construction was 3 years. Calculations were conducted on an EBITDA-basis (Earnings Before Interest, Taxes, Depreciations and Amortizations). The aim here was to find a Levelized Cost of Production for different metal concentrates. The prices of these concentrates are given as a fraction of the pure metal price, thus indicating the possible margin of the Jarogain process.

Technical assessment was conducted with the HSC-Sim tool, [19] utilising hydrometallurgical unit operations. Economic assessments were conducted using Microsoft Excel.

A qualitative validation of this study was conducted by presenting this report to the experts of Boliden, Outotec and VTT. The report was refined on the basis of the key comments of these experts.

This study is a concept level feasibility study including considerable uncertainty. More detailed pre-feasibility and feasibility studies need to be conducted at a later date in order to ensure the viability of the process before any investment decision.

2. Process design and cost estimation details

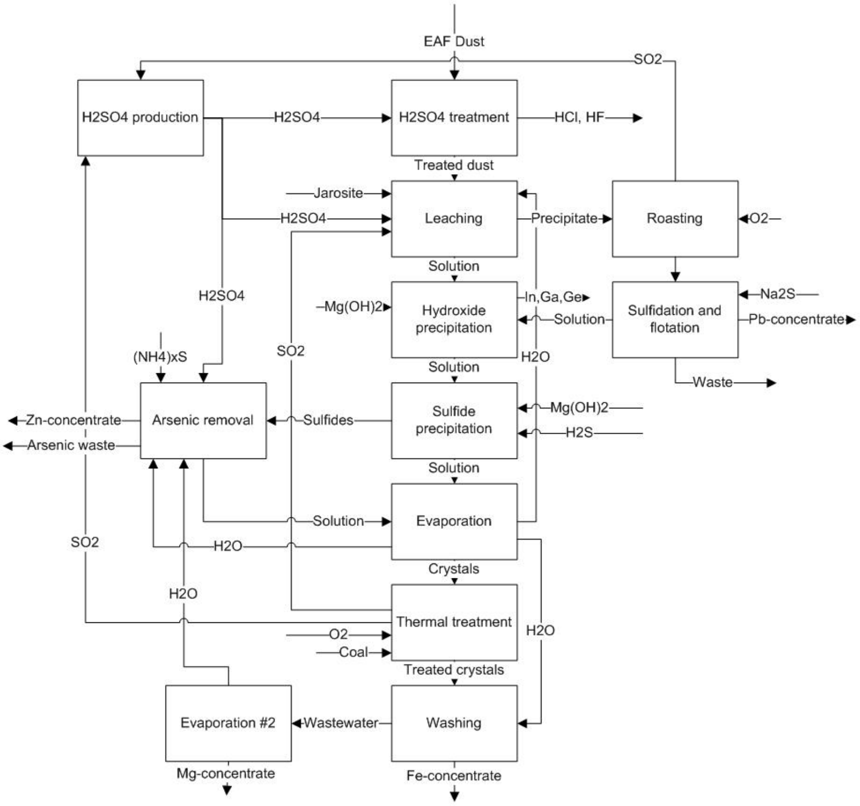


Figure 1. The Jarogain process for treating 400 000 tonnes of jarosite and 50 000 tonnes of EAF-dust annually.

The Jarogain-process is a hydrometallurgical concept for treating zinc-containing wastes and side-streams from zinc- and steel-making plants. The possible raw materials are jarosite and goethite, coupled with electric arc furnace (EAF) dust. The aim is a zero or near-zero process concept for valorising the metal content of treated streams.

The Jarogain process treats 400 000 tonnes of jarosite annually during 8000 h of operation. Of this amount, 200 000 tonnes are assumed to be fresh from the zinc factory and 200 000 tonnes from the jarosite heap. The process also treats 50 000 t of EAF-dust annually.

The overall block diagram of the Jarogain process is illustrated in Figure 1.

The following inside battery limits areas (ISBL) are considered during the technical evaluation:

- Area 100 – Sulfuric acid treatment
- Area 200 – Leaching
- Area 300 – Roasting, sulfidation and flotation
- Area 400 – Hydroxide precipitation
- Area 500 – Sulfide precipitation
- Area 600 – Arsenic removal
- Area 700 – Evaporation and crystallization
- Area 800 – Thermal treatment and washing
- Area 900 – Evaporation and crystallization #2

Following outside battery limits (OSBL) are considered here:

- Area 1100 – Sulfuric acid plant
- Area 1200 – Hydrogen sulfide generator
- Area 1300 – Waste water treatment plant
- Area 1400 – Boiler
- Area 1500 – MgO and CaO preparation

3. Raw materials

The Jarogain process treats 400 000 tonnes of jarosite annually. Half of the treated jarosite, 200 000 t/a, is fresh zinc process residue from the modern zinc RLE process (TEA #1 in Table 1). The modern process includes recovery of lead, silver and gold as well as indium within the zinc plant. In addition, direct leaching with additional elemental sulfur is assumed.

One fourth of the jarosite, 100 000 t/a, is slightly older jarosite from the jarosite heap. It is assumed that this fraction is from a process in which the direct leaching process has been utilised and thus the amount of sulfur remains higher. Lead, silver, gold and indium have not been recovered during the processing and their content in the jarosite feed is estimated accordingly (TEA #2 in Table 1).

The last quarter of the raw material (100 000 t/a) is also considered to be old jarosite from the heap. Here the valuable metals, lead, silver, gold and indium, are present and the sulfur content is lower as only the roasting-leaching process was utilised when this fraction was produced.

The three fractions illustrate typical jarosite waste characteristics available within the zinc industry. The comparison of applied materials (TEA #1 – 3) and industrial jarosites can be found in Table 1. There are naturally wide variations between different sites, as the original zinc concentrates as well as the applied processes have varied. In addition, the samples from the jarosite are usually obtained from fixed positions on the heap and thus there might be wide variations within a single site.

Table 1. Composition of different industrial jarosites and those used for the techno-economic assessment. [w-%]

	Boliden, Kokkola	**[a]Nyrstar, Budel**	**Trepça, Kosovo**	**HZL, Debari**	**Gegamines, Kolwezi**
Ref	[20–24]	[25]	[26]	[27]	[28]
Ag	0.007-0.012	0.052	0.0001		0.008-0.016
Al	0.3-1.0	1.4	0.8	3.6	
As	0.1-0.6		0.5		0.39
Au	0.00005				
Ba			0.06		
Bi					
Ca	1.5-5.0	4.0		4.8	
Cd	0.01-0.07	0.05	0.22		0.12-0.16
Cl	<0.005				
Co	0.002-0.010	0.0004	0.003		
Cr			0.04		
Cu	0.1-0.2 (6.2)	0.60	0.92		2.7-2.9
F					

Fe	8-32	11.5	31.3	23.7	26.6-32.8
Ga					0.045-0.11
Ge	0.003-0.004	0.019			0.047-0.049
Hg	0.0006-0.01				
In	0.006-0.009				
K	0.5	0.9		0.6	
Li					
Mg	0.1-0.3			1.10	
Mn	0.01-0.2 (1.8)	0.06	0.63	0.20	
Mo	0.004				
Na	0.3-1.7	0.30		0.70	
NH_4			0.6	1.9	
Ni	0.010	0.002	0.009		
Pb	1-6	13.1	7.5	1.9	2.1-2.4
S	3-35	10.5	6.6	12.2	4.0
Sb	0.01-0.08				
Se	0.0003-0.003				
Si	6.8	5	2.9	3.4	
Sn					
Sr			0.014		
Tl	0.0006-0.0012	0.01			
Zn	2-4 (16)	3.7	10.2	8.2	16.8-19.4

Table 1. Continues.

	Unkn. [Creedy]	**Unkn. [Karumb]**	**TEA #3**	**TEA #2**	**TEA #1**
Ref	[1]	[29]			
Ag	0.008-0.06	0.011	0.02	0.02	0.0066
Al		0.27	0.5	0.5	0.5
As		0.07	0.5	0.5	0.5
Au		0.0138	0.00005	0.00005	0.00002
Ba			0.01	0.01	0.01
Bi		0.007			
Ca		3.07	4	4	4
Cd		0.02	0.05	0.05	0.05
Cl			0.006	0.006	0.006
Co			0.005	0.005	0.005
Cr		0.011			

Cu		0.09	0.2	0.2	0.2
F					
Fe	25.0	18.7	21.4	20.9	20.4
Ga		0.0061	0.005	0.005	0.005
Ge		0.008	0.005	0.005	0.005
Hg					
In		0.025	0.01	0.01	0.0033
K		0.31	0.5	0.5	0.5
Li		0.2			
Mg			0.2	0.2	0.2
Mn		0.09	0.1	0.1	0.1
Mo		0.0033			
Na		1.98	1	1	1
NH4			0.5	0.5	0.5
Ni		0.016	0.01	0.01	0.01
Pb	2-5	1.5	4	4	1.32
S	13.0		10	20.9	24.4
Sb		0.005	0.05	0.05	0.05
Se					
Si	1-12		4	4	4
Sn		0.0062	0.01	0.01	0.01
Sr		0.0146	0.01	0.01	0.01
Tl		0.004			
Zn	3-5	1.39	3.5	3.5	3.5

Wide variations can be also observed for the electric arc furnace dust (EAF-dust), as illustrated in Table 2. For example, zinc content in the EAF-dust varies between 3 and 79 w-%. The amount of processed stainless steel affects the zinc content of the dust. For the jarogain process, dusts with higher Zn contents are preferred. Similarly, the amount of chlorides and fluorides depends on the extent to which plastic components among the recycled metal are treated in the furnace.

On the basis of the reported industrial compositions of the EAF-dust, the composition applied within this study was chosen (as TEA in Table 2). Within the plant, there are two sources for the EAF-dust as typically the availability of dust from a single steel plant is limited. However, the composition is identical here for both dusts in this study. Within this analysis the zinc content is estimated to be 35 w-% of dust, the chlorine content 2 w-% and the fluorine content 0.2%.

Table 2. Composition of different industrial Electric Arc Furnace (EAF) dusts and the dusts used for techno-economic assessment. [w-%]

	Unkn.	**Unkn. Romania**	**Unkn. USA**	**Unkn. GER**	**Unkn. [Grillo]**	**Unkn. [Nakayama]**
Ref	[1]	[30]	[30]	[30]	[31]	[32]
Al	1.4	0.7-6.4	0.6-6.9	0.1-1.5	1.0-5.3	
Ca	5	3.8-7.6	2.6-16	6.6-15	0.2-1.2	
Cd	0.005				0.8-1.0	
Cl						5.1
Co	0.0005					
Cr		0.2-0.3	<8.2	<0.1		
Cu	0.3					
F						
Fe	20	35-42	16-39	22-44	8-15 (53)	30.9
Ge	<0.005					
K	1				1.2-2.2	1.4
Mg		1.7-2.7	1.2-9	1.0-4.5	0.4-1.0	
Mn	3	3.4-4.1	2.3-9	0.9-4.8		3.0
Mo						
Na	2					1.5
Ni	<0.005		<2.4			
Pb	3		<3.7	1.3-5.0	3.1-7.6	1.9
S	1	0.6-2.2	<1.0	0.3-1.1		
Si	3	2-3	0.9-4.2	0.9-1.7	1.1-3.0	
Tl	0.01					
Zn	30	3-20	<35	5.8-26	63-79 (36)	32.3

Table 2. Continues.

	Unkn. US [Xia]	**Unkn. FR [Xia]**	**Unkn. SP [Xia]**	**Siderúrgica Rio-Grandense**	**Colakoglu Met., Istanbul**	**Kasemsakdi Co., Thailand**	**TEA #1 & #2**
Ref	[33]	[33]	[33]	[34]	[35]	[36]	
Al			0.44	0.0002	0.65	0.24	1.0
Ca	1.9-10	12.8	3.5	0.0039	0.9	5.6	4
Cd	<0.01		0.1	0.05	0.04		
Cl	0.51-2.4	1.75	3.43		0.65	9.8	2

Co							
Cr	0.39	0.37	0.31	0.03		0.5	
Cu	0.06-2.3	0.25	0.54			0.2	0.3
F	0.01-0.88						0.2
Fe	28.5	21.8	25.9	21	27	36	20
Ge							
K	0.06-1.1	2.1	1.2	0.002	1.2	3.5	1.5
Mg	0.8-2.9		1.5	0.001	1.3	1.5	1
Mn	2.5-4.6	2.5	2.8	1.5	2.7	2.7	3
Mo	<0.02-0.08						
Na	0.3-2.3	2.2	1.3		2.5		2
Ni	0.01-0.02	0.1	0.07	1			0.01
Pb	2.1	3.6	3.6	1	3.2	1.7	3
S				0.8	0.7	0.2	
Si	1.35-2.5		1.65	0.02	3.3	1.2	2
Tl							
Zn	19	21.8	18.6	23	29	36	35

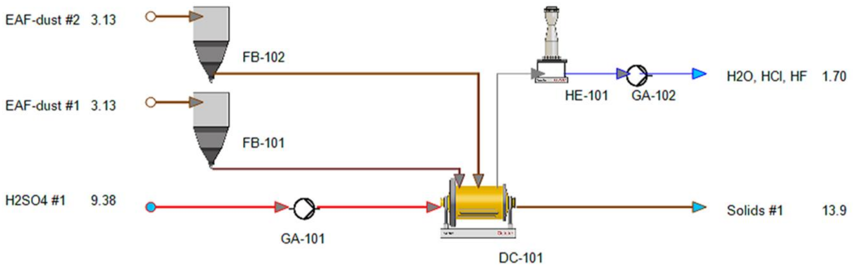
The compositions of raw materials, namely jarosite and EAF-dust, presented in Tables 1 and 2 are converted to possible species in order to be used in the process simulation. The main species within the jarosite fractions are different sulfates ($MFe_3(SO_4)_2(OH)_6$, where M is Na, K or NH_4) and the main species within EAF-dust are oxides. The conversion from elemental composition to species is made with the HSC Species Converter. The feed compositions are illustrated below in Table 3.

Table 3. Input species and the mass fractions [w-%] in the process simulation study.

	Jarosite			**EAF-Dust**
Species	TEA #3	TEA #2	TEA #1	TEA #1 & 2
AgCl	0.028	0.026	0.009	
Al_2O_3	1.030	0.945	0.945	1.904
As_2O_3	0.720	0.660	0.660	
Au	0.000	0.000	0.000	
$BaSO_4$	0.019	0.017	0.017	
CaF_2				0.000
CaO				5.640
$CaSO_4*2H_2O$	18.741	17.183	17.184	
$CdFe_2O_4$	0.140	0.128	0.128	

CoO	0.007	0.006	0.006	
$CuFe_2O_4$	0.821	0.753	0.753	
CuO				0.378
Fe_2O_3				28.810
$Fe_2(SO_4)_3$	3.571	0.002	0.003	
Ga_2O_3	0.007	0.007	0.007	
GeO_2	0.008	0.007	0.007	
In_2O_3	0.013	0.012	0.004	
KF				0.625
$KFe_3(SO_4)_2(OH)_6$	6.985	6.403	6.404	
K_2O				1.314
MgO	0.362	0.332	0.332	1.671
MnO	0.141	0.129	0.129	3.904
NaCl	0.000	0.000	0.006	3.322
Na_2O				0.955
$NaFe_3(SO_4)_2(OH)_6$	22.994	21.079	21.028	
$NH_4Fe3(SO_4)_2(OH)_6$	14.503	13.286	13.292	
NiO	0.014	0.013	0.013	0.013
PbO				3.257
$PbSO_4$	6.385	5.854	1.932	
S	0.000	11.701	15.635	
Sb_2O_3	0.065	0.060	0.060	
SiO_2	9.333	8.557	8.557	4.312
SnO_2	0.014	0.013	0.013	
$SrSO_4$	0.023	0.021	0.021	
$ZnFe_2O_4$	14.075	12.905	12.905	
ZnO				43.895

4. Area 100 - Sulfuric acid treatment



Variable	Unit	EAF-dust #1	EAF-dust #2	H2SO4 #1	Solids #1	H2O, HCl, HF
Temperature	°C	25	25	25	381	25
Pressure	bar	1.0	1.0	1.0	1.0	1.0
Amount	t/h	3.13	3.13	9.38	13.93	1.70
Enthalpy	kWh	-5106	-5106	-21630	-26200	-5954

Figure 2. PDF of Area 100 – Sulfuric acid treatment

4.1 Area 100 - Process description

Target: The EAF-dust contains chlorides (20 mg/g) and fluorides (2 mg/g), which are unwanted elements within the zinc process due to their harmful effects during the electrolysis. Thus, chlorides and fluorides need to be effectively removed from the raw materials.

Process description: The EAF-dust from the steelworks is preheated to 150 °C and mixed with heated (250 °C) sulfuric acid. Effective mixing is applied in order to ensure the complete reactions of halogens to HCl and HF. Simultaneously oxides in the dust form sulfates. Water, hydrochloric acid and hydrogen fluoride evaporate rapidly from the mixture. Good separation efficiency has been reported during the experimental studies, see Table 4. The reactions are exothermic (adiabatic temperature up to 440 °C) and they are listed in Appendix B.

The sulphuric acid treatment is performed in a rotating drum reactor for maximum contact between the zinc dust and acid, see Table 5. It is assumed that only water, hydrochloric acid and hydrogen fluoride exit in the gas phase. The composition of the EAF-dust applied here is presented in Table 2 and contains 35% of zinc. The same composition of dust is applied for both bins in Figure 3. The total amount of treated EAF-dust is 50 000 t annually, resulting in 110 000 t of sulfatised dust. The consumption of sulphuric acid is 1.5 t acid / t of EAFD.

Table 4. Area 100 - Key reaction efficiencies within experiments and applied in TEA.

	Exp 1*	Exp 2	TEA
Cl	< 5 %	5 %	5%
F	< 5 %	60 %	5%*
* Experiments conducted before the Jarogain project also show good separation of F.			

Table 5. Area 100 - Key process parameters within experiments and applied in TEA.

	Exp 1	Exp 2	TEA
H_2SO_4 dosage (kg/t EAF-dust)	n/a	1.4 – 1.5	1.5
Temperature (°C)	> 200	> 200	380
Reaction time (h)	n/a	0.5	0.5

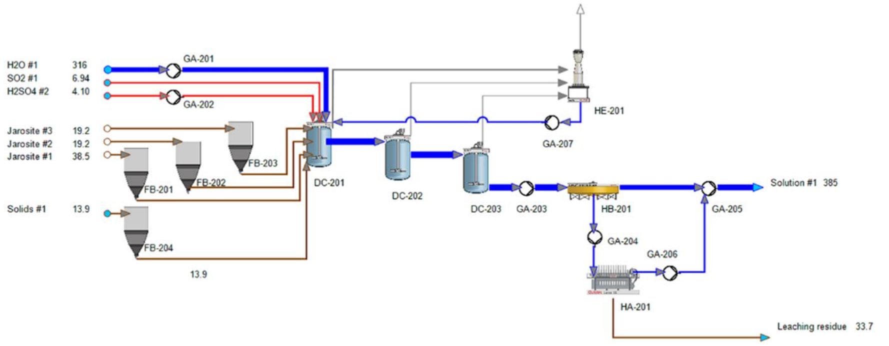
4.2 Area 100 – Cost estimation

Cost Estimation: As this is not a common equipment, the reactor was sized according to a Pug Mill twin spiral mixer. Based on the mass flow, the required capacity of the reactor is 350 ton/d. The conservative cost estimate of corresponding pug mill is 5 M€ [37]. The two silos are based on mass flow and a 2 hour residence time. The dust density is assumed to be 1.992 t/m^3 [38]. The scrubber is sized according to the volumetric flow through it and the cost correlation is obtained for a wet dynamic scrubber [39]. The pumps are sized according to the volumetric flow and their cost is obtained from a cost correlation for centrifugal pumps [40].

Table 6. Area 100 – Main process units within sulfuric acid treatment.

EQ #	Description	T (°C)	pH	Material	Size		Cost (€)	Ref
FB-101	EAF Dust silo 1	25	7	CS	4.0	m^3	10 000 €	[41]
FB-102	EAF Dust silo 2	25	7	CS	4.0	m^3	10 000 €	[41]
DC-101	Drum reactor	381	0.5	SS 316	350	t/d	5 000 000 €	[42]
HE-101	Scrubber	381	7	SS 316	1.0	m^3/s	16 000 €	[39]
GA-101	H_2SO_4 pump	25	0.5	SS 316	1.5	l/s	11 000 €	[41]
GA-102	HCl & HF pump	25	7	SS 316	0.5	l/s	11 000 €	[41]

5. Area 200 – Leaching



Variable	Unit	Jarosite #1	Jarosite #2	Jarosite #3	Solids #1	H2O #1	SO2 #1	H2SO4 #2	Leaching residue	Solution #1
Temperature	°C	25	25	25	381	25	25	25	90	90
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Amount	t/h	38.46	19.24	19.23	13.93	316.27	6.94	4.10	33.66	384.51
Enthalpy	kWh	-111174	-56012	-59209	-26200	-1393867	-8936	-9464	-91913	-1557974

Figure 3. PDF of Area 200 – Leaching.

5.1 Area 200 – Process description

Target: The aim of the leaching step is to dissolve most of the metals as sulfates and to reduce ferric iron to ferrous iron. The leaching residue contains lead, silver and gold to be recovered as a value-added concentrate.

Process description: Jarosite and the sulfatised EAF-dust are cooled down to 90 °C and fed to reactor, where materials are leached with sulphuric acid. pH is 0.5 - 1.0. Most of the metals are dissolved as sulfates but Pb, Ag and Au remain in the solid residue. During the leaching process, sulfur dioxide is fed to the reactor in order to provide reductive process conditions and to facilitate the dissolution, but also to reduce iron from Fe(III) to Fe(II). This is beneficial for the further processing of solutions, as ferrous iron remains in solution during the subsequent precipitation steps.

The leaching is performed in three continuous stirred tank reactors (CSTR) in series. Reaction time is 3 hours. After the leaching, the solid and liquid products are separated in a thickener and further water removal is conducted in a press. The reactions used in the process model can be seen in Appendix B. The consumption of SO_2 is 7 t/h, corresponding to ~ 110 kg of SO_2 per ton of raw material (jarosite + EAFD). Water is added so that the solid content is 220 kg/m3, leading to a water consumption of 316 t/h.

A total of 400 000 tonnes of jarosite are treated annually within the plant. Three different sources for the jarosite are used, as indicated in Table 1: first fresh jarosite from zinc production (200 000 t/a), second jarosite from the existing jarosite newer heap (100 000 t/a), and third jarosite from the older heap (100 000 t/a). In addition, the sulfatised EAF-dust is processed and thus an additional 14 t/h material is introduced to the process.

Table 7. Area 200 - Key reaction efficiencies for leaching.

	Exp 1	Exp 2	TEA
Pb	100%	99%	100%
Ag	n/a	100%	100%
Au	n/a	n/a	100%
Ca	92%	85%	90%
Si	100%	92%	100%
Zn	12%	8%	10%
Fe	8%	5%	5%
In	77%	0%	0%
Ga	33%	78%	50%
Ge	51%	0%	0%

Table 8. Area 200 – Key process parameters for leaching.

	Exp 1	Exp 2	TEA
pH	0.4-0.6	0.9-1.7	< 1.0
Temperature (°C)	90	85-90	90
Reaction time (h)	24	20-24	3
H_2SO_4 dosage (kg/t raw material)	80-90	50-100	80
SO_2 dosage (kg/t raw material)	760-840	600	110
Solid content (kg raw material/m^3)	260 - 280	160-220	220
Solids after thickener	-	-	25%
Solids after filter	-	-	75%

5.2 Area 200 - Cost estimation

Cost Estimation: Based on the feed and residence time, the required reactor volume is 2400 m^3 (assuming a 90% fill rate, 0.97 t/m^3 density at 90 °C [43]). Three 400-m3 reactors are sufficient. The cost of the reactors was obtained through correlation with reactor costs provided by Outotec [42].

Separation of the solid and liquid phase is effected through settling. It is assumed that a minimum retention time of 90 minutes is required for sufficient separation [44]. The volume of the tank is chosen so that the minimum retention time is met. The volume of the tank is thus dependent on the inlet flowrate. The dimensions should also be within standard measures [45]. A tank with a depth of 3.5 m, width 6 m and length 31 m gives a sufficient retention time. For rectangular settlers no price correlation was found. Instead, price correlations for circular settlers based on diameter were selected. The price was obtained through correlation with Outotec's high rate thickeners [42].

Table 9. Area 200 – Main process units within leaching.

EQ #	Description	T (°C)	pH	Mate-rial	Size		Cost (€)	Ref
FB-201	Jarosite silo 1	25	7	CS	30.0	m^3	22 000 €	[41]
FB-202	Jarosite silo 2	25	7	CS	14.0	m^3	16 000 €	[41]
FB-203	Jarosite silo 3	25	7	CS	14.0	m^3	16 000 €	[41]
FB-204	Treated dust silo	381	7	CS	16.0	m^3	7 000 €	[41]
DC-201	Leaching reactor 1	90	0.5	SS 316	800	m^3	721 000 €	[42]
DC-202	Leaching reactor 2	90	0.5	SS 316	800	m^3	721 000 €	[42]
DC-203	Leaching reactor 3	90	0.5	SS 316	800	m^3	721 000 €	[42]
HB-201	Settler	90	0.5	SS 316	15.0	m	973 000 €	[42]
HE-201	Scrubber	90	7	SS 316	2.00	m^3/s	23 000 €	[39]
HA-201	Filter	90	0.5	SS 316	40	m^2	520 000 €	[39]
GA-201	Water pump	25	7	CS	90.0	l/s	22 000 €	[41]
GA-202	H_2SO_4 pump	25	0.5	SS 316	1.0	l/s	11 000 €	[41]
GA-203	Solution pump	90	0.5	SS 316	120.0	l/s	34 000 €	[41]
GA-204	Filter pump	90	0.5	SS 316	30.0	l/s	17 000 €	[41]
GA-205	Solution pump	90	0.5	SS 316	110.0	l/s	32 000 €	[41]
GA-206	Solution pump	90	0.5	SS 316	20.0	l/s	15 000 €	[41]
GA-207	Scrubber condensate pump	25	7	SS 316	1.0	l/s	11 000 €	[41]

Some evaporation is assumed to occur in the reactors and thus scrubbers are required to prevent potentially harmful substances such as hydrogen sulfide from leaking. The scrubbers are assumed to condense the gas and feed the liquid back to the reactors. The calculations are based on the relative moisture of air (assumed to be 50%) and the moisture holding capacity of effluent air based on temperature.

The prices are scaled according to a price correlation based on volumetric flow [39]. Table 10 shows temperature, moisture-holding capacity at said temperature and volumetric flow for each process step that requires scrubbers, also in the other process areas.

Table 10. Scrubber CAPEX.

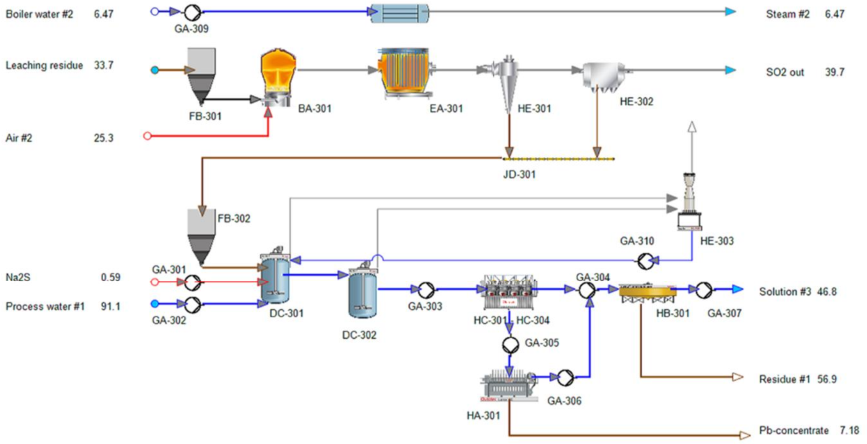
	Temperature	Air moisture holding capacity (kg/kg)		Volumetric flow	
Leaching	90	1.1	kg H_2O/kg air	1.66	m^3/s
Hydroxide precipitation	70	0.28	kg H_2O /kg air	0.27	m^3/s
Sulfide precipitation	67	0.28	kg H_2O /kg air	0.20	m^3/s
Sulfidation	70	0.28	kg H_2O /kg air	0.11	m^3/s
Arsenic removal	45	0.05	kg H_2O /kg air	0.02	m^3/s
Washing	43	0.05	kg H_2O /kg air	0.16	m^3/s

The filter used for the final solid-liquid separation is assumed to be a rotary drum filter. The price is obtained through a price correlation based on filter area [39]. As no data concerning the separation rates for the Jarogain process exists, the separation rates were assumed based on values found in literature [46]. The assumed filtration rates can be seen in Table 11.

Table 11. Assumed filtration rates

Filter	Assumed filtration rate (kg/m^2h)
HA-201	2800
HA-301	500
HA-401	2800
HA-501	300
HA-601	300
HA-602	300
HA-801	12000

6. Area 300 - Roasting, sulfidation and flotation



Variable	Unit	Leaching residue	Air #2	Na2S	Process water #1	Boiler water #2	Pb-concentrate	Residue #1	Solution #3	SO2 out	Steam #2
Temperature	°C	90	25	25	25	90	25	25	25	250	150
Pressure	bar	1.0	1.0	1.0	1.0	5.0	1.0	1.0	1.0	1.0	5.0
Amount	t/h	33.66	25.27	0.59	91.10	6.47	7.18	56.93	46.80	39.71	6.47
Enthalpy	kWh	-91913	0	-942	-401478	-28027	-15572	-235946	-204052	-44782	-23703

Figure 4. PFD of Area 300 – Roasting, sulfidation and flotation.

6.1 Area 300 – Process description

Target: The aim is to remove the calcium (gypsum) and silicates from the Pb-concentrate and thus to upgrade the value of this concentrate further for use by lead smelters.

Process description: As the residue from the leaching stage contains some elemental sulfur, this will be removed by roasting it in a furnace, where the elemental sulphur is oxidized to sulphur dioxide and can be further utilized in the sulfuric acid plant. The temperature of the furnace must not exceed 600 °C (risk of formation of Pb-silicates). The reaction is exothermic, so it is assumed that it can be sustained without the addition of fuel. The process contains a furnace, recovery boiler, cyclone and electrostatic precipitator. Heat (5 MW) is recovered from the boiler as steam.

After roasting, the mixture is mixed with water. Sodium sulphide is added in an equivalent amount in order to form lead and silver sulfides. This is performed in two CSTRs. The Na_2S-solution consumption is 0.6 t/h. After the sulfidation, the flotation is performed in four flotation tanks at room temperature (25 °C). Flotation aid is needed for ensuring better fractionation during the process. The lead and silver sulphides and gold float are separated from the foam. These are also the main products of the whole Jarogain process. Here a positive assumption is made for the recovery efficiencies of lead, silver and gold, see Table 12, as suggested by prior experiments [47]. The press is utilized for further removing water from the product, Pb-concentrate The total amount of wet Pb-concentrate is 7.2 t/h. Pb content was up to 40% in experiments. When optimized process is considered, Pb content of 50-60% is assumed.

The un-floated part is fed into a thickener, where the liquid and remaining solids are separated. The solids constitute a waste, that is sent to landfill or tailings dam. The remaining liquid is sent back to the main process (hydroxide precipitation). The applied reactions within the roasting and sulfidation are illustrated in Appendix B.

Table 12. Area 300 - Key reaction efficiencies during roasting, sulfidation and flotation.

	Prior Exp[47]	**Exp 1**	**Exp 2**	**Exp 3**	**Exp 4**	**TEA**
Pb	~ 85%	45%	55%	17%	79%	90%
Ag	~ 95%	25%	64%	13%	71%	90%*
Au	~ 85%	28%	72%	25%	88%	90%
Zn	~ 5%	32%	66%	21%	89%	90%
Ca		n/a	n/a	n/a	5%	0%
Si		37%	48%	13%	57%	0%*
* Positive assumption applied here for TEA.						

Table 13. Area 300 - Key process parameters for leaching.

	Exp 1	**Exp2**	**Exp 3**	**Exp 4**	**TEA**
Temperature in roasting(°C)	-	850	900	550	600
Yield in roasting (%)	-	52%	51%		75%
Reaction time in roasting (h)	-	n/a	2	>12	2
pH in sulfidation	3.2->7.4	6.3->7.7	2.0	2.0	2
Reaction time in sulfidation (h)	3	1	2	1	2
Solid content in sulfidation (kg/m^3)	n/a	n/a	n/a	n/a	220
Na_2S charge (kg/t raw material)	n/a	n/a	16	100	30
pH in flotation	7.5-7.8	3	2-3	2-3	2
Reaction time in flotation (h)	0.5	1	1	0.5	1
Solid content in flotation (kg/m^3)	n/a	n/a	n/a	n/a	220
Foaming agent (kg/t raw mat.)	0.1	2.2	0.4	4	n/a
Collector chemical (kg/t raw mat.)	0.2	3.1	1.5	50	n/a
Solids after thickener	-	-	-	-	25 %
Solids after filter	-	-	-	-	75 %

6.2 Area 300 - Cost estimation

Cost Estimation: The leaching residues are roasted in a furnace. The investment cost of the furnace was obtained from a similar zinc roasting process [17]. The cost evaluation is based on an overall roasting process, without looking at the individual parts, as these are assumed to be similar and to scale accordingly. The prices of two equal processes with different scales can be compared according to

$$C_B = C_A \cdot \left(\frac{S_B}{S_A}\right)^n, \tag{1}$$

Where C is cost, S is size and n is a size factor (assumed to be 0.6 if more precise data is not available). Here the reference plant capacity is 220 000 t/a and has a price of 20.7 M € [17]. The flow through the Jarogain process is 269 000 t/a. Thus the price according to equation 1 is 24 M €. Dividing by 3.2 (other ISBL costs) gives the purchased equipment cost of 7.5 M €. This price includes gas-handling equipment: recovery boiler, cyclone, electrostatic precipitator as well as a conveyor for the treated dust.

The CSTRs are calculated in the same way as in section 5.2 for a residence time of 1 hour. Two 22 m^3 reactors provide sufficient volume. The reactors cost 0.9 M € [40].

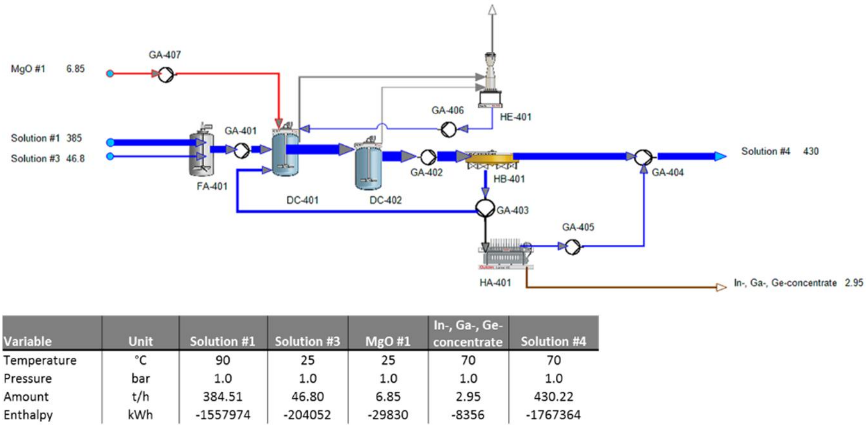
The flotation system was not sized but has a capacity of 50 t/h or 0.33 million gallons per day (MGD).The cost of the flotation tank was calculated by rescaling. A 1 MGD system costs 215 000 $ and a 15 MGD system costs 1.2 M [16]. These two installations can be matched according to equation 1. This yields a size factor of 0.63. Matching equation 1 to the 0.2 MGD flotation cell in the Jarogain process, we get an equipment cost of 83 000 $ (in 1994). The settler after the flotation is calculated according to section 5.2 and has the dimensions 3.5x1x16 m.

Table 14. Area 300 – Main process units within roasting, sulfidation and flotation.

EQ #	Description	T (°C)	pH	Material	Size		Cost (€)	Ref
FB-301	Leaching residue silo	90	3	SS 316	25	m^3	28 000 €	[41]
FB-302	Roasted residue silo	150	3	SS 316	25	m^3	28 000 €	[41]
BA-301	Roasting furnace, price also includes EA-301, HE-301, HE-302 and JD-301	600	3	SS 316	35	t/h	7 457 000 €	[17]
EA-301	Waste heat recovery boiler	600	3	SS 316			- €	[17]
HE-301	Cyclone		4	SS 316			- €	[17]
HE-302	Electrostatic precipitator		4	SS 316			- €	[17]

JD-301	Conveyor		3	SS 316			- €	[17]
DC-301	Sulfidation reactor 1	70	3	SS 316	60	m^3	137 000 €	[42]
DC-302	Sulfidation reactor 2	70	3	SS 316	60	m^3	137 000 €	[42]
HC-301	Flotator 1	70	3	SS 316	860	m^3/d	159 000 €	[16]
HC-302	Flotator 2	70	3	SS 316	860	m^3/d	159 000 €	[16]
HC-303	Flotator 3	70	3	SS 316	860	m^3/d	159 000 €	[16]
HC-304	Flotator 4	70	3	SS 316	860	m^3/d	159 000 €	[16]
HB-301	Settler	25	3	SS 316	8	m	504 000 €	[42]
HE-303	Scrubber	70	3	SS 316	0.1	m^3/s	5 000 €	[39]
HA-301	Filter	25	3	SS 316	100	m^2	1 463 000 €	[39]
GA-301	Na2S pump	25	13	SS 316	0.2	l/s	11 000 €	[41]
GA-302	Water pump	25	7	SS 316	26	l/s	16 000 €	[41]
GA-303	Solution pump	70	3	SS 316	32	l/s	18 000 €	[41]
GA-304	Flotation underflow pump	25	3	SS 316	30	l/s	17 000 €	[41]
GA-305	Filter pump	25	3	SS 316	15	l/s	14 000 €	[41]
GA-306	Solution pump	25	3	SS 316	13	l/s	14 000 €	[41]
GA-307	Solution pump	25	3	SS 316	14	l/s	14 000 €	[41]
GA-309	Boiler water pump	25	3	SS 316	2	l/s	11 000 €	[41]
GA-310	Scrubber condensate pump	25	3	SS 316	0.3	l/s	11 000 €	[41]

7. Area 400 – Hydroxide precipitation



Variable	Unit	Solution #1	Solution #3	MgO #1	In-, Ga-, Ge-concentrate	Solution #4
Temperature	°C	90	25	25	70	70
Pressure	bar	1.0	1.0	1.0	1.0	1.0
Amount	t/h	384.51	46.80	6.85	2.95	430.22
Enthalpy	kWh	-1557974	-204052	-29830	-8356	-1767364

Figure 5. PFD of Area 400 – Hydroxide precipitation.

7.1 Area 400 - Process description

Target: The aim of this process stage is to precipitate indium, gallium and germanium selectively from the solution as hydroxide concentrates. The hydroxide mix will be further purified in current commercial processes or in new process concepts developed by Aalto University (see appendix D).

Process description: The solutions from the leaching and flotation process are mixed. The hydroxide precipitation of indium, gallium and germanium is conducted by adjusting the pH up to 4.5. Magnesium oxide is utilised as a neutralizing agent (but ZnO is also a possible option). In order to ensure proper precipitation of germanium, some hydrogen peroxide is added for oxidizing a small amount of iron. Peroxide addition will facilitate the co-precipitation of $Fe(OH)_3$ and $Ge(OH)_2$, thus increasing the germanium yield in the precipitate.

Temperature during the precipitation step is 70 °C and the consumption of $Mg(OH)_2$ is 4 kg/m3 solution. The precipitation is conducted in two CSTRs, after which the liquid phase and precipitate are separated in a thickener. Additional water removal from the hydroxide precipitate is conducted in a filter. The reactions applied during the hydroxide precipitation step are illustrated in Appendix B.

In-, Ga-, Ge-precipitate is one of the products of the Jarogain process. The total amount of this precipitate is 3.0 t/h, where the amount of In is 970 ppm, Ga 390 ppm and Ge 620 ppm. This precipitate includes large amounts of Zn, Al and Fe, but also of As. Possible methods for further purifying In-Ga-Ge concentrate are discussed in Appendix D.

Table 15. Area 400 - Key reaction efficiencies during hydroxide precipitation.

	Exp 1	Exp 2	Exp 3	Exp 4	TEA
In	94 %	87 %	74 %	77 %	80 %
Ga	65 %	100 %	84 %	85 %	90 %
Ge	12 %	48 %	71 %	70 %	67 %
Al	88 %	99 %	87 %	83 %	90 %
Zn	7 %	26 %	3 %	4 %	5 %
Fe	0 %	6 %	5 %	7 %	5 %
As	7%	-	51 %	51 %	50 %

Table 16. Area 400 - Key process parameters for hydroxide precipitation.

	Exp 1	Exp 2	Exp 3	Exp 4	TEA
Temperature (°C)	60	60	90	93	70
pH	0.8 → 4.5	1.3 → 4.8	1.1 → 4.8	1.2 → 4.8	4.5
Reaction time (h)	1.5	1.5-4	3	2	2
ZnO dosage (kg/m^3)	25	-	-	-	-
MgO dosage (kg/m^3)	-	19	19	19	4
H_2O_2 dosage (g/m^3)	-	0.3	0.6	0.6	0.5
Solids after reactors (kg/m^3)	-	-	-	-	80
Solids after thickener	-	-	-	-	25 %
Solids after filter	-	-	-	-	75 %

7.2 Area 400 - Cost Estimation

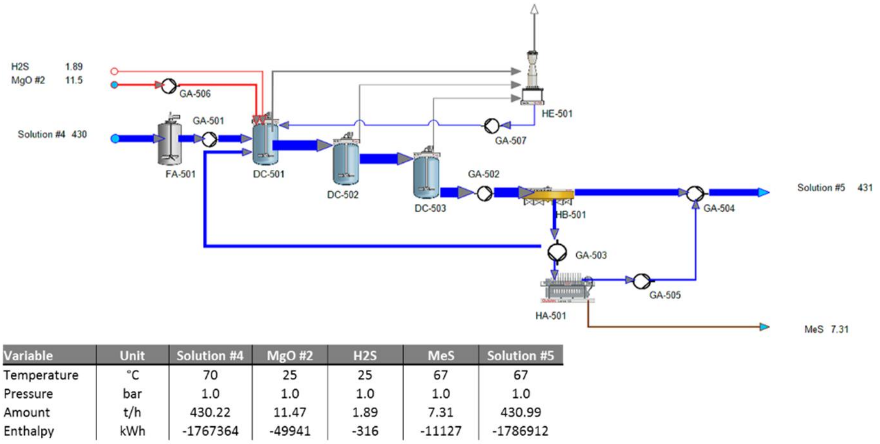
Cost Estimation: The mixing tank is sized through the volumetric flows into it and assuming a residence time of 0.1 h, thus obtaining the required volume. Assuming a power requirement of 0.04 kW/m^3 [48] for the agitation, the cost of the mixing tank is made up from the tank and agitator, found from price correlations [40]. All other equipment costs are calculated as in previous sections.

Table 17. Area 400 – Main process units within hydroxide precipitation.

EQ #	Description	T (°C)	pH	Material	Size		Cost (€)	Ref
FA-401	Mixing tank	90	3	SS 316	45	m^3	62 000 €	[41]
DC-401	Precipitation reactor 1	70	4.5	SS 316	245	m^3	334 000 €	[42]
DC-402	Precipitation reactor 2	70	4.5	SS 316	245	m^3	334 000 €	[42]

HB-401	Settler	70	4.5	SS 316	16	m	981 000 €	[42]
HE-401	Scrubber	70	4.5	SS 316	0.3	m^3/s	14 000 €	[39]
HA-401	Filter	70	4.5	SS 316	3	m^2	250 000 €	[39]
GA-401	Solution pump	82	4.5	SS 316	125	l/s	35 000 €	[41]
GA-402	Solution pump	70	4.5	SS 316	175	l/s	43 000 €	[41]
GA-403	Filter pump	70	4.5	SS 316	50	l/s	21 000 €	[41]
GA-404	Solution pump	70	4.5	SS 316	125	l/s	34 000 €	[41]
GA-405	Solution pump	70	4.5	SS 316	2	l/s	11 000 €	[41]
GA-406	Scrubber condensate pump	25	7	SS 316	0.1	l/s	10 000 €	[41]
GA-407	MgO solution pump	25	9	SS 316	2	l/s	11 000 €	[41]

8. Area 500 - Sulfide precipitation



Variable	Unit	Solution #4	MgO #2	H2S	MeS	Solution #5
Temperature	°C	70	25	25	67	67
Pressure	bar	1.0	1.0	1.0	1.0	1.0
Amount	t/h	430.22	11.47	1.89	7.31	430.99
Enthalpy	kWh	-1767364	-49941	-316	-11127	-1786912

Figure 6. PFD of Area 500 – Sulfide precipitation.

8.1 Area 500 – Process Description

Target: Zinc is precipitated from the solution as sulfide in this stage and Zn-concentrate is formed as one of the main products of the Jarogain process.

Process description: The remaining solution from hydroxide recovery is the raw material of this step. Hydrogen sulphide gas is applied as precipitation chemical and pH is controlled by utilizing MgO as neutralizing agent. Zinc is the main element to be precipitated, but aluminium, arsenic, cadmium, tin, antimony and remains of indium, gallium and germanium also appear in the solids. The concentrate is thus a mixture of different sulfides. The reactions of this step are illustrated in Appendix B.

The precipitation is performed in three CSTRs at a temperature of 70 °C. Magnesium hydroxide is applied as neutralizing agent as sulfuric acid is formed during the precipitation. pH is set to ~ 3.0. The H_2S consumption is 5 kg/m^3 solution and that of MgO is 6 kg/m^3 solution. The solution and precipitate are separated in a thickener and further water is removed from the mixed sulfide precipitate in a press. Mixed sulfide precipitate is further processed in order to remove arsenic.

Table 18. Area 500 - Key reaction efficiencies during sulfide precipitation.

	Exp 1	Exp 2	TEA
Zn	100 %	97 %	100 %
As	100 %	100 %	100 %
Cd	99 %	99 %	100 %
Sb	90 %	-	90 %

Table 19 Area 500 - Key process parameters for sulfide precipitation.

	Exp 1	Exp 2	TEA
Temperature (°C)	50	60	70
pH	1.3 → 2.4	3.8 →1.9	3
Reaction time (h)	8	9-10	1
H_2S dosage (kg/m^3)	20	7	5
NaOH dosage (kg/m^3)	35	-	-
MgO dosage (kg/m^3)	-	20	6
Solids after reactors (kg/m^3)	-	-	110
Solids after thickener	-	-	25 %
Solids after filter	-	-	75 %

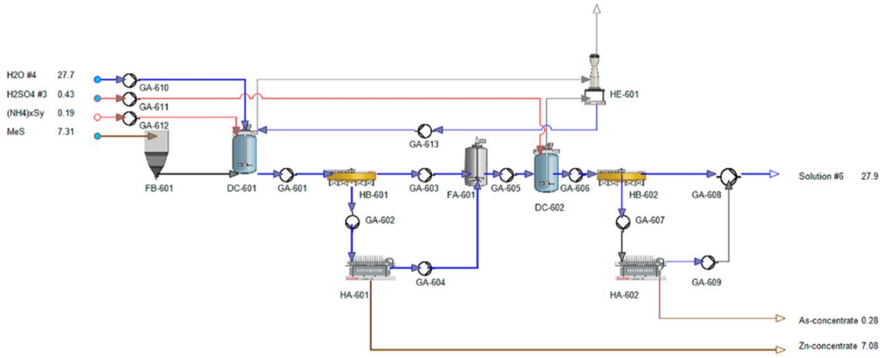
8.2 Area 500 – Cost Estimation

Cost Estimation: Equipment is calculated as in previous sections.

Table 20. Area 500 – Main process units within sulfide precipitation.

EQ #	Description	T (°C)	pH	Material	Size		Cost (€)	Ref
FA-501	Mixing tank	70	2.4	SS 316	45	m^3	62 000 €	[41]
DC-501	Precipitation reactor 1	67	2.4	FRP	85	m^3	187 000 €	[42]
DC-502	Precipitation reactor 2	67	2.4	FRP	85	m^3	187 000 €	[42]
DC-503	Precipitation reactor 3	67	2.4	FRP	85	m^3	87 000 €	[42]
HB-501	Settler	67	2.4	SS 316	16	m	998 000 €	[42]
HE-501	Scrubber	67	2.4	SS 316	0.2	m^3/s	7 000 €	[39]
HA-501	Filter	67	2.4	SS 316	80	m^2	1 237 000 €	[39]
GA-501	Solution pump	70	2.4	SS 316	125	l/s	34 000 €	[41]
GA-502	Solution pump	67	2.4	SS 316	185	l/s	45 000 €	[41]
GA-503	Filter pump	67	2.4	SS 316	65	l/s	24 000 €	[41]
GA-504	Solution pump	67	2.4	SS 316	125	l/s	34 000 €	[41]
GA-505	Solution pump	67	2.4	SS 316	5	l/s	12 000 €	[41]
GA-506	MgO solution pump	25	9	SS 316	4	l/s	11 000 €	[41]
GA-507	Scrubber condensate pump	25	7	SS 316	0.1	l/s	10 000 €	[41]

9. Area 600 - Arsenic Removal



Variable	Unit	MeS	(NH4)xSy	H2SO4 #3	H2O #4	Zn-concentrate	As-concentrate	Solution #6
Temperature	°C	67	25	25	25	40	45	45
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Amount	t/h	7.31	0.19	0.43	27.66	7.08	0.28	27.95
Enthalpy	kWh	-11127	-138	-995	-121902	-11205	-318	-120946

Figure 7 - PFD of Area 600 – Arsenic removal.

9.1 Area 600 – Process Description

Target: Zinc sulfide concentrate contains unwanted species, particularly arsenic, which need to be removed from the concentrate before its utilization in the zinc plant. The aim of this process step is to separate arsenic from the sulfide precipitate.

Process Description: The mixed sulfide precipitate from sulphide precipitation is mixed with ammonium sulphides or polysulfides in order to dissolve the arsenic, antimony and tin. The process is conducted in a CSTR tank, to which an equivalent amount of ammonium sulfide or polysulfide is fed to the reactor. The reaction time is 1 hour and the reaction takes place at a slightly elevated temperature of 40 °C and pH 13. The phase separation is conducted in a thickener and finally additional water is removed from the Zn-concentrate using a filter. The amount of ammonium sulfide is 6 kg/m^3 solution. The solids content within the reactor is 180 kg/m^3.

The remaining solution is then mixed with sulfuric acid to back-precipitate arsenic, antimony and tin. Here the pH is low, < 2, and the temperature is 40 °C. The delay in the CSTR reactor is 1 hour. Again, the phases are separated in a thickener and liquid phase is removed from the arsenic concentrate using a filter. The solid product is treated as toxic waste. The remaining liquid phase is sent back to the evaporation and crystallization phases of the main process. The consumption of sulphuric acid is 16 kg/m^3 solution. The reactions for this process step can be seen in Appendix B.

Zn-concentrate is a product of the Jarogain process. The amount of this concentrate is 7.1 t/h and the zinc content is 47 %. The amount of toxic As-concentrate is 0.3 t/h and the arsenic content is 35 %.

Table 21. Area 600 - Key reaction efficiencies during arsenic removal; Recovery of elements in purified Zn-concentrate.

	Exp 1	**Exp 2**	**Exp 3[a]**	**TEA**
Zn	100 %	100 %		100 %
As	95 %	96 %	0%	0 %[b]
Cd	100 %	84%		100 %
Sb	77 %	100%		0 %[b]
[a]The experiment 3 is a qualitative experiment where all arsenic sulfide was dissolved using ammoniumsulfide. [b]A positive assumption is made here for arsenic removal efficiency.				

Table 22. Area 600 - Key process parameters for arsenic removal.

	Exp 1	**Exp 2**	**Exp 3[a]**	**TEA**
Temperature, PS-treatment (°C)	25	43	40	40
pH, PS-treatment	12.7	9.4	10.2	13
Reaction time, PS-treatment (h)	1	1	4.5	1
K_2S_X dosage (kg/kg precipitate)	2.6	-		-
$(NH_4)_2S_X$ dosage (kg/m^3 solution)	-	50	50	6
Temperature, precipitation (°C)	n/a	25	25	40
pH during precipitation	12.7 → 1.6	9.6 → 1-3	10.2 → 1.6	1.6
Reaction time, precipitation (h)	n/a	-	-	1
H_2SO_4 charge (kg/m^3)	20	14	23	16
Solids after thickener	-	-	-	25 %
Solids after filter	-	-	-	75 %
[a]The experiment 3 is a qualitative experiment where all arsenic sulfide was dissolved using ammoniumsulfide.				

9.2 Area 600 – Cost Estimation

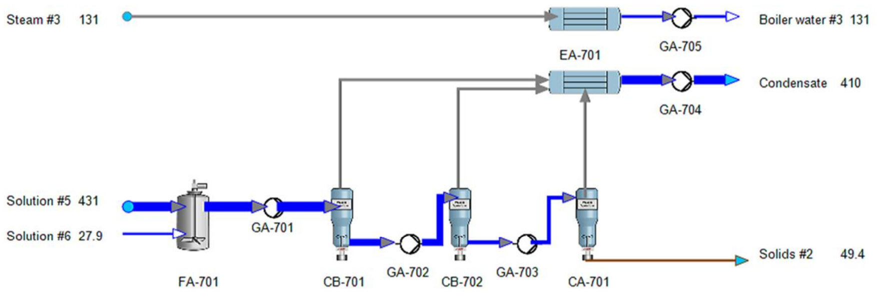
Cost estimation: Equipment is calculated as in previous sections.

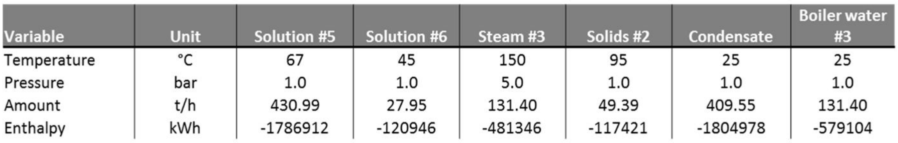
Table 23. Area 600 – Main process units within arsenic removal.

EQ #	**Description**	**T (°C)**	**pH**	**Material**	**Size**		**Cost (€)**	**Ref**
FB-601	Precipitate silo	67	2.4	SS 316	9	m^3	17 000 €	[41]
DC-601	Zn precipitation reactor	40	12.7	SS 316	17	m^3	62 000 €	[42]
HB-601	Settler 1	45	12.7	SS 316	5	m	303 000 €	[42]

HE-601	Scrubber	45	7	SS 316	0.2	m^3/s	2 000 €	[39]
HA-601	Filter 1	40	12.7	SS 316	80	m^2	1 212 000 €	[39]
FA-601	Mixer	40	12.7	SS 316	3	m^3	34 000 €	[41]
DC-602	As precipitation reactor	40	1.7	SS 316	15	m^3	56 000 €	[42]
HB-602	Settler 2	45	1.7	SS 316	4	M	285 000 €	[42]
HA-602	Filter 2	45	1.7	SS 316	3	m^2	246 000 €	[39]
GA-601	Solution pump	40	12.7	SS 316	10	l/s	13 000 €	[41]
GA-602	Filter pump	40	12.7	SS 316	6	l/s	12 000 €	[41]
GA-603	Solution pump	40	12.7	SS 316	4	l/s	12 000 €	[41]
GA-604	Solution pump	40	12.7	SS 316	4	l/s	12 000 €	[41]
GA-605	Solution pump	40	12.7	SS 316	8	l/s	12 000 €	[41]
GA-606	Solution pump	45	1.7	SS 316	8	l/s	13 000 €	[41]
GA-607	Filter pump	45	1.7	SS 316	0.2	l/s	11 000 €	[41]
GA-608	Solution pump	45	1.7	SS 316	8	l/s	13 000 €	[41]
GA-609	Solution pump	45	1.7	SS 316	0.2	l/s	11 000 €	[41]
GA-610	Water pump	25	7	CS	8	l/s	10 000 €	[41]
GA-611	H_2SO_4 pump	25	0.5	SS 316	0.1	l/s	11 000 €	[41]
GA-612	$(NH_4)_S$ pump	25	13	SS 316	0.1	l/s	10 000 €	[41]
GA-613	Scrubber condensate pump	25	7	SS 316	0.01	l/s	10 000 €	[41]

10. Area 700 - Evaporation and Crystallization





Variable	Unit	Solution #5	Solution #6	Steam #3	Solids #2	Condensate	Boiler water #3
Temperature	°C	67	45	150	95	25	25
Pressure	bar	1.0	1.0	5.0	1.0	1.0	1.0
Amount	t/h	430.99	27.95	131.40	49.39	409.55	131.40
Enthalpy	kWh	-1786912	-120946	-481346	-117421	-1804978	-579104

Figure 8. PFD of Area 700 – Evaporation and crystallization.

10.1 Area 700 – Process Description

Target: The remaining solution, containing mainly iron, is evaporated and finally crystalized. During the process, iron is precipitated as $FeSO_4$.

Process description: The solutions from sulfide precipitation and arsenic removal are mixed. This final solution is evaporated and crystallized in steam-driven three-stage counter-current evaporators/crystallizers. The main component of the crystalized solution is $FeSO_4$ but sodium, potassium and magnesium sulfates are also present. Particularly the magnesium content can be high, if MgO is used as a neutralizing agent during hydroxide and sulfide precipitation steps.

The amount of evaporated water is 410 t/h. The evaporation is conducted in a three-stage steam-driven counter-current evaporation train. Steam consumption here is one third of the evaporated water, 130 t/h. The evaporators use 150 °C low pressure steam. The condensed water is then recycled back to the process for dilution during previous process steps.

The applied steam is mainly generated in a boiler, but some steam is available from Areas 200 and 800, where thermal treatments of dissolving residue and iron oxide are conducted.

Table 24. Area 700 - Key process parameters for evaporation and crystallization.

	Exp 1	**TEA**
Evaporation temperature (°C)	90	95
Pressure within evaporation (mbar)	300 → 90	-
Reaction time (h)	n/a	2-3
Steam temperature (°C)	n/a	150

10.2 Area 700 – Cost Estimation

Cost estimation: The cost of the evaporator was obtained through Towler and Sinnots price correlation for evaporators, based on heat exchange area [41]. The area was obtained through

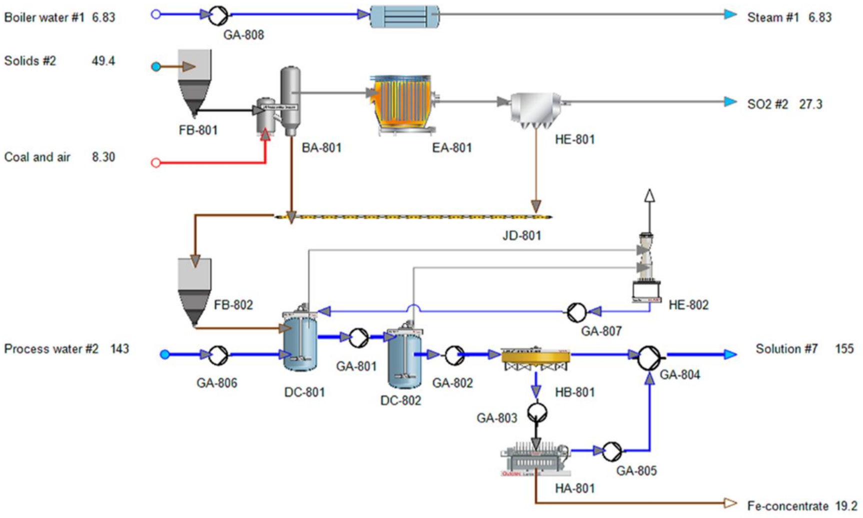
$$Q = UAT \tag{2}$$

where Q is the amount of heat transferred over the evaporator, U is the overall heat transfer coefficient (here assumed to be 1.5 kW/m^2K), A is the evaporator area and T is the temperature difference between the sides of the evaporators (55 °C assumed). The required heat was obtained from the HSC Sim-tool.

Table 25 Area 700 – Main process units within evaporation and crystallization.

EQ #	**Description**	**T (°C)**	**pH**	**Material**	**Size**		**Cost (€)**	**Ref**
FA-701	Mixer	67	2.4	SS 316	50	m^3	64 000 €	[41]
CB-701	Crystallizer 1	95	2.4	SS 316	885	m^2	2 154 000 €	[41]
CB-702	Crystallizer 2	95	2.4	SS 316	775	m^2	2 005 000 €	[41]
CA-701	Evaporator	95	2.4	SS 316	800	m^2	2 032 000 €	[41]
EA-701	Heat exchanger	95	2.4	SS 316	3600	m^2	1 141 000 €	[41]
GA-701	Solution pump	66	2.4	SS 316	135	l/s	36 000 €	[41]
GA-702	Solution pump	95	2.4	SS 316	95	l/s	29 000 €	[41]
GA-703	Solution pump	95	2.4	SS 316	55	l/s	22 000 €	[41]
GA-704	Condensate pump	25	7	SS 316	120	l/s	33 000 €	[41]
GA-705	Boiler water pump	25	7	CS	40	l/s	14 000 €	[41]

11. Area 800 - Thermal Treatment and Washing



Variable	Unit	Solids #2	Coal and air	Process water #2	Boiler water #1	Fe-concentrate	Solution #7	SO2 #2	Steam #1
Temperature	°C	95	25	25	90	43	43	250	150
Pressure	bar	1.0	1.0	1.0	5.0	1.0	1.0	1.0	5.0
Amount	t/h	49.39	8.30	143.38	6.83	19.22	154.57	27.27	6.83
Enthalpy	kWh	-117421	0	-631889	-29564	-41315	-654841	-57829	-25003

Figure 9. PDF of Area 800 – Thermal treatment and washing.

11.1 Area 800 – Process Description

Target: The final step here is the thermal treatment of $FeSO_4$-concentrate to form gaseous SO_2 and hematite, with Fe_2O_3 as the solid product. Sulfur dioxide is recycled to the sulfuric acid plant and solids are washed in order to purify iron precipitate.

Process description: The crystallized mixture is fed to a furnace for thermal treatment at 750 °C. Additional fuel is needed to support the process. Here coal is used as fuel. The reactions occurring during the thermal treatment can be seen in Appendix B. The coal consumption is 50 kg/t solids. Heat recovery from thermal treatment is 7 MW as steam.

The solids are washed after thermal treatment in order to purify the Fe-concentrate. Sodium, potassium and magnesium salts are dissolved, whereas hematite remains solid. The dissolving/washing is conducted in two CSTRs in series. The solid content here is 85 kg/m^3. Solids are separated in a thickener and further in a filter.

Fe-concentrate is another product of the Jarogain process. The amount of this concentrate is 19 t/h and the iron content is 52 %.

Table 26. Area 800 - Key reaction efficiencies during thermal treatment and washing.

	Exp 1	TEA
Fe	38 %	95 %*
Mg	10 %	0 %
Na	12 %	0 %
K	13 %	0 %
* A positive assumption is made here for arsenic removal efficiency.		

Table 27. Area 800 - Key process parameters for thermal treatment and washing.

	Exp 1	TEA
Temperature (°C)	750	750
Reaction time (h)	11	1
Coal (kg/t solids)	-	50
Solids content during dissolving/washing (kg/m^3)	120	85
Solids after thickener	-	25 %
Solids after filter	-	75 %

11.2 Area 800 - Cost Estimation

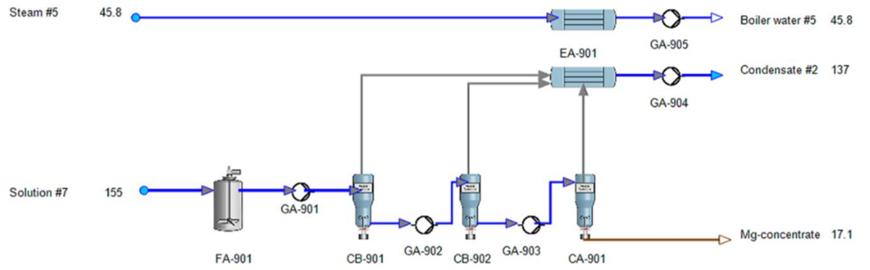
Cost estimation: The equipment costs are calculated in the same way as in the previous sections.

Table 28 Area 800 – Main process units within thermal treatment.

EQ #	Description	T (°C)	pH	Material	Size		Cost (€)	Ref
FB-801	Crystal silo	95	2.4	SS 316	40	m^3	34 000 €	[41]
BA-801	Thermal treatment furnace	750	2.4	SS 316	50	t/h	13 124 000 €	[17]
EA-801	Waste heat recovery boiler	750	2.4	SS 316			- €	[17]
HE-801	Electrostatic precipitator		2.4	SS 316			- €	[17]
JD-801	Conveyor		2.4	SS 316			- €	[17]
FB-802	Treated crystal silo	150	2.4	SS 316			- €	[17]

DC-801	Washing reactor	43	7	CS	200	m^3	293 000 €	[42]
DC-802	Washing reactor	43	7	CS	200	m^3	293 000 €	[42]
HB-801	Settler	43	7	CS	10	m	648 000 €	[42]
HE-802	Scrubber	43	7	CS	0.2	m^3/s	5 000 €	[39]
HA-801	Filter	43	7	CS	5	m^2	286 000 €	[39]

12. Area 900 - Evaporation and Crystallization #2



Variable	Unit	Process water #3	Steam #5	Mg-concentrate	Condensate #2	Boiler water #5
Temperature	°C	43	25	95	25	25
Pressure	bar	1.0	1.0	1.0	1.0	1.0
Amount	t/h	154.56	45.81	17.12	137.44	45.81
Enthalpy	kWh	-654813	-170828	-51177	-605738	-201913

Figure 10. PFD of Area 900 – Evaporation and crystallization #2.

12.1 Area 900 – Process Description

Target: The final solution from the Fe-concentrate, containing mainly magnesium, is evaporated and finally crystalized. During the process, magnesium is precipitated as $MgSO_4$*H_2O.

Process description: The solutions from thermal treatment and washing of Fe-concentrate are evaporated and crystallized in steam-driven three-stage counter-current evaporators/crystallizers. The main component of the crystalized solution is $MgSO_4$, but sodium and potassium sulfates are also present.

The amount of evaporated water is 140 t/h. The evaporation is conducted in a three-stage steam-driven counter-current evaporation train. Steam consumption here is one third of the evaporated water, 46 t/h. The evaporators use 150 °C low pressure steam. The condensed water is then recycled back to the process for dilution during previous process steps. Applied steam is mainly generated in a boiler, but some steam is available from Areas 200 and 800, in which thermal treatments of dissolving residue and iron oxide are conducted.

Table 29 Area 700 - Key process parameters for arsenic removal. No experiments were conducted for this final step.

	TEA
Evaporation temperature (°C)	95
Pressure within evaporation (mbar)	-
Reaction time (h)	2-3
Steam temperature (°C)	150

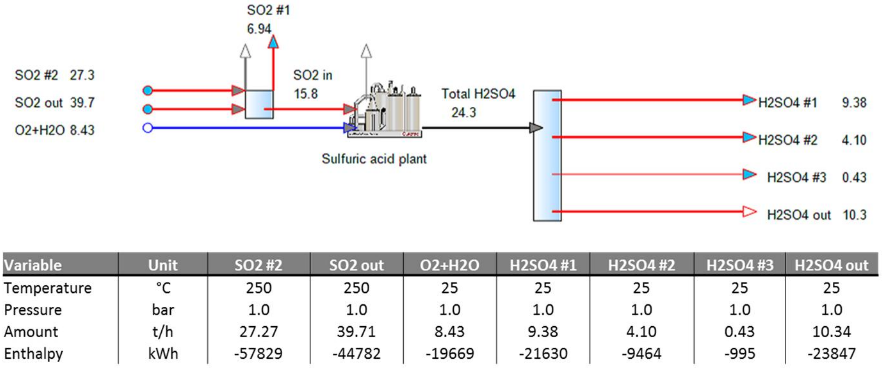
12.2 Area 900 – Cost Estimation

Cost estimation: The cost of the equipment was obtained in the same way as that for area 700, through Towler and Sinnott's price correlations. The assumptions (heat transfer coefficient 1.5 kW/m^{2}K, and temperature difference 55 °C between the sides of the evaporators) remained the same.

Table 30. Area 900 – Main process units within evaporation and crystallization #2.

EQ #	Description	T (°C)	pH	Material	Size		Cost (€)	Ref
FA-901	Mixer	43	7	SS 316	16	m^3	45 000 €	[41]
CB-901	Crystallizer 1	95	7	SS 316	325	m^2	1 243 000 €	[41]
CB-902	Crystallizer 2	95	7	SS 316	260	m^2	1 094 000 €	[41]
CA-901	Evaporator	95	7	SS 316	265	m^2	1 112 000 €	[41]
EA-901	Heat exchanger	95	7	SS 316	1200	m^2	389 000 €	[41]
GA-901	Solution pump	43	7	SS 316	45	l/s	20 000 €	[41]
GA-902	Solution pump	95	7	SS 316	30	l/s	17 000 €	[41]
GA-903	Solution pump	95	7	SS 316	18	l/s	15 000 €	[41]
GA-904	Condensate pump	25	7	SS 316	40	l/s	19 000 €	[41]
GA-905	Boiler water pump	25	7	CS	13	l/s	11 000 €	[41]

13. Area 1100 – Sulfuric Acid Plant (OSBL)



Variable	Unit	SO2 #2	SO2 out	O2+H2O	H2SO4 #1	H2SO4 #2	H2SO4 #3	H2SO4 out
Temperature	°C	250	250	25	25	25	25	25
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Amount	t/h	27.27	39.71	8.43	9.38	4.10	0.43	10.34
Enthalpy	kWh	-57829	-44782	-19669	-21630	-9464	-995	-23847

Figure 11 PFD of Area 1100 – Sulfuric acid plant.

Target: Sulfuric acid is needed during the Jarogain process. In addition, SO_2 is released from raw materials during the thermal treatments. Thus, a sulfuric acid plant is mandatory in the near vicinity of the process. This is considered as an Outside Boundary Limit (OSBL) unit.

Process description: Using the contact process, sulfuric acid can be produced from sulphur dioxide as shown below.

$$2\,SO_2 + O_2 = 2\,SO_3$$

$$2\,H_2SO_4 + 2\,SO_3 = 2\,H_2SO_7$$

$$2\,H_2SO_7 + 2\,H_2O = 4\,H_2SO_4$$

The sulphuric acid plant takes sulphur dioxide from the roasting and thermal treatment and distributes sulphuric acid to the sulphuric acid treatment, leaching and arsenic removal process steps. The amount of sulphuric acid produced is greater than that consumed by the process; the excess sulphuric acid can be sold as a by-product. The amount of SO_2 available from the Jarogain process is 23 t/h, from which 35 t/h H_2SO_4 is produced. Part of this sulphuric acid is used within the Jarogain process, but ca. 40 % (10.3 t/h) can be sold elsewhere.

Cost estimation: The cost of the sulphuric acid plant was scaled according to equation 1 from the Boliden Harjavalta sulfuric acid plant. The reference plant has a capacity of 2600 t/d [49] and investment costs of 90 M€ [50]. The required capacity in the Jarogain processis 837 t/d (35 t/h), so with a scaling factor of 0.6 the cost is 46 M€.

14. Area 1200 – Hydrogen sulfide generator (OSBL)

Target: Hydrogen sulfide is needed for sulfide precipitation (Area-500), in which mainly zinc is precipitated as ZnS. This is considered as an Outside Boundary Limit (OSBL) unit.

Process description: Hydrogen sulfide can be produced from hydrogen and elemental sulfur in a quench tower. A plant can be erected to produce the required H_2S. The facility is assumed to operate according to Uniteltech's design [51]. A hydrogen production facility is also required for the production of H_2S. This is assumed to be done by steam methane reforming from natural gas [52]. The operating costs that make up the price of hydrogen sulphide can be seen in Table 31.

Table 31. - Hydrogen sulfide production costs

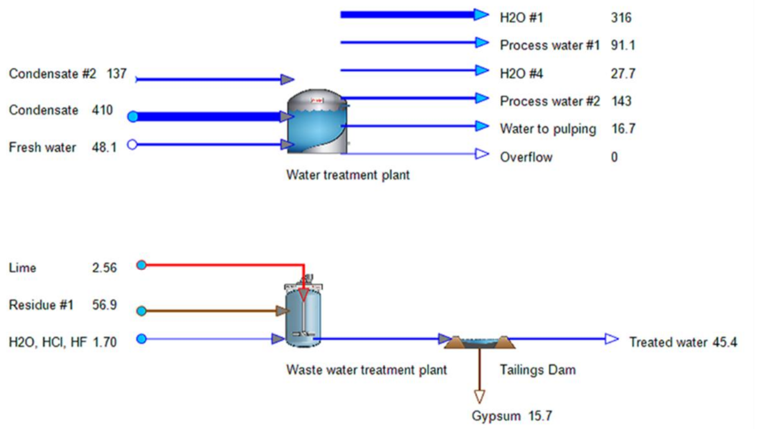
Item	**Amount**	**Unit**	**Cost per unit**			**Cost**	**Source**
Hydrogen	32	kg/h	0.64	€/kg	10.8	€/t H_2S	[53]
Molten sulfur	555	kg/h	126.55	€/t	37.2	€/t H_2S	[54]
Power	120	kW	0.07	€/kWh	4.5	€/t H_2S	[55]
Steam	400	kg/h	0.09	€/kg	18.8	€/t H_2S	[56]
Boiler water feed	200	kg/h	3.06	€/m^3	0.3	€/t H_2S	[56]
Air	1	Nm^3/h	0.46	€/m^3	0.2	€/t H_2S	[56]
Nitrogen	20	Nm^3/h	0.07	€/m^3	0.7	€/t H_2S	[57]
Cooling water	9	m^3/h	5.83	€/m^3	27.8	€/t H_2S	[56]
H_2S					100.4	€/t	

Cost estimation: The cost of the H_2S production facility was obtained as a quote from Unitel technologies, 5.5 M€ for a 13 t/d capacity. As the specifications of the process later changed, the cost was scaled according to equation 1 with a scaling factor of 0.6. The price obtained was 10.3 M€. The cost of the hydrogen production unit was obtained by comparing it to the different plants found in [52]. The cost correlation obtained was

$$C = 228 \cdot S + 162180 \tag{3}$$

where S is the capacity of the plant in kg/h. The obtained cost was 170 000 $.

15. Area 1300 – Water treatment plant (OSBL)



Variable	Unit	Condensate	Condensate #2	Fresh water	Residue #1	H2O, HCl, HF	Lime	H2O #1	Process water #1	H2O #4	Process water #2	Water to pulping	Overflow	Treated water	Gypsum
Temperature	°C	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Amount	t/h	409.54	137.44	48.11	56.93	1.70	2.56	316.27	91.10	27.66	143.37	16.70	0.00	45.45	15.74
Enthalpy	kWh	-1804939	-605738	-212049	-235946	-7093	-10627	-1393867	-401478	-121910	-631870	-73600	0	-199190	-54645

Figure 12. PFD of Area 1300 Water treatment plant.

Target: To provide process water and to treat effluents from the process. Water and wastewater treatment plants are considered as Outside Boundary Limit (OSBL) units.

Process description: The fresh water intake to the Jarogain process is 48 m^3/h, whereas the amount of treated effluent to be purged out from the mill is 45 m^3/h.

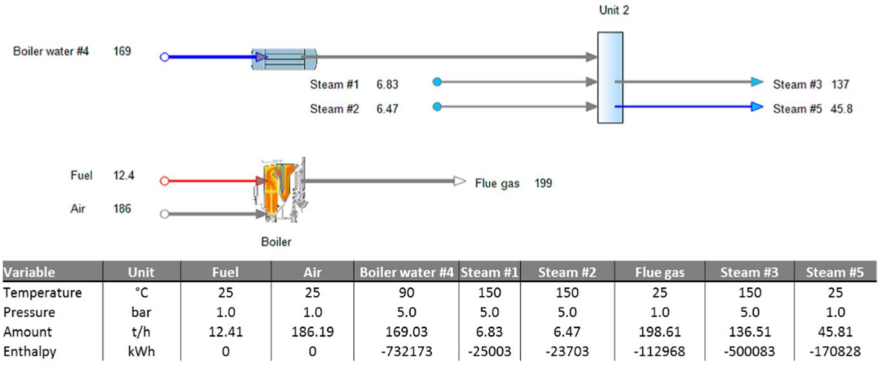
The water treatment plant mainly utilises condensate from the evaporation and crystallization plant (Area-700) for providing process water to the plant. 90% of the total water amount is recycled through two evaporation trains. The main usage of process water is leaching, followed by the washing of iron precipitate.

A wastewater treatment process is required to treat the effluents from the Jarogain mill. The main source of effluents are the residues from the sulfidation and flotation. In addition, a smaller wastewater fraction comes from the sulfuric acid treatment of EAF-dust. Chlorides and fluorides are also present in this stream.

Lime is utilised for neutralising the effluents and to precipitate gypsum and magnesium hydroxide. The amount of precipitated silicates and gypsum is 16 t/h, which is 30% of the amount of treated jarosite (50 t/h). A conservative assumption is made that the gypsum silicate mixture cannot be used as construction material and thus needs to be stored in the tailings dam.

Cost estimation: The cost of the wastewater treatment plant was obtained from Towler & Sinnott's correlation for ion exchange water treatment plants based on capacity [40]. For the required capacity of 155 t/h, the corresponding price is 209 000 €.

16. Area 1400 – Boiler (OSBL)



Variable	Unit	Fuel	Air	Boiler water #4	Steam #1	Steam #2	Flue gas	Steam #3	Steam #5
Temperature	°C	25	25	90	150	150	25	150	25
Pressure	bar	1.0	1.0	5.0	5.0	5.0	1.0	5.0	1.0
Amount	t/h	12.41	186.19	169.03	6.83	6.47	198.61	136.51	45.81
Enthalpy	kWh	0	0	-732173	-25003	-23703	-112968	-500083	-170828

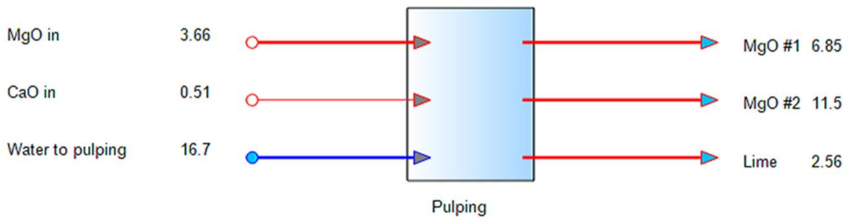
Figure 13 PFD of Area 1400 – Boiler.

Target: Evaporation and crystallisation requires steam. An additional boiler is needed for providing this steam. This area is considered Outside Boundary Limits (OSBL).

Process description: A coal fired power plant is installed nearby the Jarogain process for providing the needed heat. The thermal power of this boiler is 113 MW and coal consumption is 12.4 t/h.

Cost estimation: The cost of the boiler was calculated on the basis of power input. The cost estimate obtained was 969 $/kW [58]. As the reference cost was for electricity generation, the price was halved, assuming a better efficiency (80 % vs. 40 % for electricity generation). The cost was adjusted to Euros and to a European location by multiplying by 1.11 [40]. The cost thus obtained was 55 M€.

17. Area 1500 – MgO + CaO Slurry preparation (OSBL)



Variable	Unit	MgO in	CaO in	Water to pulping	MgO #1	MgO #2	Lime
Temperature	°C	25	25	25	25	25	25
Pressure	bar	1.0	1.0	1.0	1.0	1.0	1.0
Amount	t/h	3.66	0.51	16.70	6.85	11.47	2.56
Enthalpy	kWh	-15189	-1609	-73600	-29830	-49941	-10627

Figure 14. PFD of Area 1500 – MgO + CaO Slurry Preparation.

Target: The Jarogain process uses two neutralising agents, MgO and CaO, which are utilised as slurries. A separate preparation area is needed for bothMgO and CaO for mixing the dry solids with water before the slurries can be used in the process.

Cost estimation: The cost of the mixing unit was obtained through price correlations for a tank and agitator [40]. The obtained price was 366 000 €.

18. Products, chemicals, utilities and waste

The main products from the Jarogain process are concentrates, see Table 32. The amount of Pb-Ag-concentrate is 7.2 t/h, with a Pb-content of 20% and Ag ca. 1000 ppm. Zn-concentrate production is 7.1 t/h and the Zn content is 47%. Mixed In-, Ga-, Ge-hydroxide concentrate is precipitated at 3.0 t/h with an In content of 970 ppm, Ga 390 ppm and Ge 620 ppm. Finally, Fe-concentrate is produced at 19.2 t/h with an Fe content of 52% (Fe_2O_3 content is 74%). The assumed moisture content in Table 32 is 25% H_2O for each concentrate. The fifth product from the Jarogain plant is sulphuric acid. Net acid to be sold outside the plant is 10.3 t/h.

The chemicals consumption of the Jarogain process is presented inTable 33. As H_2SO_4 and SO_2 are recycled within the process, the key chemical used in the process is MgO as a neutralising agent in hydroxide and sulphide precipitation. A total of 3.7 t/h MgO is utilised in the process, resulting in almost 30 000 t annual consumption. In addition, a significant amount of heat is needed for the evaporation and crystallisation steps and thus a boiler is needed for running the Jarogain process. The coal consumption is 11.2 t/h (90 000 t/h), resulting in annual CO_2-emissions of 330 000 t/a.

Other wastes (Table 34) from the Jarogain process include residue from flotation (14.2 t/h), gypsum from the wastewater treatment plant (15.7 t/h) and arsenic waste, 0.3 t/h, as a toxic waste fraction. In addition, 46 m^3/h of treated wastewater is purged from the Jarogain process.

Utilities needed for the Jarogain process are mainly process and boiler water. Condensate from the evaporation plant is mainly used for providing process water, but an additional 48 m^3/h of fresh process water is needed. The amount of used boiler water is 169 m^3/h. However, here it assumed that boiler water is fully recycled (only indirect heating is used).

The amount of electricity used is based on the BAT document [59] and is 300 kWh/h. This estimate is based on literature data and was not estimated within this techno-economic assessment.

Table 32. Products as different concentrates from the Jarogain process [t/h].

	Pb-concentrate		**In-Ga-Ge-concentrate**		**Zn-concentrate**	
	[t/h]	[% or ppm]	[t/h]	[% or ppm]	[t/h]	[% or ppm]
Total	7.18		2.95		7.08	
Water	1.79	25 %	0.66	22 %	1.74	25 %
Pb	1.40	20 %/27%^{d}				
Ag	0.01	850/1130^d				
Au	0.00	2.2/2.9^d				
In			0.00	966/1236^d		
Ga			0.00	394/504^d		
Ge			0.00	620/794^d		

Zn					3.32	47 %/63%^{d}
Fe						
Mg						
Others	3.98	55 %	2.28	77 %	2.02	28 %

Table 32. Continues.

	Fe-concentrate*		**Mg-concentrate****	
	[t/h]	[% or ppm]	[t/h]	[% or ppm]
Total	19.22		17.12	
Water	4.32	22 %	0.0	0%
Pb				
Ag				
Au				
In				
Ga				
Ge				
Zn				
Fe	9.96	52 %/67%^{d}		
Mg			2.17	13%^{d}
Others	4.94	26 %	14.95	87%
*Fe as Fe_2O_3; **Mg as $MgSO_4$*H_2O; ^{d}dry basis				

Table 33. Chemicals utilised in the Jarogain process [t/h].

	Area-100	**Area-200**	**Area-300**	**Area-400**	**Area-500**	**Area-600**
	[t/h]	[t/h]	[t/h]	[t/h]	[t/h]	[t/h]
H_2SO_4	9.38*	4.10*				0.43*
SO_2		6.94*				
Na_2S			0.59			
MgO				1.37	2.29	
H_2S					1.89	
$(NH_4)_2S_y$						0.20
Coal						
Lime						

Table 33. Continues.

	Area-700	**Area-800**	**Area-900**	**Area-1300**	**Area-1400**	**Total**
	[t/h]	[t/h]	[t/h]	[t/h]	[t/h]	[t/h]
H_2SO_4						13.9*
SO_2						6.9*
Na_2S						0.6
MgO						3.7
H_2S						1.9
$(NH_4)_2S_y$						0.2
Coal		2.58			12.4	15.0
Lime				2.56		2.6
*H_2SO_4 and SO_2 are produced on site, not purchased from outside.						

Table 34. Waste fraction from the Jarogain process [t/h].

	As-concentrate		**Gypsum (WWTP)**		**Treated water (WWTP)**	
	[t/h]	[% or ppm]	[t/h]	[% or ppm]	[t/h]	[% or ppm]
	0.28		15.7		45.5	
Water	0.07	25 %	0.16	1 %	44.8	98 %
Gypsum			10.1	64 %		
SiO_2			4.65	30 %		
As	0.10	35 %				
Others	0.11	40 %	0.79	5 %	0.7	2 %

19. Capital expenditure (CAPEX)

The cost of equipment is updated with factors for material, location and time and changed from dollars to euros [60].The costs for equipment in price correlations are for carbon steel. The material is updated to stainless steel 316 to cope with the acidic conditions. The factor is 1.3. All equipment price correlations are for the U.S. Gulf Coast. The costs are adjusted to European currency by multiplying by a factor of 1.11. The cost of the equipment is dated and can be adjusted to the year 2016 with the chemical plant cost indices according to

$$C_B = C_A \cdot \frac{I_B}{I_A}, \qquad (4)$$

where C is cost and I index for year n. The index for 2016 is 541.7, 2014 = 576.1, 2010 = 532.9, 2002 = 390.4 and 1994 = 368.1.

The purchased equipment cost only constitutes part of the total plant costs. Other costs include installation of the equipment, piping, instrumentation and control, electrical, civil, structures and buildings, lagging and painting, offsite costs, design and engineering and contingency costs. The total cost of the plant can be obtained by multiplying the price of the equipment by 6.05 for solid-liquid processes [40].

19.1 Working capital & other CAPEX

Other investment costs include a spare parts inventory, which is calculated as 1 % of the total plant cost, start-up costs which is calculated as 2 % of the total cost, operation and management costs which is calculated as 3 months of fixed operational costs, and raw material in stock, which is calculated as 1 month of variable operational costs.

The working capital is calculated as 30 days' worth of raw material costs plus 15 days' worth of sales costs, to account for raw material and product storage. The working capital is released at the end of the process life span. A summary of capital costs can be seen in Table 35. Construction of the plant is assumed to take 4 years.

Table 35. Summary of capital expenditure. (thousand €)

	Cost (k€)	**-3**	**-2**	**-1**	**1**
Main Process Units					
H_2SO_4 treatment	5058	2023	2276	506	253
Leaching	3892	1557	1751	389	195
Hydroxide precipitation	2140	856	963	214	107
Sulfide precipitation	3035	1214	1366	304	152
Evaporation	7530	3012	3389	753	377
Thermal treatment & washing	14782	5913	6652	1478	739

Roasting, sulfidation and foaming	10521	4208	4734	1052	526
Evaporation 2	3965	1586	1784	397	198
Arsenic removal	2367	947	1065	237	118
Total main units	53290	21316	23981	5329	2665
Others (ISBL)					
Installation (50 % of main process units)	26645	10658	11990	2665	1332
Piping (50 % of main process units)	26645	10658	11990	2665	1332
Instrumentation and control (30 % of main process units)	15987	6395	7194	1599	799
Electrical (20 % of main process units)	10658	4263	4796	1066	533
Civil (30 % of main process units)	15987	6395	7194	1599	799
Structures and buildings (20 % of main process units)	10658	4263	4796	1066	533
Lagging, insulation and paint (10 % of main process units)	5329	2132	2398	533	266
Mill infrastructure (OSBL)					
Storage, Handling, Utilities, Offices, etc. (20 % of ISBL costs)	33040	13216	14868	3304	1652
H_2SO_4 plant	45591	18236	20516	4559	2280
H_2S plant	10545	4218	4745	1054	527
MgO and CaO preparation	366	146	165	37	18
Boiler	55000	22000	24750	5500	2750
Water treatment plant	209	84	94	21	10
Project Overheads					
Project contingencies (10 % of TIC)	30995	12398	13948	3099	1550
Design & engineering (10 % of TIC)	30995	12398	13948	3099	1550
Total Plant Cost (TPC)	371939	148776	167373	37194	18597
Other CAPEX					
Spare Parts (3 % of TPC)	11158	4463	5021	1116	558
Start-Up & Commissioning Cost					
Start Up CAPEX (2 % of TPC)	7439	2976	3347	744	372
O&M (3 month worth of fixed costs)	5	2	2	0	0

Raw materials and chemicals (1 month worth of variable costs)	5	2	2	0	0
Capital requirement (excl. Working and Recurring Capital)	390546	156218	175746	39055	19527
Working Capital	9				9
Total Capital Requirement (TCR)	390555	156222	175750	39055	19528
		Year -3	Year -2	Year -1	Year 1
Capital Expenditure Scheduling Assumptions		40 %	45 %	10 %	5 %

20. Operational expenditures (OPEX)

This section presents the operational costs taken into account for the techno-economic evaluation. The operational costs consist of fixed operational costs and variable operational costs. Fixed operational costs are labour costs, property taxes, insurance, land rental, charges for environmental emissions and maintenance costs. Variable costs consist of raw material costs, chemical expenses, utility costs, heat and electricity costs and cost of waste treatment.

20.1 Fixed costs

The labour costs are estimated for the entire plant requiring 50 operators, 5 shift supervisors, 5 senior operation managers and 20 maintenance personnel each month. The operators are assumed to have a median salary of 3 500 € per month, shift supervisors and senior staff 4 500 € per month and maintenance staff 4 500 € per month. The plant also has 20 support personnel (secretaries, lab personnel, kitchen etc.) with an average salary of 4250 €/month. The indirect costs, consisting of items such as health insurance, pensions and costs of professional society memberships, are assumed to be 44 % of the direct labour costs.

Property taxes and insurance are estimated as 1 % of the ISBL capital investment, land rental as 1 % of ISBL and OSBL capital investment and environmental charges as 1 % of the ISBL capital investment. The cost of maintenance for a liquid-solid process is assumed to be 4 % of the capital investment for ISBL process units, 3 % for OSBL process units and 1 % of capital investment for other OSBL units such as storages and offices. A summary of maintenance costs can be seen in Table 36. A summary of fixed operational costs can be seen in Table 37.

Table 36. Maintenance costs as percentages of capital investments [€ million].

	[% TIC]	**TIC [MEUR]**	**[MEUR]**
Main Process Units			
H_2SO_4 treatment	4 %	15.7	0.63
Leaching	4 %	12.1	0.48
Hydroxide precipitation	4 %	6.6	0.27
Sulfide precipitation	4 %	9.4	0.38
Evaporation	4 %	23.3	0.93
Thermal treatment & washing	4 %	45.8	1.83
Roasting, Sulfidation and foaming	4 %	32.6	1.30
Arsenic removal	4 %	7.3	0.29
Evaporation 2	4 %	12.3	0.49
Total	4 %	165.2	6.61
Mill infrastructure (OSBL)			

Storage, Handling, Utilities, Offices, etc.	1 %	33.0	0.33
H_2SO_4 plant	3 %	45.6	1.37
H_2S plant	3 %	10.5	0.32
MgO preparation	3 %	0.4	0.01
Boiler	3 %	55.0	1.65
Water treatment plant	3 %	0.2	0.01

Table 37. Fixed operating costs in [€ million per year].

	Base [MEUR/y]	**NPV (during 3 + 30 years)**
Direct labour	4.9	39.2
Indirect labour	2.2	17.2
Property taxes & insurance	1.7	13.1
Land rental	3.1	24.6
Environmental charges	1.7	13.1
Maintenance	6.1	48.5
Total Fixed O&M Costs	**19.7**	**155.7**

20.2 Variable costs

The costs of raw materials, chemicals, utilities and waste treatment per ton of jarosite can be seen in Table 38. The cost of jarosite is an expert opinion on the transport of material from the heap to the process. Obtaining EAF-dust is assumed to have no additional charges. The cost of sulphur dioxide was assumed to be zero as it is produced in the process. The amount of utility water was obtained from the process model. The amount of cooling water was calculated from the heat of the condensers, from which the flow of water can be obtained (assuming 5 °C water heated to 80 °C). The cost of solid waste was assumed according to landfill costs in Finland; arsenic is treated as a toxic waste. A summary of variable operational costs can be seen in Table 39.

Table 38. Unit consumptions per ton of jarosite and consequent unit costs.

	Amount	**Cost**	**Ref**
Raw Materials	kg/t	€/t	
Jarosite	1000	5	VTT opinion
EAF-dust	125	0	VTT opinion
Chemicals	t/t	€/t	
H_2SO_4	0.7	27.63	[61]
SO_2	0.1	0	
Na_2S	0.012	500	VTT opinion

Flotation aid	0.003	1315	[62]
MgO	0.073	400	VTT opinion
H_2S	0.038	100	Table 29
C	0.300	71	[63]
NaOH	0.0006	539	[62]
$(NH_4)_xS_y$	0.004	500	VTT Opinion
Lime	0.010	170	[64]
Utilities	t/t	€/t	
Process water	9	0.1	[65]
Cooling water	77	0.05	[65]
Energy	kWh/t	€/kWh	
Electricity	300.00	0.0710	[55]
Waste	t/t	€/t	
Solid waste	0.31	50	[66]
As-concentrate	0.006	550	[67]
Waste water	0.9	0.1	[40]
Molten sulfur	0.001	550	[67]

Table 39. Variable operating costs in M€/a.

	Base [MEUR/y]	**NPV (during 3 + 30 years)**
Raw Materials		
Jarosite	2.0	15.5
EAF-dust	0.0	0.0
Chemicals		
H_2SO_4	7.71	59.8
SO_2	0	0.0
NaHS	2.4	18.4
Flotation aid	1.5	11.9
MgO	11.7	90.9
H_2S	1.5	11.8
C	8.6	66.3
NaOH	0.1	1.0
$(NH_4)_2S_X$	0.8	5.9
Lime	0.7	6.4
Utilities		
Process water	0.4	2.9

Cooling water	1.5	11.9
Energy		
Heat	0.0	0.0
Electricity	8.520	66.1
Waste		
Solid waste	6.30	48.8
As-concentrate	1.22	9.5
Waste water	0.04	0.3
Total Variable O&M Costs	55.0	427.5

21. Revenue and cash flow

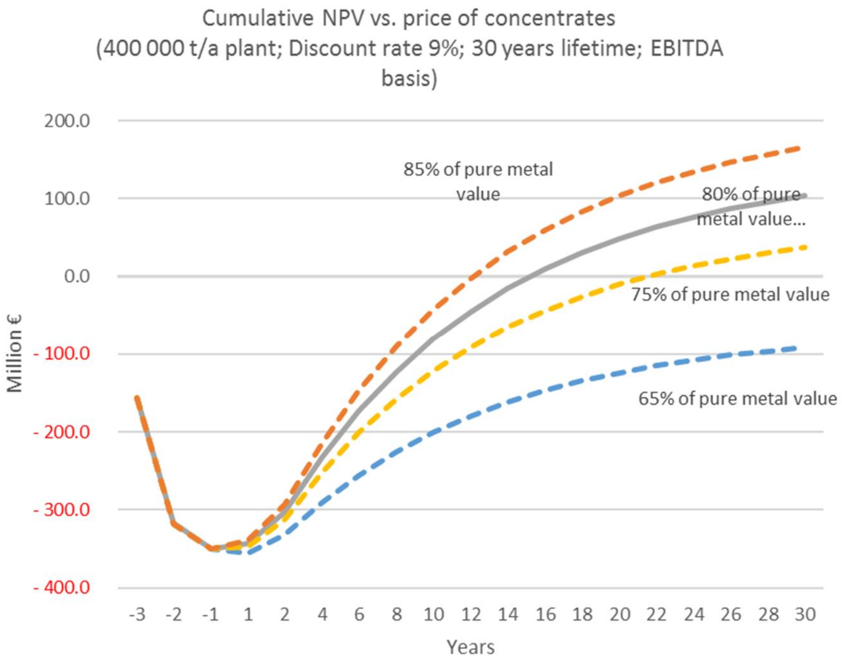


Figure 15. Cumulative NPV vs. price of concentrates.

The economic feasibility of the Jarogain process was evaluated on the basis of the Discounted Cash Flow (DCF) methodology on an EBITDA basis (Earnings Before Interest, Taxes, Depreciation and Amortization). A 30-year lifetime was assumed for the plant and the applied discount rate was 9%. The investment estimate includes both ISBL and OSBL areas.

The main products from the process are the Pb-concentrate, also containing silver and gold, the concentrate with indium, gallium and germanium, the Zn-concentrate also containing copper and cadmium, the Fe-concentrate and the Mg-concentrate. It is also assumed that some revenue comes from the treatment of jarosite and EAF-dust. The product streams and prices can be seen in Table 40. The prices shown are those of pure metals. The cost of sales and distribution is assumed to be 20 €/t.

The levelized cost of production (LCOP) for concentrates is estimated on the basis of the DCF analysis. LCOP of concentrates are given as fractions of metal values within the concentrates. LCOP is calculated in such a way that net present value (NPV) during the 15-year payback time of the plant is set to zero and the corresponding LCOP values are solved as fractions of metal values.

The estimate of LCOP for concentrates is 80 %, see Figure 15. In the same figure, the DCF values of 65%, 75% and 85% metal values are illustrated. For example, if the values of concentrates were 85% of the pure metal values, the payback time of the Jarogain process would be 12 years.

Table 40. Main product amounts per ton of jarosite and their prices. Prices of each metal are given as the average of pure metal value in 2015-2016. The prices of concentrates are given on the basis of the calculated LCOP (80% of pure metal price).

	kg/t	€/kg	Ref
Pb-concentrate	143.5	0.7	
Pb	28.0	1.8	[68]
Ag	0.1	550	[69]
Au	0.0003	33000	[70]
In-Ga-Ge-concentrate	58.9	0.9	
In	0.06	400	[71]
Ga	0.02	350	[72]
Ge	0.04	1000	[73]
Zn-concentrate	141.6	0.8	
Zn	66.6	2.0	[74]
Fe-concentrate	384.4	0.04	
Fe	199.2	0.10	[75]
Mg-concentrate	342.4	0.08	
Mg	342.4	0.10	VTT opinion on fertilizer price
Sulfuric acid	419	0.05	VTT opinion

21.1 Revenues

Jarosite is the key raw material of the process, with significant values of different metals as illustrated in Figure 16. The most important metals in jarosite are zinc, silver, lead and germanium. The processed EAF-dust increases the value of raw materials by introducing a significant amount of zinc to the process. The availability of this material is limited and thus the total potential of this raw material cannot be utilised.

When revenues from the Jarogain process are considered, the Zn- and Pb-concentrates are the key fractions for successful operation of the process. In, Ga, Ge-concentrate provides additional revenue for the operator, but the value of this stream is only 20% compared to the total value of Zn- and Pb-concentrates. The value of Fe-concentrate is lower. The revenues from Mg-concentrate are omitted from Figure 16, as a large part of the magnesium is introduced to the process as a neutralizing chemical and not as a raw material. In addition, the exported sulfuric acid and possible revenues from treating jarosite and EAF-dust would increase the amount of revenue from the Jarosite process. All these smaller revenue streams are important for the operator of the Jarogain process, although the most valuable streams are the Zn- and Pb-concentrates.

The revenues from different concentrates are illustrated in Figure 16. Here the levelized cost of production is based on the 80% value of concentrates compared to the pure metal prices.

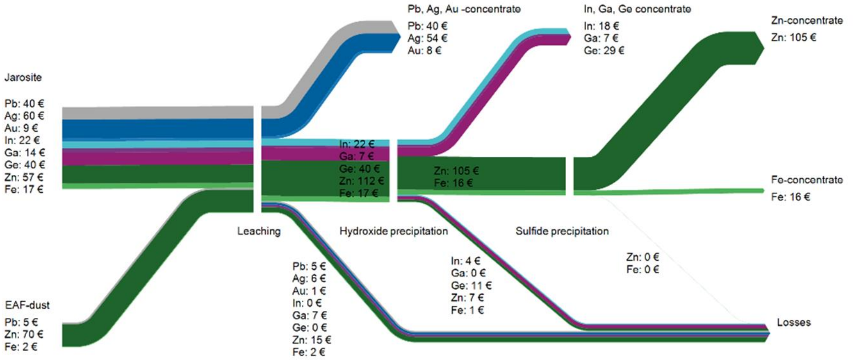


Figure 16. Revenues from different concentrates when the value of concentrates is 80 % of pure metal prices (average of 2015-2016) [€/ton of treated jarosite]. *Mg-concentrate and sulfuric acid are omitted, as well as possible revenues from the treatment costs of jarosite and EAF-dust.*

21.2 Cost factors

Capital costs are the largest cost factor related to the Jarogain process, 37% of total production costs. The costs related to the Outside Boundary Limit (OSBL) units are almost as high as those of the main Jarogain process. Especially the sulfuric acid plant and power boiler are expensive OSBL units, increasing the total capital investment significantly. When the Jarogain process is considered, the capital costs related to treatment of $FeSO_4$ and $MgSO_4$ solution at the end of the process represent 50% of the investment costs.

The second largest cost factor is chemical costs, 30% of total costs. Magnesium oxide used as neutralizing chemical is the most expensive chemical to be used. However, magnesium is recovered from the process as magnesium sulfate thus generating additional revenue. Energy, coal and electricity are needed for operating the process. Possible mixed gypsum/SiO2 waste to be stored as well as toxic arsenic waste together generate 7% of total costs. Similar costs are also due to labour, logistics and maintenance.

Figure 17 illustrates fractions of the different expenditures as percentages of total costs calculated on the basis of the discounted cash flow analysis (DCF) as previously discussed.

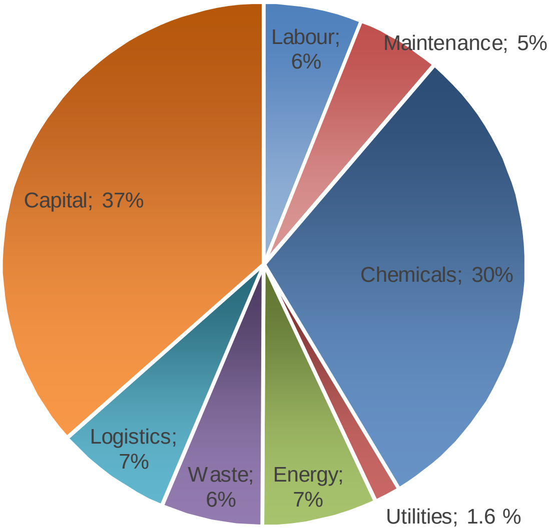


Figure 17. Cost breakdown of factors contributing to NPV.

21.3 Sensitivity analysis

A partial sensitivity analysis was conducted in order to illustrate the effects of key economic factors on the feasibility of the Jarogain process. The studied factors were: i) yields of the concentrates, ii) prices of chemicals, energy, waste and utilities and iii) capital investment. The studied factors were varied ±25% and the levelized costs of production as fractions of pure metal prices were calculated. Here the baseline was the above-mentioned case in which the LCOP values of concentrate values were 80% of pure metal prices. The results of the sensitivity analysis are presented in Figure 18.

Based on this sensitivity analysis, the most critical factor here is the capital investment. If 25% lower investment costs are obtained, the break-even cost of metal prices is 71%. Correspondingly, with 25% higher costs, the break-even price is 89%. The yields of Pb- and Zn-concentrates are the second most critical aspect here. If a 25% lower yield is obtained, the LCOP of concentrate prices increases to 88%.

On the other hand, changes in costs of the utilities, waste, electricity and yield of Fe-concentrate have only a minor effect on the break-even cost of concentrates.

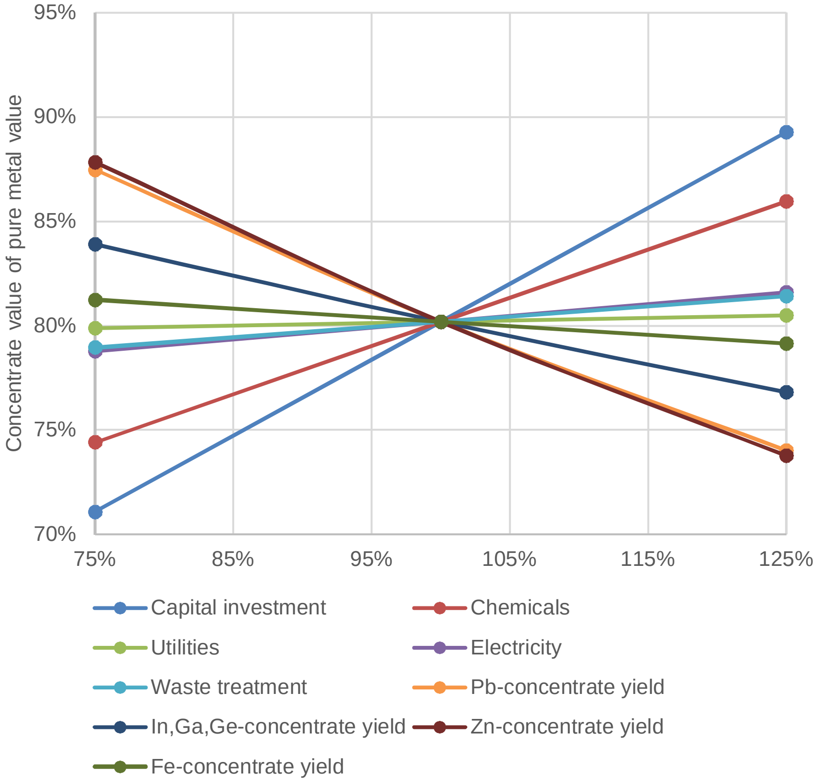


Figure 18. Sensitivity analysis for selected process parameters.

22. Discussion

22.1 Process design

The raw materials and their composition greatly affect the capacities of different areas of the Jarogain process. Within this study, a theoretical composition based on the several published jarosite and EAF-dust compositions was utilised. However, in reality the composition of these residues might vary within a single site due to changes in the raw materials and in the main process over the years. It might be necessary to mix different raw material fractions similar to the customary way in the RLE zinc process in order to maintain a more stable composition of raw materials to the Jarogain process. However, the process design must be revised on the basis of each particular case, if there are large changes in the composition or availability of raw materials.

The process design presented in this document utilises standard unit operations applied in the hydrometallurgical industry. Many of the unit operations are available from the machine supplier. Some new reactor development may be needed for the Area 100 – Sulfuric acid treatment. Here the mechano-chemical reaction of solids and hot sulphuric acid is conducted. In this document, reference is made to a pug mill mixer, which might not be suitable as such for this purpose. Particularly if operated in large scale, the issues relating to heat transfer, release of gases and proper mixing would need to be discussed.

The thermal treatment of leaching residue (Area 300 – Roasting, sulfidation and flotation) is another unit operation to be discussed. Here the temperature of the reactor needs to be below 600°C (preferably close to 500°C) in order to evaporate/fume the elemental sulfur but to limit the formation of lead silicates. After the reactor, the sublimated sulfur must be burned in an after-burner. This may result in a more complex design for the thermal treatment.

The separation rate of different precipitates (and leaching residue) has not been experimentally validated. Especially the settling of hydroxide precipitate (Area 400 – Hydroxide precipitation) and filtration might be challenging. Correspondingly, the particle size of leaching residue (Area 200 – Leaching) might set challenges for the separation steps. It is essential to evaluate the settling properties of this solid fraction in order to fully assess the investment cost related to these separation steps.

Arsenic removal is successfully conducted with ammoniumsulfide but utilising polysulphide treatment (Area 600 – Arsenic removal) must be experimentally validated in the next phase of studies. In addition, the arsenic sulfide might be incorporated in the same particles as zinc sulfide resulting in inefficient removal. One option would be to omit this step and to utilise the current arsenic removal methods in the RLE zinc process to which Zn-concentrate is fed.

Two evaporation trains (Area 700 – Evaporation and Crystallization and Area 900 – Evaporation and Crystallization #2) need to be assessed when the amount of available steam and electricity and their prices are known. If steam economy is critical, it is possible to use multi-effect evaporation trains. However, this will result in increased capital costs. Another option is to use mechanical vapour evaporators (MVR) if additional or cheap electricity is available at the site. Usually MVR evaporators result in lower investment costs.

This process design utilises magnesium oxide or hydroxide as neutralizing agent (Area 400 – Hydroxide precipitation and Area 500 – Sulfide precipitation). The amount of magnesium introduced to the system is however large, and magnesium must be separated from the final solution (Area 900 – Evaporation and Crystallization). Other options for neutralizing agent are NaOH (caustic) and ZnO (even as Waelz oxide). If zinc oxide is utilised, it can later be separated in the process with other zinc (Area 500 – Sulfide precipitation). No additional treatment for magnesium is needed, but the capacity of the sulfide precipitation step is then higher. Correspondingly, if caustic soda is utilised as neutralising agent, the remaining aqueous effluent from the plant contains a large amount of dissolved sodium sulfate.

The composition of concentrates to be used in primary metal processes should be evaluated in the future while further optimising the Jarogain process. For example, the leaching process should be optimised in such way that the amount of zinc and iron remaining in the leaching residue is minimized. This can be done by adjusting pH and other process conditions in the forthcoming studies, preferably including continuous pilot operation.

Additionally, the purity of applied chemicals should be considered. For example, if impurities such as chlorides are introduced to the process with chemicals, there might be a need for additional cleaning steps for removing detrimental substances. The properties and mineralogical composition of concentrates and waste fraction also need to be assessed and optimized.

Another issue related to the Jarogain process is the expensive outside boundary limit (OSBL) units needed for successful operation of the plant (Area 1100 – Sulfuric acid plant and Area 1400 - Boiler). Thus, when moving forward, it will be essential to make a process design based on the case mills and the availability / capacity of the current sulphuric acid plant / power boiler.

22.2 Economics

The levelized cost of metal concentrate compared to pure metal prices was set at 80% in this assessment. Examples of prices for the primary concentrates are for example 95% for Pb-concentrate and 85% for Zn-concentrate. However, here a treatment cost is usually applied, resulting in a lower price to be paid for the mines. Much uncertainty is involved in the value of In-Ga-Ge-concentrate. The concentrations of these metals are low and their market values may fluctuate significantly.

The biggest cost factor is the capital costs. It must be noted that nearly half of the capital costs are due to the units in the outside boundary limits (OSBL). The most expensive ones are the sulfuric acid plant and power boiler, both entailing costs in excess of 50 M€. If such capacity is already available nearby, for example at an RLE zinc process, the economic feasibility of Jarogain is greatly improved.

When the Jarogain process itself is considered, it can be seen that a large share of the overall capital costs is due to the treatment of aqueous solution containing iron (and magnesium) sulfate. The revenues from these streams are limited, but both processes are required for the proposed near waste-free Jarogain process. Magnesium oxide is the most expensive chemical used in the Jarogain process, but if magnesium is recovered as magnesium sulfate, there is a possibility to sell this for the production of magnesium fertilizers. Thus, the chemical costs will be partly covered by this by-product. If magnesium is replaced by zinc oxide (Waelz oxide), there is no need for the final Evaporation and crystallization step (Area-900) and the capital costs are reduced. It would be a subject of further study to estimate whether such a combined strategy for treating jarosite and zinc-containing dusts could be realistic.

The greatest uncertainty in the capital costs is related to the separation of solids (clarifiers and filters). During the experimental part, the settling of solids was not evaluated. Due to this, the capital investment related to the solids separation is an approximate estimate only. These properties can be evaluated with a continuously operating bench scale or pilot process, and means for improving filtration properties can then be applied (such as recycling of solids to reactors).

The economic feasibility was estimated on the basis of the discounted cash flow analysis. The payback time was set to 15 years, which might be considered somewhat long. The interest rate was set to 9%. It must be noted that the calculations were made on an EBITDA basis. This means that depreciation was not considered. This is because different companies, and countries where companies operate, have different rules for depreciations. However, when assessing the feasibility of the Jarogain process to a particular case, the depreciation should also be considered.

The capital investments in this study were based on the main process units. The price estimates were mainly based on corresponding models from the literature. However, some quotations from the suppliers were obtained. During the next phase, it must be considered whether to conduct a pre-feasibility study of the Jarogain process or to move straight to the more expensive feasibility study.

22.3 Conclusions

Within this report, the basic process design of jarosite recycling in the Jarogain process is illustrated and the economics of the process are assessed. The overall feasibility of the process is fair. However, the Jarogain process is a rather complex hydrometallurgical process and the investment costs are correspondingly high. If installed, the Jarogain process is in any case a capital-intensive investment.

The next step for the development would be a continuous pilot run of the main hydrometallurgical process. The target would be to confirm that the process can be run in continuous mode with the proof-of-concept yields. It might be necessary to conduct some batch experiments for fine-tuning the process conditions prior to the continuous pilot. In addition, a more comprehensive pre-feasibility study of the proposed Jarogain process needs to be performed for any particular site where the Jarogain process is to be implemented.

The Jarogain process can be seen as a promising alternative for treating zinc-containing side-streams and residues in a near waste free manner and further studies for optimising the process are therefore recommended.

Acknowledgements

Jarogain project was funded by Tekes – the Finnish Funding Agency for Innovation, VTT Technical Research Centre of Finland and Aalto University during years 2016-2017. The financial support is acknowledged. The project group is also grateful for the support and advices given by the experts of Finnish metallurgical industry.

References

[1] Creedy, S., Glinin, A., Matusewics, R., Hughes, S. & Reuter, M. 2013. Outotec Ausmelt Technology for Treating Zinc Residues. World Metall. - ERZMETALL 66(4), 230–235.

[2] Goodwin, F.E. 2012. Zinc and Zinc Alloys, in: Kirk-Othmer Encycl. Chem. Technol., Hoboken, NJ, USA.doi:10.1002/0471238961.2609140307151504.a01.pub3

[3] Lausch, H. & Lommert, H. 1999. Method for processing metalliferous sludge, EP 0709472 B1, 1999

[4] Befasa n.d. The SDHL-Waelz Process http://www.befesa-steel.com/web/en/nuestra_tecnologia/detalle/The-SDHL-Waelz-Process/

[5] Hughes, S., Reuter, M.A., Baxter, R., Kaye, A., Hughes, S., Reuter, M.A., et al. 2008. Ausmelt Technology for Lead and Zinc Processing, in: Lead Zinc 2008

[6] Outotec 2016. Successful Zinc Residue Smelter Project for Xingan. , . http://www.outotec.com/en/Search-material/Customer-newsletter-Smelting-News/Smelting-Newsletter-Issue-1-April-2016/Successful-residue-smelter-project-for-XingAn/

[7] UNEP 2013. Metal Recycling: Opportunities, Limits, Infrastructure.doi:978-92-807-3267-2

[8] Ju, S., Zhang, Y., Zhang, Y., Xue, P. & Wang, Y. 2011. Clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazardous jarosite residues produced during zinc hydrometallurgy. J. Hazard. Mater. 192(2), 554–8. doi:10.1016/j.jhazmat.2011.05.049

[9] Ju, S., Zhang, L., Peng, J., Shi, Z., Guo, S., Liu, B., et al. 2013. Thermodynamics of leaching roasted jarosite residue from zinc hydrometallurgy in NH4Cl system. Trans. Nonferrous Met. Soc. China 23(4), 1179–1183. doi:10.1016/S1003-6326(13)62581-9

[10] Han, H., Sun, W., Hu, Y., Jia, B. & Tang, H. 2014. Anglesite and silver recovery from jarosite residues through roasting and sulfidization-flotation in zinc hydrometallurgy. J. Hazard. Mater. 278, 49–54. doi:10.1016/j.jhazmat.2014.05.091

[11] Elgersma, F. 1992. Integrated Hydrothermal Jarosite Treatment, TU Delft.

[12] Swain, M., Sahu, K.K. & Roy, B.N. 2016. Recycling of Jarosite For Recovery of Valuable Metals and its Utilisation. Int. J. Sci. Tech. Res. Eng. 1(4), 36–46.

[13] Rastas, J., Saikkonen, P. & Honkala, R. 1982. Process for the treatment of a raw material which contains oxide and ferrite of zinc, copper and cadmium, US 4355005 A, 1982

[14] Rastas, J., Järvinen, A., Hintikka, V. & Leppinen, J. 1989. Recovery of lead, silver and gold in the zinc process and possibility of non-waste technology in zinc production, in: VTT Symp. - Non-Waste Technol., Vol. 2,

[15] Rastas, J., Saikkonen, P., Hintikka, V. & Koukkari, P. 2016. Processing of Industrial Metal-containing waste materials, Finnish Patent Application FI20165972, 2016

[16] Benemann, J.R. & Oswald, W.J. 1996. Systems and economic analysis of microalgae ponds for conversion of CO{sub 2} to biomass. Final report, Pittsburgh, PA, and Morgantown, WV.doi:10.2172/493389

[17] BATEMAN 2011. Desktop Study Report - Citronen Zinc Project - Greenland. http://ironbark.gl/wp-content/uploads/2015/08/M6034-1700-001-Rev-0-Citronen-Zinc-Desktop-Study-Report.pdf

[18] U.S. Environmental Protection Agency 2003. Air Pollution Control Technology Fact Sheet - Spray-Chamber & Spray-Tower Wet Scrubber (EPA-452/F-03-016).

[19] Outotec 2015. HSC Chemistry

[20] Pöyry 2016. Boliden Kokkola Oy - Vaarallisen jätteen kaatopaikan laajentaminen - Ympäristövaikutusten arviointiohjelma. , . http://www.ymparisto.fi/fi-FI/Asiointi_luvat_ja_ymparistovaikutusten_arviointi/Ymparistovaikutusten_arviointi/YVAhankkeet/Boliden_Kokkola_Oyn_vaarallisen_jatteen_kaatopaikan_laajentaminen_Kokkola

[21] Länsi-Suomen ympäristölupavirasto 2008. Boliden Kokkola Oy:n Kokkolan sinkkitehtaan ympäristölupahakemus. http://www.ymparisto.fi/download/noname/%7BD40AD4E3-D99F-4EBB-8C92-88A2CC6FE431%7D/83709

[22] Länsi- ja Sisä-Suomen Aluehallintovirasto 2013. Boliden Kokkola Oy:n sinkkitehtaan toiminnalle 14.5.2008 myönnetyn ympä- ristölupapäätöksen lupamääräyksien 24 ja 34 muuttaminen.

https://www.avi.fi/documents/10191/56864/Issavi_paatos_134_2013_1_2013_09_03.pdf/fd373114-1559-42c0-b71e-ec31cce4139d

[23] Fugleberg, S. 1999. Finnish expert report on best available techniques in zinc production. https://helda.helsinki.fi/bitstream/handle/10138/43123/FE_315.pdf?sequence=1

[24] Toropainen, A. 2017. A Computational Thermodynamic Model for Conversion of Jarosite Residue into an Inert Slag via a Pyrometallurgical Process, Aalto University.

[25] Bergfald 2014. Nyrstar Hoyanger - Environmental impact of a new raw material, Oslo, Norway. http://www.miljodirektoratet.no/Global/dokumenter/horinger/horing2013-86-1_mra.pdf

[26] Kerolli-Mustafa, M. & Ćurković, L. 2016. Analysing the characteristics and application potentials of jarosite waste in Kosovo. Glob. Nest J. 18(1), 89–97.

[27] Pappu, A., Saxena, M. & Asolekar, S.R. 2006. Jarosite characteristics and its utilisation potentials. Sci. Total Environ. 359(1–3), 232–243. doi:10.1016/j.scitotenv.2005.04.024

[28] Ngenda, R.B., Segers, L. & Kongolo, P.K. 2009. Base metals recovery from zinc hydrometallurgical plant residues by digestion method. Hydrometallurgy , 17–30.

[29] Karumb, E.T. n.d. THE RECOVERY OF INDIUM FROM MINING WASTES, Colorado School of Mines. https://dspace.library.colostate.edu/bitstream/handle/11124/170446/TshijikKarumb_mines_0052N_11126.pdf?sequence=1

[30] Sofilić, T., Rastovčan-Mioč, A., Cerjan-Stefanović, Š., Novosel-Radović, V. & Jenko, M. 2004. Characterization of steel mill electric-arc furnace dust. J. Hazard. Mater. 109(1–3), 59–70. doi:10.1016/j.jhazmat.2004.02.032

[31] Grillo, F.F., Coleti, J.L., Espinosa, D.C.R., Oliveira, J.R. & Ten^|^oacute;rio, J. a. S. 2014. Zn and Fe Recovery from Electric Arc Furnace Dusts. Mater. Trans. 55(2), 351–356. doi:10.2320/matertrans.M2013385

[32] Michio Nakayama 2009. New Eaf Dust Treatment Process : Esrf. https://steelplantech.com/wp-

content/uploads/2013/11/201105_EAF_DustTreatment_byNewProcess.pdf

[33] Xia, K. 1997. Recovery of Zinc From Zinc Ferrite and Electric Arc Furnace Dust, Queen’s University. http://www.collectionscanada.gc.ca/obj/s4/f2/dsk3/ftp04/nq38338.pdf

[34] Lenz, D.M. & Martins, F.B. 2007. Lead and zinc selective precipitation from leach electric arc furnace dust solutions. Matéria (Rio Janeiro) 12(3), 503–509. doi:10.1590/S1517-70762007000300011

[35] Morcali, M.H., Yucel, O., Aydin, A. & Derin, B. 2012. Carbothermic reduction of electric arc furnace dust and calcination of waelz oxide by semi-pilot scale rotary furnace. J. Min. Metall. Sect. B Metall. 48(2), 173–184. doi:10.2298/JMMB111219031M

[36] Wannakamb, S., Manuskijsamrun, S. & Buggakupta, W. 2013. the Use of Electric Arc Furnace Dust From Steel Recycling in Ceramic Glaze. Suranaree J. Sci. Technol. 20(4), 329–337.

[37] Saikkonen, P. 2017. Personal discussion

[38] The Engineering Toolbox n.d. Densities of some Common Materials. , . https://www.engineeringtoolbox.com/

[39] Matches n.d. Matches’ Process Equipment Cost Estimates

[40] Towler, G. & Sinnott, R. 2013. Chemical engineering design, 2nd ed., Oxford.

[41] Towler, G. & Sinnott, R. 2013. Chemical Engineering Desing - Principles, Practices and Economics of Plant and Process Design, 2nd ed.

[42] van der Meer, T. 2017. Email correspondance

[43] The Engineering Toolbox n.d. Water - Density and Specific Weight. , . https://www.engineeringtoolbox.com/

[44] King County 2016. Minimum standards for sedimentation tank design. , . http://www.kingcounty.gov/services/environment/wastewater/industrial-waste/business/construction/sedimentation-tanks.aspx

[45] Darthmouth Collage 2006. Sedimentation basins (“ clarifiers ”).

[46] Matteson, M.J. & Orr, C. 1987. Filtration : principles and practices.

[47] Rastas, J., Saari, K., Väinö, H., Leppinen, J. & Järvinen, A. 1983.

Flotation recovery of lead, silver and gold as sulfides from electrolytic zinc process residues, US4385038, 1983

[48] Golam, S. & Oinas, P. 2016. CHEM-C7200 DESIGN PROJECT GUIDE

[49] Varsinais-Suomen ELY-keskus 2014. Boliden Harjavalta Oy:n uuden rikkihappotehtaan YVA-selostuksesta on annettu yhteysviranomaisen lausunto 3.9.2014.

[50] Luukka, T. 2015. Harjavaltaan 90 miljoonan euron investointi: Ruotsalaisyhtiö rakentaa uuden tehtaan. Helsingin Sanomat , . https://www.hs.fi/talous/art-2000002873421.html

[51] Unitel n.d. HYDROGEN SULFIDE (H2S) PRODUCTION TECHNOLOGY, 2–5.

[52] Basye, L. & Swaminathan, S. 1997. Hydrogen Production Costs - A Survey, Bethesda.

[53] Basye, L. & Swaminathan, S. 1997. Hydrogen production costs -- A survey, Golden, CO.doi:10.2172/674693

[54] Argus 2016. Argus FMB Sulphur. (16–42), . http://www.argusmedia.com/fertilizer/argus-sulphur/

[55] Eurostat 2016. Electricity prices for industrial consumers - bi-annual data (from 2007 onwards).

[56] Ulrich, G.D. & Vasudevan, P.T. 2006. How to estimate utility costs. Chem. Eng. 113(4), 66–69.

[57] Paul Humphreys 2011. Weigh the benefits of on-site nitrogen generation | Plant Engineering.

[58] Eia 2017. Cost and Performance Characteristics of New Generating Technologies, Annual Energy Outlook 2017.

[59] European IPPC Bureau 2014. Best available techniques (BAT) reference document for the non-ferrous metals industries. http://eippcb.jrc.ec.europa.eu/reference/BREF/NFM_Final_Draft_10_2014.pdf

[60] XE 2017. XE Currency Converter: USD to EUR

[61] King, M.J., Davenport, W.G., Moats, M.S., King, M.J., Davenport, W.G. & Moats, M.S. 2013. Costs of sulfuric acid production, in: Sulfuric Acid Manuf., doi:10.1016/B978-0-08-098220-5.00032-0

[62] ICIS 2006. Indicative Chemical Prices A-Z. https://www.icis.com/chemicals/channel-info-chemicals-a-z/

[63] Trading Economics 2017. Coal | 2009-2017 | Data | Chart | Calendar | Forecast | News. , . https://tradingeconomics.com/

[64] Intratec 2017. Calcium Hydroxide Price History in USA, Europe, Asia. , . https://www.intratec.us/chemical-markets/calcium-hydroxide-price

[65] Kangas, P., Kaijaluoto, S. & Määttänen, M. 2014. Evaluation of future pulp mill concepts - Reference model of a modern Nordic kraft pulp mill. Nord. Pulp Pap. Res. J. 29(4), 620–634. doi:10.3183/NPPRJ-2014-29-04-p620-634

[66] CEWEP 2014. Landfill taxes & bans. http://www.cewep.eu/information/data/landfill/index.html

[67] Puhas Oy 2017. Yrityksille vaarallisten jätteiden hinnasto - Jätehuoltoyhtiö Puhas Oy. , . http://www.puhas.fi/hinnat/kontiosuon-jatekeskus/yrityksille-vaarallisten-jatteiden-hinnasto.html

[68] U.S. Geological Survey 2017. LEAD. Miner. Commod. Summ.

[69] U.S. Geological Survey 2017. SILVER. Miner. Commod. Summ.

[70] U.S. Geological Survey 2017. GOLD. Miner. Commod. Summ.

[71] U.S. Geological Survey 2017. INDIUM. Miner. Commod. Summ.

[72] U.S. Geological Survey 2017. GALLIUM. Miner. Commod. Summ.

[73] U.S. Geological Survey 2017. GERMANIUM. Miner. Commod. Summ.

[74] U.S. Geological Survey 2017. ZINC. Miner. Commod. Summ.

[75] U.S. Geological Survey 2017. IRON ORE. Miner. Commod. Summ.

Appendix A: Cash flow for the Jarogain process

Table A1 Cash flow for the Jarogain process over a 30-year life-span using 80 % metal value. PV and NPV are based on 9 % discount rate. Every second year is omitted for simplicity.

Period	NPV	-3	-2	-1	1	2
Sales	1 085.2	0.0	0.0	0.0	104.9	139.9
Selling and distribution expenses	-66.4	0.0	0.0	0.0	-6.4	-8.6
Net Sales Revenue (€ million)					98.5	131.4
Variable costs	-426.4	0.0	0.0	0.0	-41.3	-55.0
Gross Margin (€ million)					57.2	76.4
Fixed costs	-155.7	0.0	0.0	0.0	-19.6	-19.6
Net Margin (€ million)					37.6	56.7
Capital expenditure	-335.2	-156.2	-175.7	-39.1	-19.5	0.0
Working capital	-5.8	0.0	0.0	0.0	-8.9	0.0
EBITDA (€ Million)		-156.2	-175.7	-39.1	9.2	56.7
PV		-156.2	-161.2	-32.9	7.1	40.2
CUM NPV		-156.2	-317.5	-350.3	-343.2	-303.0

Table A1. Continues; Years 4-16.

Period	4	6	8	10	12	14	16
Sales	139.9	139.9	139.9	139.9	139.9	139.9	139.9
Selling and distribution expenses	-8.6	-8.6	-8.6	-8.6	-8.6	-8.6	-8.6
Net Sales Revenue (€ million)	131.4	131.4	131.4	131.4	131.4	131.4	131.4
Variable costs	-55.0	-55.0	-55.0	-55.0	-55.0	-55.0	-55.0
Gross Margin (€ million)	76.4	76.4	76.4	76.4	76.4	76.4	76.4
Fixed costs	-19.6	-19.6	-19.6	-19.6	-19.6	-19.6	-19.6
Net Margin (€ million)	56.7	56.7	56.7	56.7	56.7	56.7	56.7

Capital expenditure	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Working capital	0.0	0.0	0.0	0.0	0.0	0.0	0.0
EBITDA (€ Million)	56.7	56.7	56.7	56.7	56.7	56.7	56.7
PV	33.8	28.5	24.0	20.2	17.0	14.3	12.0
CUM NPV	-232.3	-172.8	-122.7	-80.5	-45.0	-15.2	10.0

Table A1. Continues; Years 18-30.

Period	18	20	22	24	26	28	30
Sales	139.9	139.9	139.9	139.9	139.9	139.9	139.9
Selling and distribution expenses	-8.6	-8.6	-8.6	-8.6	-8.6	-8.6	-8.6
Net Sales Revenue (€ million)	131.4	131.4	131.4	131.4	131.4	131.4	131.4
Variable costs	-55.0	-55.0	-55.0	-55.0	-55.0	-55.0	-55.0
Gross Margin (€ million)	76.4	76.4	76.4	76.4	76.4	76.4	76.4
Fixed costs	-19.6	-19.6	-19.6	-19.6	-19.6	-19.6	-19.6
Net Margin (€ million)	56.7	56.7	56.7	56.7	56.7	56.7	56.7
Capital expenditure	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Working capital	0.0	0.0	0.0	0.0	0.0	0.0	8.9
EBITDA (€ Million)	56.7	56.7	56.7	56.7	56.7	56.7	65.6
PV	10.1	8.5	7.2	6.0	5.1	4.3	4.2
CUM NPV	31.1	49.0	64.0	76.6	87.2	96.1	104.2

Appendix B: Key reactions and extent of reactions

Table B1 Key reactions applied in the process modelling (HSC-Sim) and respective extent of these reactions.

Area 100 - H_2SO_4 treatment					
Progress %	**REACTANTS**			**PRODUCTS**	
95.00	**NaCl**	**H2SO4(l)**	**=**	**Na2SO4**	**HCl(g)**
Coef.	2	1		1	2
kmol/h	3.38	1.69		1.69	3.38
t/h	0.20	0.17		0.24	0.12
100.00	**Na2O**	**H2SO4(l)**	**=**	**Na2SO4**	**H2O(g)**
Coef.	1	1		1	1
kmol/h	0.96	0.96		0.96	0.96
t/h	0.06	0.09		0.14	0.02
95.00	**KF**	**H2SO4(l)**	**=**	**K2SO4**	**HF(g)**
Coef.	2	1		1	2
kmol/h	0.64	0.32		0.32	0.64
t/h	0.04	0.03		0.06	0.01
100.00	**K2O**	**H2SO4(l)**	**=**	**K2SO4**	**H2O(g)**
Coef.	1	1		1	1
kmol/h	0.87	0.87		0.87	0.87
t/h	0.08	0.09		0.15	0.02
100.00	**MgO**	**H2SO4(l)**	**=**	**MgSO4**	**H2O(g)**
Coef.	1	1		1	1
kmol/h	2.59	2.59		2.59	2.59
t/h	0.10	0.25		0.31	0.05
95.00	**CaF2**	**H2SO4(l)**	**=**	**CaSO4**	**HF(g)**
Coef.	1	1		1	2
kmol/h	0.00	0.00		0.00	0.00
t/h	0.00	0.00		0.00	0.00
100.00	**CaO**	**H2SO4(l)**	**=**	**CaSO4**	**H2O(g)**
Coef.	1	1		1	1
kmol/h	6.29	6.29		6.29	6.29
t/h	0.35	0.62		0.86	0.11
100.00	**Al2O3**	**H2SO4(l)**	**=**	**Al2(SO4)3**	**H2O(g)**
Coef.	1	3		1	3
kmol/h	1.17	3.50		1.17	3.50
t/h	0.12	0.34		0.40	0.06
100.00	**MnO**	**H2SO4(l)**	**=**	**MnSO4**	**H2O(g)**
Coef.	1	1		1	1

kmol/h	3.44	3.44		3.44	3.44		
t/h	0.24	0.34		0.52	0.06		
100.00	**ZnO**	**H2SO4(l)**	**=**	**ZnSO4**	**H2O(g)**		
Coef.	1	1		1	1		
kmol/h	33.71	33.71		33.71	33.71		
t/h	2.74	3.31		5.44	0.61		
100.00	**CuO**	**H2SO4(l)**	**=**	**CuSO4**	**H2O(g)**		
Coef.	1	1		1	1		
kmol/h	0.30	0.30		0.30	0.30		
t/h	0.02	0.03		0.05	0.01		
100.00	**NiO**	**H2SO4(l)**	**=**	**NiSO4**	**H2O(g)**		
Coef.	1	1		1	1		
kmol/h	0.01	0.01		0.01	0.01		
t/h	0.00	0.00		0.00	0.00		
100.00	**CoO**	**H2SO4(l)**	**=**	**CoSO4**	**H2O(g)**		
Coef.	1	1		1	1		
kmol/h	0.00	0.00		0.00	0.00		
t/h	0.00	0.00		0.00	0.00		
100.00	**PbO**	**H2SO4(l)**	**=**	**PbSO4**	**H2O(g)**		
Coef.	1	1		1	1		
kmol/h	0.91	0.91		0.91	0.91		
t/h	0.20	0.09		0.28	0.02		
100.00	**Fe2O3**	**H2SO4(l)**	**=**	**Fe2(SO4)3**	**H2O(g)**		
Coef.	1	3		1	3		
kmol/h	11.28	33.83		11.28	33.83		
t/h	1.80	3.32		4.51	0.61		
100.00	**H2O(l)**		**=**	**H2O(g)**			
Coef.	1			1			
kmol/h	0.21			0.21			
t/h	0.00			0.00			

Area 200 - Leaching

Progress **%**	**REACTANTS**			**PRODUCTS**			
100.00	**SO2(g)**		**=**	**SO2(a)**			
Coef.	1			1			
kmol/h	108.38			108.38			
t/h	6.94			6.94			
100.00	**H2SO4(l)**		**=**	**H(+a)**	**SO4(-2a)**		
Coef.	1			2	1		
kmol/h	48.99			97.98	48.99		
t/h	4.80			0.10	4.71		
95.00	**NH4Fe3(SO4)2(OH)6**	**SO2(a)**	**=**	**NH4(+a)**	**Fe(+2a)**	**SO4(-2a)**	**H2O(l)**

Coef.	1	1.5			1	3	3.5	3
kmol/h	13.46	20.19			13.46	40.38	47.11	40.38
t/h	6.46	1.29			0.24	2.25	4.53	0.73
95.00	**NaFe3(SO4)2(OH)6**	**SO2(a)**		**=**	**Na(+a)**	**Fe(+2a)**	**SO4(-2a)**	**H2O(l)**
Coef.	1	1.5			1	3	3.5	3
kmol/h	21.10	31.65			21.10	63.30	73.85	63.30
t/h	10.23	2.03			0.49	3.54	7.09	1.14
95.00	**KFe3(SO4)2(OH)6**	**SO2(a)**		**=**	**K(+a)**	**Fe(+2a)**	**SO4(-2a)**	**H2O(l)**
Coef.	1	1.5			1	3	3.5	3
kmol/h	6.21	9.32			6.21	18.63	21.74	18.63
t/h	3.11	0.60			0.24	1.04	2.09	0.34
95.00	**Fe2(SO4)3**	**SO2(a)**	**H2O(l)**	**=**	**Fe(+2a)**	**H(+a)**	**SO4(-2a)**	
Coef.	1	1	2		2	4	4	
kmol/h	11.77	11.77	23.55		23.55	47.10	47.10	
t/h	4.71	0.75	0.42		1.32	0.05	4.52	
90.00	**ZnFe2O4**	**SO2(a)**	**H(+a)**	**=**	**Zn(+2a)**	**Fe(+2a)**	**SO4(-2a)**	**H2O(l)**
Coef.	1	1	4		1	2	1	2
kmol/h	24.64	24.64	98.54		24.64	49.27	24.64	49.27
t/h	5.94	1.58	0.10		1.61	2.75	2.37	0.89
0.00	**CuFe2O4**	**SO2(a)**	**H(+a)**	**=**	**Cu(+2a)**	**Fe(+2a)**	**SO4(-2a)**	**H2O(l)**
Coef.	1	1	4		1	2	1	2
kmol/h	0.00	0.00	0.00		0.00	0.00	0.00	0.00
t/h	0.00	0.00	0.00		0.00	0.00	0.00	0.00
90.00	**CdFe2O4**	**SO2(a)**	**H(+a)**	**=**	**Cd(+2a)**	**Fe(+2a)**	**SO4(-2a)**	**H2O(l)**
Coef.	1	1	4		1	2	1	2
kmol/h	0.20	0.20	0.82		0.20	0.41	0.20	0.41
t/h	0.06	0.01	0.00		0.02	0.02	0.02	0.01
67.00	**Al2O3**	**H(+a)**		**=**	**Al(+3a)**	**H2O(l)**		
Coef.	1	6			2	3		
kmol/h	3.17	19.05			6.35	9.52		
t/h	0.32	0.02			0.17	0.17		
75.00	**MgO**	**H(+a)**		**=**	**Mg(+2a)**	**H2O(l)**		
Coef.	1	2			1	1		
kmol/h	3.16	6.31			3.16	3.16		
t/h	0.13	0.01			0.08	0.06		
99.00	**MnO**	**H(+a)**		**=**	**Mn(+2a)**	**H2O(l)**		
Coef.	1	2			1	1		
kmol/h	0.92	1.84			0.92	0.92		
t/h	0.07	0.00			0.05	0.02		
80.00	**NiO**	**H(+a)**		**=**	**Ni(+2a)**	**H2O(l)**		
Coef.	1	2			1	1		
kmol/h	0.07	0.14			0.07	0.07		
t/h	0.01	0.00			0.00	0.00		
80.00	**CoO**	**H(+a)**		**=**	**Co(+2a)**	**H2O(l)**		

Coef.	1	2		1	1
kmol/h	0.03	0.07		0.03	0.03
t/h	0.00	0.00		0.00	0.00
95.00	**As2O3**	**H2O(l)**	**=**	**H3AsO3(a)**	
Coef.	1	3		2	
kmol/h	1.62	4.86		3.24	
t/h	0.32	0.09		0.41	
10.00	**Sb2O3**	**H2O(l)**	**=**	**HSbO2(a)**	
Coef.	1	1		2	
kmol/h	0.01	0.01		0.02	
t/h	0.00	0.00		0.00	
0.00	**SnO2**	**SO2(a)**	**=**	**Sn(+2a)**	**SO4(-2a)**
Coef.	1	1		1	1
kmol/h	0.00	0.00		0.00	0.00
t/h	0.00	0.00		0.00	0.00
100.00	**GeO2**	**SO2(a)**	**=**	**Ge(+2a)**	**SO4(-2a)**
Coef.	1	1		1	1
kmol/h	0.04	0.04		0.04	0.04
t/h	0.00	0.00		0.00	0.00
100.00	**In2O3**	**H(+a)**	**=**	**In(+3a)**	**H2O(l)**
Coef.	1	6		2	3
kmol/h	0.01	0.09		0.03	0.04
t/h	0.00	0.00		0.00	0.00
50.00	**Ga2O3**	**H(+a)**	**=**	**Ga(+3a)**	**H2O(l)**
Coef.	1	6		2	3
kmol/h	0.01	0.05		0.02	0.03
t/h	0.00	0.00		0.00	0.00
0.00	**H2O(g)**		**=**	**H2O(l)**	
Coef.	1			1	
kmol/h	0.00			0.00	
t/h	0.00			0.00	
67.00	**Al2(SO4)3**		**=**	**Al(+3a)**	**SO4(-2a)**
Coef.	1			2	3
kmol/h	0.78			1.56	2.35
t/h	0.27			0.04	0.23
100.00	**CaF2**		**=**	**Ca(+2a)**	**F(-a)**
Coef.	1			1	2
kmol/h	0.00			0.00	0.00
t/h	0.00			0.00	0.00
100.00	**NaCl**		**=**	**Na(+a)**	**Cl(-a)**
Coef.	1			1	1
kmol/h	0.21			0.21	0.21
t/h	0.01			0.00	0.01
100.00	**KF**		**=**	**K(+a)**	**F(-a)**

Coef.	1			1	1	
kmol/h	0.03			0.03	0.03	
t/h	0.00			0.00	0.00	
10.00	**CaSO4*2H2O**		**=**	**Ca(+2a)**	**SO4(-2a)**	**H2O(l)**
Coef.	1			1	1	2
kmol/h	5.10			5.10	5.10	10.21
t/h	0.88			0.20	0.49	0.18
1.00	**H2O(l)**		**=**	**H2O(g)**		
Coef.	1			1		
kmol/h	194.11			194.11		
t/h	3.50			3.50		
90.00	**ZnSO4**		**=**	**Zn(+2a)**	**SO4(-2a)**	
Coef.	1			1	1	
kmol/h	30.34			30.34	30.34	
t/h	4.90			1.98	2.91	
100.00	**Na2SO4**		**=**	**Na(+a)**	**SO4(-2a)**	
Coef.	1			2	1	
kmol/h	2.65			5.30	2.65	
t/h	0.38			0.12	0.25	
100.00	**K2SO4**		**=**	**K(+a)**	**SO4(-2a)**	
Coef.	1			2	1	
kmol/h	1.19			2.38	1.19	
t/h	0.21			0.09	0.11	
67.00	**SrSO4**		**=**	**Sr(+2a)**	**SO4(-2a)**	
Coef.	1			1	1	
kmol/h	0.04			0.04	0.04	
t/h	0.01			0.00	0.00	

Area 300 - Roasting

Progress **%**	**REACTANTS**			**PRODUCTS**
100.00	**S**	**O2(g)**	**=**	**SO2(g)**
Coef.	1	1		1
kmol/h	167.51	167.51		167.51
t/h	5.37	5.36		10.73
100.00	**C**	**O2(g)**	**=**	**CO2(g)**
Coef.	1	1		1
kmol/h	0.00	0.00		0.00
t/h	0.00	0.00		0.00
100.00	**H2O(l)**		**=**	**H2O(g)**
Coef.	1			1
kmol/h	503.41			503.41
t/h	9.07			9.07

100.00	**CaSO4*2H2O**		=	**CaSO4**	**H2O(l)**	
Coef.	1			1	2	
kmol/h	45.93			45.93	91.86	
t/h	7.91			6.25	1.65	

Area 300 - Sulfidation

Progress %	**REACTANTS**			**PRODUCTS**		
100.00	**PbSO4**	**Na2S(ia)**	=	**PbS**	**Na(+a)**	**SO4(-2a)**
Coef.	1	1		1	2	1
kmol/h	7.55	7.55		7.55	15.10	7.55
t/h	2.29	0.59		1.81	0.35	0.73
100.00	**Ag2SO4**	**Na2S(ia)**	=	**Ag2S**	**Na(+a)**	**SO4(-2a)**
Coef.	1	1		1	2	1
kmol/h	0.00	0.00		0.00	0.00	0.00
t/h	0.00	0.00		0.00	0.00	0.00
100.00	**AgCl**	**Na2S(ia)**	=	**Ag2S**	**Na(+a)**	**Cl(-a)**
Coef.	2	1		1	2	2
kmol/h	0.06	0.03		0.03	0.06	0.06
t/h	0.01	0.00		0.01	0.00	0.00
1.00	**H2O(l)**		=	**H2O(g)**		
Coef.	1			1		
kmol/h	50.02			50.02		
t/h	0.90			0.90		
100.00	**CaSO4**	**H2O(l)**	=	**CaSO4*2H2O**		
Coef.	1	2		1		
kmol/h	52.22	104.43		52.22		
t/h	7.11	1.88		8.99		

Area 400 - Hydroxide precipitation

Progress %	**REACTANTS**			**PRODUCTS**	
99.00	**MgO**	**H2O(l)**	=	**Mg(+2a)**	**OH(-a)**
Coef.	1	1		1	2
kmol/h	33.97	33.97		33.97	67.94
t/h	1.37	0.61		0.83	1.16
80.00	**In(+3a)**	**OH(-a)**	=	**In(OH)3**	
Coef.	1	3		1	
kmol/h	0.02	0.07		0.02	
t/h	0.00	0.00		0.00	
90.00	**Ga(+3a)**	**OH(-a)**	=	**Ga(OH)3**	
Coef.	1	3		1	
kmol/h	0.02	0.05		0.02	

t/h	0.00	0.00		0.00	
67.00	**Ge(+2a)**	**OH(-a)**	**=**	**Ge(OH)2**	
Coef.	1	2		1	
kmol/h	0.03	0.05		0.03	
t/h	0.00	0.00		0.00	
90.00	**Al(+3a)**	**OH(-a)**	**=**	**Al(OH)3**	
Coef.	1	3		1	
kmol/h	7.21	21.63		7.21	
t/h	0.19	0.37		0.56	
5.00	**Zn(+2a)**	**OH(-a)**	**=**	**Zn(OH)2**	
Coef.	1	2		1	
kmol/h	3.46	6.93		3.46	
t/h	0.23	0.12		0.34	
5.00	**Fe(+2a)**	**OH(-a)**	**=**	**Fe(OH)2**	
Coef.	1	2		1	
kmol/h	12.32	24.65		12.32	
t/h	0.69	0.42		1.11	
50.00	**H(+a)**	**OH(-a)**	**=**	**H2O(l)**	
Coef.	1	1		1	
kmol/h	10.13	10.13		10.13	
t/h	0.01	0.17		0.18	
1.00	**H2O(l)**		**=**	**H2O(g)**	
Coef.	1			1	
kmol/h	278.68			278.68	
t/h	5.02			5.02	
50.00	**H3AsO3(a)**		**=**	**As2O3**	**H2O(l)**
Coef.	2			1	3
kmol/h	1.81			0.90	2.71
t/h	0.23			0.18	0.05

Area 500 - Sulfide precipitation

Progress %	REACTANTS			PRODUCTS	
100.00	**H2S(g)**		**=**	**H2S(a)**	
Coef.	1			1	
kmol/h	55.46			55.46	
t/h	1.89			1.89	
100.00	**MgO**	**H2O(l)**	**=**	**Mg(+2a)**	**OH(-a)**
Coef.	1	1		1	2
kmol/h	56.90	56.90		56.90	113.81
t/h	2.29	1.03		1.38	1.94
100.00	**H3AsO3(a)**	**H2S(a)**	**=**	**As2S3**	**H2O(l)**
Coef.	2	3		1	6

kmol/h	1.40	2.10		0.70	4.19
t/h	0.18	0.07		0.17	0.08
100.00	**HSbO2(a)**	**H2S(a)**	**=**	**Sb2S3**	**H2O(l)**
Coef.	2	3		1	4
kmol/h	0.02	0.03		0.01	0.04
t/h	0.00	0.00		0.00	0.00
100.00	**Sn(+2a)**	**H2S(a)**	**=**	**SnS**	**H(+a)**
Coef.	1	1		1	2
kmol/h	0.00	0.00		0.00	0.00
t/h	0.00	0.00		0.00	0.00
100.00	**Cu(+2a)**	**H2S(a)**	**=**	**CuS**	**H(+a)**
Coef.	1	1		1	2
kmol/h	0.00	0.00		0.00	0.00
t/h	0.00	0.00		0.00	0.00
100.00	**Cd(+2a)**	**H2S(a)**	**=**	**CdS**	**H(+a)**
Coef.	1	1		1	2
kmol/h	0.20	0.20		0.20	0.40
t/h	0.02	0.01		0.03	0.00
100.00	**Zn(+2a)**	**H2S(a)**	**=**	**ZnS**	**H(+a)**
Coef.	1	1		1	2
kmol/h	50.85	50.85		50.85	101.71
t/h	3.32	1.73		4.96	0.10
100.00	**Al(+3a)**	**SO4(-2a)**	**=**	**Al2(SO4)3**	
Coef.	2	3		1	
kmol/h	0.62	0.93		0.31	
t/h	0.02	0.09		0.11	
10.00	**Co(+2a)**	**SO4(-2a)**	**=**	**CoSO4**	
Coef.	1	1		1	
kmol/h	0.00	0.00		0.00	
t/h	0.00	0.00		0.00	
100.00	**Ge(+2a)**	**OH(-a)**	**=**	**Ge(OH)2**	
Coef.	1	2		1	
kmol/h	0.01	0.02		0.01	
t/h	0.00	0.00		0.00	
100.00	**In(+3a)**	**OH(-a)**	**=**	**In(OH)3**	
Coef.	1	3		1	
kmol/h	0.00	0.01		0.00	
t/h	0.00	0.00		0.00	
100.00	**Ga(+3a)**	**OH(-a)**	**=**	**Ga(OH)3**	
Coef.	1	3		1	
kmol/h	0.00	0.00		0.00	
t/h	0.00	0.00		0.00	
100.00	**H(+a)**	**OH(-a)**	**=**	**H2O(l)**	
Coef.	1	1		1	

kmol/h	109.94	109.94			109.94		
t/h	0.11	1.87			1.98		
1.00	**H2O(l)**			=	**H2O(g)**		
Coef.	1				1		
kmol/h	292.66				292.66		
t/h	5.27				5.27		
1.00	**Fe(+2a)**	**OH(-a)**		=	**Fe(OH)2**		
Coef.	1	2			1		
kmol/h	2.42	4.84			2.42		
t/h	0.14	0.08			0.22		

Area 600 - Arsenic removal

Progress %	**REACTANTS**				**PRODUCTS**		
100.00	**As2S3**	**(NH4)2S(ia)**	**S**	=	**(NH4)3AsS4(ia)**		
Coef.	1	3	2		2		
kmol/h	0.70	2.10	1.40		1.40		
t/h	0.17	0.14	0.04		0.36		
100.00	**Sb2S3**	**(NH4)2S(ia)**	**S**	=	**(NH4)3SbS4(ia)**		
Coef.	1	3	2		2		
kmol/h	0.01	0.03	0.02		0.02		
t/h	0.00	0.00	0.00		0.01		
100.00	**SnS**	**(NH4)2S(ia)**	**S**	=	**(NH4)2SnS3(ia)**		
Coef.	1	1	1		1		
kmol/h	0.00	0.00	0.00		0.00		
t/h	0.00	0.00	0.00		0.00		
0.00	**(NH4)3AsS4(ia)**	**H2SO4(ia)**		=	**As2S5**	**(NH4)2SO4(ia)**	**H2S(a)**
Coef.	2	3			1	3	3
kmol/h	0.00	0.00			0.00	0.00	0.00
t/h	0.00	0.00			0.00	0.00	0.00
0.00	**(NH4)3SbS4(ia)**	**H2SO4(ia)**		=	**Sb2S5**	**(NH4)2SO4(ia)**	**H2S(a)**
Coef.	2	3			1	3	3
kmol/h	0.00	0.00			0.00	0.00	0.00
t/h	0.00	0.00			0.00	0.00	0.00
0.00	**(NH4)2SnS3(ia)**	**H2SO4(ia)**		=	**SnS2**	**(NH4)2SO4(ia)**	**H2S(a)**
Coef.	1	1			1	1	1
kmol/h	0.00	0.00			0.00	0.00	0.00
t/h	0.00	0.00			0.00	0.00	0.00
0.00	**H2SO4(l)**			=	**H2SO4(ia)**		
Coef.	1				1		
kmol/h	0.00				0.00		
t/h	0.00				0.00		
1.00	**H2O(l)**			=	**H2O(g)**		

Coef.	1				1		
kmol/h	16.27				16.27		
t/h	0.29				0.29		

Area 600 - Arsenic removal - H_2SO_4 precipitation

Progress %	**REACTANTS**				**PRODUCTS**		
100.00	**H2SO4(l)**			**=**	**H(+a)**	**SO4(-2a)**	
Coef.	1				2	1	
kmol/h	4.40				8.79	4.40	
t/h	0.43				0.01	0.42	
100.00	**(NH4)3AsS4(ia)**	**H(+a)**		**=**	**As2S5**	**NH4(+a)**	**H2S(a)**
Coef.	2	6			1	6	3
kmol/h	1.31	3.94			0.66	3.94	1.97
t/h	0.34	0.00			0.20	0.07	0.07
100.00	**(NH4)3SbS4(ia)**	**H(+a)**		**=**	**Sb2S5**	**NH4(+a)**	**H2S(a)**
Coef.	2	6			1	6	3
kmol/h	0.02	0.06			0.01	0.06	0.03
t/h	0.01	0.00			0.00	0.00	0.00
100.00	**(NH4)2SnS3(ia)**	**H(+a)**		**=**	**SnS2**	**NH4(+a)**	**H2S(a)**
Coef.	1	2			1	2	1
kmol/h	0.00	0.00			0.00	0.00	0.00
t/h	0.00	0.00			0.00	0.00	0.00

Area 700 - Evaporation and crystallization

Progress %	**REACTANTS**				**PRODUCTS**
100.00	**Fe(+2a)**	**SO4(-2a)**	**H2O(l)**	**=**	**FeSO4*H2O**
Coef.	1	1	1		1
kmol/h	178.41	178.41	178.41		178.41
t/h	9.96	17.14	3.21		30.32
100.00	**Mn(+2a)**	**SO4(-2a)**	**H2O(l)**	**=**	**MnSO4*H2O**
Coef.	1	1	1		1
kmol/h	0.91	0.91	0.91		0.91
t/h	0.05	0.09	0.02		0.15
100.00	**Ni(+2a)**	**SO4(-2a)**	**H2O(l)**	**=**	**NiSO4*H2O**
Coef.	1	1	1		1
kmol/h	0.07	0.07	0.07		0.07
t/h	0.00	0.01	0.00		0.01
100.00	**Co(+2a)**	**SO4(-2a)**	**H2O(l)**	**=**	**CoSO4*H2O**
Coef.	1	1	1		1
kmol/h	0.03	0.03	0.03		0.03
t/h	0.00	0.00	0.00		0.01

100.00	**Al(+3a)**	**SO4(-2a)**	**H2O(l)**	**=**	**Al2(SO4)3*6H2O**			
Coef.	2	3	6		1			
kmol/h	0.00	0.00	0.00		0.00			
t/h	0.00	0.00	0.00		0.00			
100.00	**NH4(+a)**	**SO4(-2a)**		**=**	**(NH4)2SO4**			
Coef.	2	1			1			
kmol/h	17.28	8.64			8.64			
t/h	0.31	0.83			1.14			
100.00	**Na(+a)**	**SO4(-2a)**		**=**	**Na2SO4**			
Coef.	2	1			1			
kmol/h	34.04	17.02			17.02			
t/h	0.78	1.63			2.42			
100.00	**K(+a)**	**SO4(-2a)**		**=**	**K2SO4**			
Coef.	2	1			1			
kmol/h	8.52	4.26			4.26			
t/h	0.33	0.41			0.74			
100.00	**H2O(l)**			**=**	**H2O(g)**			
Coef.	1				1			
kmol/h	7435.09				7435.09			
t/h	133.95				133.95			
100.00	**Mg(+2a)**	**SO4(-2a)**	**H2O(l)**	**=**	**MgSO4*H2O**			
Coef.	1	1	1		1			
kmol/h	92.21	92.21	92.21		92.21			
t/h	2.24	8.86	1.66		12.76			
100.00	**OH(-a)**	**Mg(+2a)**		**=**	**Mg(OH)2**			
Coef.	2	1			1			
kmol/h	3.41	1.70			1.70			
t/h	0.06	0.04			0.10			

Area 800 - Thermal treatment

Progress %	REACTANTS				PRODUCTS			
100.00	**FeSO4*H2O**			**=**	**Fe2O3**	**SO2(g)**	**O2(g)**	**H2O(g)**
Coef.	4				2	4	1	4
kmol/h	178.41				89.21	178.41	44.60	178.41
t/h	30.32				14.25	11.43	1.43	3.21
100.00	**MgSO4*H2O**			**=**	**MgSO4**	**H2O(g)**		
Coef.	1				1	1		
kmol/h	92.21				92.21	92.21		
t/h	12.76				11.10	1.66		
100.00	**MnSO4*H2O**			**=**	**MnO**	**SO2(g)**	**O2(g)**	**H2O(g)**
Coef.	2				2	2	1	2
kmol/h	0.91				0.91	0.91	0.46	0.91

t/h	0.15			0.06	0.06	0.01	0.02
100.00	**NiSO4*H2O**		**=**	**NiO**	**SO2(g)**	**O2(g)**	**H2O(g)**
Coef.	2			2	2	1	2
kmol/h	0.07			0.07	0.07	0.03	0.07
t/h	0.01			0.01	0.00	0.00	0.00
100.00	**CoSO4*H2O**		**=**	**CoO**	**SO2(g)**	**O2(g)**	**H2O(g)**
Coef.	2			2	2	1	2
kmol/h	0.03			0.03	0.03	0.01	0.03
t/h	0.01			0.00	0.00	0.00	0.00
100.00	**Al2(SO4)3*6H2O**		**=**	**Al2O3**	**SO2(g)**	**O2(g)**	**H2O(g)**
Coef.	1			1	3	1.5	6
kmol/h	0.00			0.00	0.00	0.00	0.00
t/h	0.00			0.00	0.00	0.00	0.00
100.00	**(NH4)2SO4**	**O2(g)**	**=**	**N2(g)**	**SO2(g)**	**H2O(g)**	
Coef.	1	1		1	1	4	
kmol/h	8.64	8.64		8.64	8.64	34.56	
t/h	1.14	0.28		0.24	0.55	0.62	
100.00	**C**	**O2(g)**	**=**	**CO2(g)**			
Coef.	1	1		1			
kmol/h	215.03	215.03		215.03			
t/h	2.58	6.88		9.46			
Area 800 - Washing							
Progress	**REACTANTS**			**PRODUCTS**			
%							
100.00	**MgSO4**		**=**	**Mg(+2a)**	**SO4(-2a)**		
Coef.	1			1	1		
kmol/h	92.21			92.21	92.21		
t/h	11.10			2.24	8.86		
100.00	**Na2SO4**		**=**	**Na(+a)**	**SO4(-2a)**		
Coef.	1			2	1		
kmol/h	17.02			34.04	17.02		
t/h	2.42			0.78	1.63		
100.00	**K2SO4**		**=**	**K(+a)**	**SO4(-2a)**		
Coef.	1			2	1		
kmol/h	4.26			8.52	4.26		
t/h	0.74			0.33	0.41		
1.00	**H2O(l)**		**=**	**H2O(g)**			
Coef.	1			1			
kmol/h	79.59			79.59			
t/h	1.43			1.43			

Appendix C: Elemental mass-based yields in solid phases

Table C1 Elemental mass-based yields in solid phases after each process step.

Element	H_2SO_4-treatment	Leaching	Flotation	Hydroxide precipitation	Sulfide precipitation
Ag	100 %	100 %	90 %	-	-
Al	100 %	33 %	0 %	90 %	100 %
As	100 %	5 %	0 %	50 %	100 %
Au	100 %	100 %	90 %	-	-
Ba	100 %	100 %	0 %	-	-
Ca	100 %	90 %	0 %	1 %	2 %
Cd	100 %	10 %	0 %	15 %	100 %
Cl	5 %	28 %	0 %	0 %	0 %
Co	100 %	20 %	0 %	2 %	10 %
Cr	100 %	0 %	0 %	100 %	-
Cu	100 %	100 %	0 %	-	-
F	5 %	0 %	0 %	0 %	0 %
Fe	100 %	5 %	2 %	5 %	1 %
Ga	100 %	50 %	0 %	90 %	100 %
Ge	100 %	0 %	0 %	67 %	100 %
Hg	100 %	100 %	0 %	-	-
In	100 %	0 %	0 %	80 %	100 %
K	100 %	10 %	0 %	1 %	1 %
Mg	100 %	25 %	0 %	1 %	4 %
Mn	100 %	1 %	0 %	1 %	0 %
Na	100 %	1 %	0 %	1 %	0 %
Ni	100 %	20 %	0 %	2 %	3 %
Pb	100 %	100 %	90 %	-	-
S	100 %	33 %	2 %	14 %	30 %
Sb	100 %	90 %	0 %	80 %	100 %
Si	100 %	95 %	2 %	100 %	-
Sn	100 %	100 %	0 %	20 %	100 %
Sr	100 %	33 %	100 %	5 %	5 %
Zn	100 %	10 %	2 %	5 %	100 %

Table C2 Continues.

Element	**Arsenic removal**	**Evaporation**	**Thermal treatment**	**Washing**	**Process total to main products**
Ag	-	-	-	-	90 %
Al	-	-	-	-	
As	0	-	-	-	
Au	-	-	-	-	90 %
Ba	-	-	-	-	
Ca	0 %	100 %	100 %	100 %	
Cd	-	-	-	-	
Cl	0 %	100 %	100 %	100 %	
Co	0 %	100 %	100 %	100 %	
Cr	-	-	-	-	
Cu	-	-	-	-	
F	0 %	100 %	100 %	100 %	
Fe	100 %	100 %	100 %	100 %	85 %
Ga	100 %	-	-	-	45 %
Ge	100 %	-	-	-	67 %
Hg	-	-	-	-	
In	100 %	-	-	-	80 %
K	0 %	100 %	100 %	100 %	
Mg	100 %	100 %	100 %	100 %	
Mn	-	100 %	100 %	100 %	
Na	-	100 %	100 %	100 %	
Ni	100 %	100 %	100 %	100 %	
Pb	-	-	-	-	90 %
S	-	100 %	100 %	100 %	
Sb	-	-	-	-	
Si	-	-	-	-	
Sn	-	-	-	-	
Sr	-	100 %	100 %	100 %	
Zn	100 %	-	-	-	86 %

Appendix D: Proposed methods for purifying In-Ga-Ge concentrate

Mari Lundström, Aalto University (mari.lundstom@aalto.fi)
Benjamin Wilson, Aalto University (ben.wilson@aalto.fi)

The focus of Jarogain project research in Aalto University focused on the investigation of In-Ga-Ge rich precipitate originating from the VTT´s Jarogain process as a side product. The precipitate (#1) investigated had In content of 3 mg/g, Ga content 0.79 mg/g and Ge content of 0.37 mg/g. In addition the sample was rich in Fe (161 mg/g), S (257 mg/g), Fe (161 mg/g), Al (49.8 mg/g), As (46.8 mg/g), Zn (34.9 mg/g), Si (18.1 mg/g), Mg (13.2 mg/g) with other elements present such as Ca, Cd, Cr, Cu, Mn, Na, Sb and Sr in trace amounts.

In, Ga and Ge are usually produced as byproducts of base metals, such as aluminum, zinc or lead. (Alfantazi, Moskalyk 2003, Moskalyk 2003). Hydrometallurgical processes have been studied for the recovery of In and Ga from zinc residues, such as Jarosite (Dutrizac, Chen 2000) and these processes often leach the material with a strong mineral acid or in some cases alkali. (F. Zhang et al. 2016, Kudo, Maruyama 2001). Leaching is followed by metal purification and separation by different methods like precipitation, cementation, solvent extraction and ion exchange (Li et al. 2015). Metallic gallium and indium is usually produced either by cementation or by electrowinning, with the final product often purified by electrorefining (Jiang, Liang & Zhong 2011, De Souza 2008).

In this work, a hydrometallurgical process was investigated as a potential recovery treatment step for the In-Ga-Ge rich precipitate of VTT, a side-product produced from jarosite and EAF dust (Kangas et al. 2016). In addition, a high temperature treatment was studied in order to observe the extraction of volatile elements. A detailed description of the experiments is presented in the Master´s Thesis of Sami Kinnunen (2017).

Experimental

The experimental part of this work consisted of raw material characterization (In-Ga-Ge rich side stream of Jarogain process), leaching experiments, preparation of synthetic solutions for solvent extraction as well as solvent extraction, scrubbing and stripping experiments. The leaching experiments were conducted in sulfuric acid media (60 g/L and 150 g/L), as well as in oxalic acid media (110 g/L).

Also pyrolysis experiments were carried out for the In-Ga-Ge rich precipitate in order to determine if In and Ga could be enriched in the raw material by evaporation of other elements. 2-hour experiments were carried out with dried precipitate samples in both 500 and 1000 ^{o}C. Pyrolysis experiments showed no significant change in indium or gallium concentrations and the only element that was removed from the material by the process was sulfur.

The analysis of solution samples and solids (after total leaching) were conducted with an Inductively Coupled Plasma-Optical Emission Spectroscope (ICP-OES). In addition to the ICP-OES analysis, the solid precipitates were analyzed with a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) detection system (Goodhew et al. 2000).

In the leaching experiments, the best indium and gallium extraction were achieved with 150 g/L sulfuric acid concentration, 55 °C temperature and oxygen purging. No significant selectivity was found in any of the experiments. Based on the composition of precipitate #1 and an assumption of a theoretical sulfuric acid leaching with 150 g/L sulfuric dissolving the precipitate with S/L ratios of 1/20 and 1/10, two synthetic solutions were prepared for In and Ga solvent extraction, Table D1.

Table D1: Compositions of the two synthetic solutions

Solution #	[Al] (g/L)	[Fe] (g/L)	[Ga] (mg/L)	[Ge] (mg/L)	[In] (mg/L)	[Mg] (mg/L)	[Zn] (g/L)
1	2.5	8	40	20	150	660	1.7
2	5	16	80	40	300	1300	3.5

The pH of the synthetic In-Ga(-Ge) containing solutions was first adjusted (with 5 M NaOH), after which ferric iron in the solution was reduced to ferrous with addition of ascorbic acid. Solvent extraction experiments with 20 v-% D2EHPA diluted in Escaid 110 were carried out, after which a scrubbing stage using 0.5 M H_2SO_4 was performed and metals were stripped using either H_2SO_4 or HCl. Optimized conditions for the solvent extraction were found to be A/O ratio of 1:1 and 5 minutes contact time, which were used for the scrubbing and stripping steps as well, Figure D1.

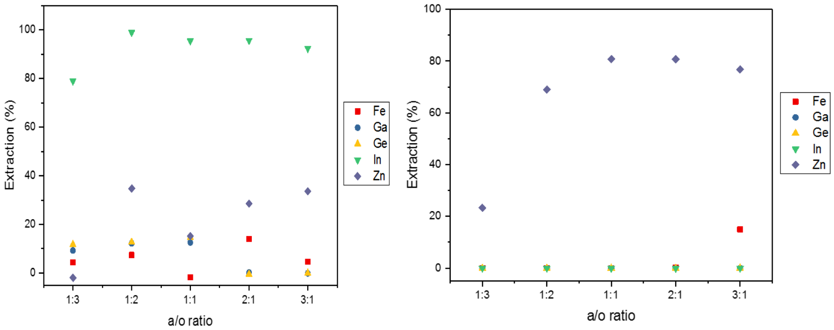


Figure D1. The effect of aqueous/organic ratio for the extraction of metals (left) into the 20 v-% D2EHPA at pH 1.2 with contact time 5 min and into (right) 0.5 M sulphuric acid from the organic (i.e. scrubbing).

In a process with optimized steps, the pH of the solution was first adjusted to 2.1, after which 250 g/L of ascorbic acid powder was added to the solution. Solvent extraction was carried out at equilibrium pH of 1.5, resulting in approximately 93% In, 22% Ga, 67% Zn, 1.2% Al and 1.6% Ge extractions. 96% of Zn was scrubbed from the organic phase, after which 66% of In was stripped with 5 M HCl.

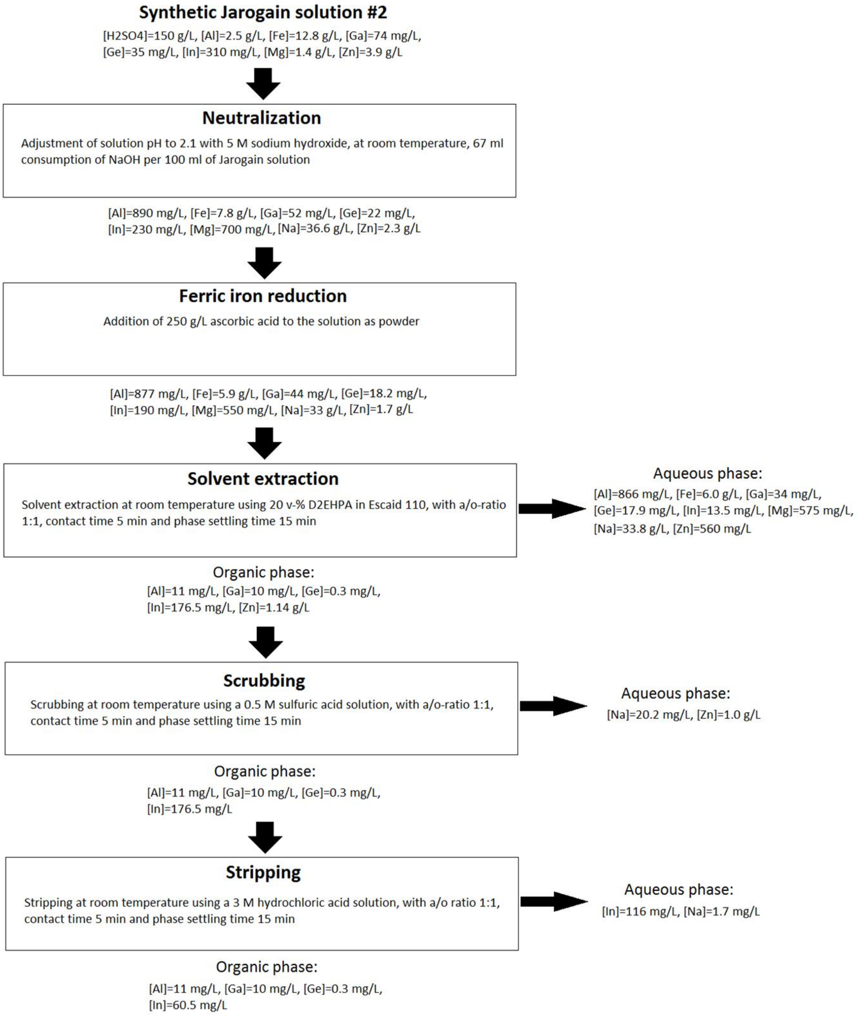


Figure D2. Flow sheet and results of a chain of unit processes carried out with Solution #2.

A block diagram of the hydrometallurgical process carried out for solution #2, Figure D2. It can be seen, that the aqueous phases from the scrubbing and stripping stages do contain zinc and indium in relatively high purity. The aqueous phases from the scrubbing and stripping stages contain both Zn and In at relatively high purity. Subsequently, Al and Fe stripping can carried out using 5 M H_2SO_4 and 5 M HCl sequentially.

Overall, the flowsheet presented (Figure 1) provides a significant basis for further development of the In and Ga recovery. The main focus in the further work need to be (i) in the use of real raw material with high S/L ratio in leaching, resulting in verified product liquid solution (PLS), (ii) testing alternative lower cost reducing agent for iron and (iii) enhancement of Ga (and Ge) extraction/stripping. Furthermore, process steps for the recovery of In and Ga (and Ge) need to be verified.

Direct recovery of In, Ga by electrochemical methods

In order to investigate electrochemical recovery of In, Ga (and Ge), synthetic solutions that contained 1500 ppm Al, 8000 ppm Zn, 100 ppm In, 20 ppm Ga and 10 g/L H_2SO_4 were investigated with a three-electrode cell set-up in order to determine the applicability of tailored electrochemical recovery for In, Ga and Ge. Initial experiments focused on the deposition and stripping peaks of Ga and In with the synthetic, two compound solution, nevertheless, the extremely low recoveries of Ga (~0.4 wt.%) and In (~0.2 wt.%) demonstrated that platinum was an unsuitable electrode material.

As an alternative to Pt, a novel electrode sensor material “3D-carbon” was used as the electrode. This was tested with a solution a containing 8 g/L Fe, 2.5 g/L Al, 1.7 g/L Zn, 660 ppm Mg, 40 ppm Ga, 20 ppm Ge and 150 ppm In (similar to the precipitate solutions provided by VTT) and the results are presented in Table D2.

Table D2: SEM-EDS results from electrochemical recovery experiments with 3D Carbon Electrodes after shorter electrodeposition (50s) and longer electrodeposition (50 000 s).

Test	Total deposition time	Ga [wt-%]	In [wt-%]	Ge [wt-%]
1	50 s	0.5	1.4	0.17
2	50 s	0.48	0.28	0.07
3	50 000 s	0.2	0.28	0.12

As it can be seen in Table D2, the level of recovery of all metals achieved with 3D carbon electrodes was found to be marginal. Overall, these results indicate that the use of electrochemical-based recovery methods is challenging for direct In and Ge recovery from Jarosite process solutions and thus hydrometallurgical flow sheet, such as presented in Figure D2 is required.

References

Alfantazi, A., Moskalyk, R. 2003, "Processing of indium: a review", *Minerals Engineering,* 16, pp. 687-694.

De Souza, A.D. 2008, *Process for producing pure metallic indium from zinc oxide and/or solution containing the metal*, U.S. Patent Application 12/601,398.

Dutrizac, J., Chen, T. 2000, "The behaviour of gallium during jarosite precipitation", *Canadian Metallurgical Quarterly,* 39, pp. 1-14.

Jiang, J., Liang, D., Zhong, Q. 2011, "Precipitation of indium using sodium tripolyphosphate", *Hydrometallurgy,* vol. 106, no. 3, pp. 165-169.

Kangas, P., Koukkari, P., Wilson, B., Lundström, M., Rastas, J.K., Saikkonen, P.J., Leppinen, J. & Hintikka, V. 2016, "Hydrometallurgical Processing of Jarosite to Value-added Products", *Konferens i Mineralteknik 2017, Luleå, Sweden*, 07/02/2017-08/02/2017.

Li, X., Deng, Z., Li, C., Wei, C., Li, M., Fan, G. & Rong, H. 2015, "Direct solvent extraction of indium from a zinc residue reductive leach solution by D2EHPA", *Hydrometallurgy,* vol. 156, pp. 1-5.

Moskalyk, R. 2003, "Gallium: the backbone of the electronics industry", *Minerals Engineering,* vol. 16, pp. 921-929.

Zhang, F., Wei, C., Deng, Z., Li, X., Li, C. & Li, M. 2016, "Reductive leaching of indium-bearing zinc residue in sulfuric acid using sphalerite concentrate as reductant", *Hydrometallurgy,* vol. 161, pp. 102-106.

Series title and number

VTT Technology 317

Title	**The Jarogain Process for Metals Recovery from Jarosite and Electric Arc Furnace Dust** Process Design and Economics
Author(s)	Petteri Kangas, Max Nyström, Inka Orko, Pertti Koukkari, Pekka Saikkonen & Jussi Rastas
Abstract	The Jarogain process provides a unique hydrometallurgical approach for treating zinc-containing side-streams and residues, in particular jarosite, gothite and electric arc furnace dust. The process is based on a sequence of steps, in which the feedstock is first leached in a reducing environment, and its metal contents are subsequently separated as hydroxide and sulfide precipitates. Finally, the remaining iron is crystallised from the solution. Key products of the Jarogain process are: i) lead concentrate, also containing silver and gold, ii) mixed indium, gallium and germanium concentrate, iii) zinc concentrate, iv) iron concentrate, and v) sulfuric acid. Gypsum silicate and a separate arsenic precipitate remain as solid residues. A purified aqueous effluent is purged from the process. A plant processing 400 000 t of jarosite and 50 000 t of EAF-dust annually would require an investment of 390 € million. The battery limit cost of the actual Jarogain process is 200 € million. Almost 50 % of the overall costs are generated by the auxiliary units such as the sulfuric acid plant and power boiler required for the operation. The economic feasibility of the Jarogain process was assessed on the basis of the discounted cash flow analysis. The levelized cost of production for the metal concentrates was estimated to be 80% of the pure metal prices. The greatest uncertainties with regard to the economic feasibility relate to the investment costs and the values of lead and zinc concentrates. According to the laboratory scale proof-of-concept results obtained, the Jarogain process remains an interesting alternative for processing residues and side-streams containing zinc. Further studies should focus on continuous piloting of the proposed concept in order to support a more rigorous feasibility study in terms of process economy.
ISBN, ISSN, URN	ISBN 978-951-38-8597-7 (Soft back ed.) ISBN 978-951-38-8596-0 (URL: http://www.vttresearch.com/impact/publications) ISSN-L 2242-1211 ISSN 2242-1211 (Print) ISSN 2242-122X (Online) http://urn.fi/URN:ISBN:978-951-38-8596-0
Date	December 2017
Language	English
Pages	75 p. + app. 21 p.
Name of the project	Jarogain
Commissioned by	
Keywords	jarosite, EAF-dust, RLE, zinc, lead, silver, gold, indium, gallium, germanium, hydrometallurgy, leaching
Publisher	VTT Technical Research Centre of Finland Ltd P.O. Box 1000, FI-02044 VTT, Finland, Tel. 020 722 111

The Jarogain Process for Metals Recovery from Jarosite and Electric Arc Furnace Dust

Process Design and Economics

Zinc-containing process residues and side-products are attractive options as secondary sources of valuable metals. Jarosite waste produced in the Roast-Leach-Electrowinning (RLE) zinc process as well as Electric Arc Furnace (EAF) dust from steel mills are abundant remainders for which novel metal recovery technologies could be utilised. By processing these materials, it is possible to gain lead and zinc but also silver, gold, indium, gallium and germanium. In addition, the amount of waste fractions could be minimized by iron separation.

The Jarogain process is multi-step hydrometallurgical process, which combines the leaching of raw materials with several precipitation and separation steps. Lead, silver and gold are obtained as enriched leach residue. Indium, gallium and germanium are separated as mixed hydroxide, zinc as sulfide and iron as hematite. In addition, sulphuric acid and magnesium oxide are produced. Waste fraction include mixed gypsum-silicate fraction and arsenic sulfide.

The process design and economic feasibility assessment are presented. Process design is based on the batch scale experiments. Feasibility is evaluated at concept level. The results indicate that the Jarogain process is an interesting alternative for holistic processing of zinc-containing residues.

ISBN 978-951-38-8597-7 (Soft back ed.)
ISBN 978-951-38-8596-0 (URL: http://www.vttresearch.com/impact/publications)
ISSN-L 2242-1211
ISSN 2242-1211 (Print)
ISSN 2242-122X (Online)
http://urn.fi/URN:ISBN:978-951-38-8596-0