

Master Thesis

# Evaluation of Excavation Methods for Jarosite Disposal Areas within Europe

Reworking of Metallurgical Tailings

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# **Declaration of Authorship**

"I declare in lieu of oath that this thesis is entirely my own work except where otherwise indicated. The presence of quoted or paraphrased material has been clearly signaled and all sources have been referred. The thesis has not been submitted for a degree at any other institution and has not yet been published."

# Acknowledgement

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# Abstract

The objective of this study is to provide an overview of possible extraction methods for the excavation of hydrometallurgical zinc production residue (jarosite) out of slurry containment embankments. The ultimate goal is cost estimation for the most suitable excavation approach, which strongly depends on geomechanical properties of the residue. The main challenge to this objective is the strong thixotropic and unstable behavior of the material.

Considering safety, efficiency, costs and viability aspects, various mining methods for material removal are suggested. Benefits and disadvantages of different approaches are assessed with the conclusion that hydraulic mining ranks amongst the best available practices, especially with regards to safety and efficiency. However, due to the fact that jarosite impoundments have not actually been excavated before, the bulk stability behavior of the material inside the impoundments is difficult to predict, therefore the considerations presented are merely theoretical.

This thesis provides the foundation for ongoing research regarding this topic, which is undeniably necessary to produce the more precise statements which a bankable feasibility study would require. Knowledge of the genuine behavior of jarosite within landfills can only be gained through true in-situ trials which are indispensable for developing proven and reliable mining approaches.

As part of a larger interdisciplinary study analyzing the recyclability of jarosite and its profitability, this work also touches on the subject areas of metallurgy and mineral processing.

## Zusammenfassung

Ziel der vorliegenden Arbeit ist es, einen Überblick über Abbaumöglichkeiten von hydrometallurgischen Zinkrückständen (Jarosit) aus Absetzbecken zu geben. Daraus folgend sollen künftig Kostenschätzungen der geeignetsten Abbauverfahren möglich sein, die ihrerseits stark von den geo-mechanischen Eigenschaften des Rückstandes abhängen. Die größte Herausforderung stellt dabei das stark thixotrope und unstabile Verhalten des Materials dar.

Unter Berücksichtigung von Sicherheits-, Effektivitäts-, Finanzierungs-, und Durchführbarkeitsaspekten werden etliche Methoden für den Materialaushub vorgeschlagen. Vor- und Nachteile der verschiedenen Herangehensweisen werden beurteilt, mit dem Ergebnis, dass hydraulischer Abbau als mitunter am vorteilhaftesten, besonders in Hinsicht auf Sicherheit und Effektivität, bewertet werden kann. Der Umstand, dass eine tatsächliche Aushebung von Jarositteichen noch nie stattgefunden hat, erklärt Wissenslücken bei der Stabilitätsbeurteilung des Materials in den Absetzbecken und führt zur Beschränkung auf theoretische Überlegungen.

Die Arbeit dient als Basis für weiterführende Untersuchungen auf diesem Themengebiet, welche zweifelsfrei für präzisere Aussagen notwendig sind, um dem Anspruch einer bankfähigen Machbarkeitsstudie zu genügen. Für die Entwicklung zuverlässiger Abbaumethoden ist Wissen über das tatsächliche Verhalten von Jarositablagerungen durch in-situ Versuche zu gewinnen.

Als Teil einer umfassenderen interdisziplinären Analyse der Recycelbarkeit von Jarosit und deren Rentabilität, befasst sich diese Studie auch mit den entsprechenden Themengebieten der Metallurgie und der mineralischen Aufbereitung.

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# **Objective of the Thesis**

The thesis is conducted in course of cooperation between the Chair of Mining Engineering and the Department of Nonferrous Metallurgy at Montanuniversitaet Leoben. First, the hydrometallurgical process for producing zinc is explained, and with it the formation of the iron precipitation residue called jarosite. Subsequently, a process for recovering valuable metals from this residue is presented thus constituting a complete recycling procedure, and possibly a solution to environmental impacts emanating from jarosite. After describing current disposal practices of this hazardous slurry, the thesis focuses on the mining related aspects of a feasibility assessment, concerning this newly developed recycling process.

Unknown variables remain regarding the retrieval of material from residual storage areas (RSA) in a safe, effective, and economic fashion. Stating the best available excavation approach for a settled body of residue slurry is the main objective of this thesis and requires elaborating on residue disposal practice, country specific legal restrictions, geo-mechanical material properties of jarosite, and its bulk behavior in storage.

To obtain the necessary information and to establish an understanding of the challenging characteristics of jarosite, two zinc smelters and their associated containment sites were visited and literature research conducted. Through interviews with landfill commissioners, analysis of jarosite storage methods and landfill structures, conclusions for the most appropriate residue extraction scheme could be drawn. Built into the considerations for an adequate mining method are also examinations of the downstream recycling process of jarosite - preparing steps for the procedure imply material enrichment through flotation.

With numerous factors influencing the benefits and disadvantages of individual excavation methods, the commitment to one single approach is not practical. Hence, strengths and weaknesses of each method are indicated. Coping well with most challenges however, hydraulic mining was discovered to be a good practice, which is consequentially explained in more detail.

A second objective of this work is the estimation of expenditures associated with the extraction. However, the vast number of cost influencing factors hampers everything but general and quantitative estimations. Difficulties arise, amongst others, from geographical, disposal, and initiation background differences as well as optional downstream mineral processing and the amount of possible mining approaches in general. These extenuating circumstances make it necessary to evaluate each recycling project individually.

# 1 Introduction

This chapter states information about initiation of the thesis, introduces basics of the hydrometallurgical zinc process, and uncovers the challenges deriving from disposal of zinc production residue. The aforementioned is important for understanding the main objective of this work.

## **1.1 Initiation Background of the Thesis**

The unmitigated dependency of Europe on foreign countries resources, especially for high-tech commodities, has driven the European Union (EU) to counteract and initiate a major development program.

Therefore, the European Institute of Innovation & Technology (EIT), an independent body of the European Union, was set up to spur innovation and entrepreneurship across Europe to overcome some of its greatest challenges. It has various flagship endeavors regarding energy, health, climate, etc. Amongst them is an initiative called "EIT Raw Materials". This initiative has the vision of turning the challenge of raw materials dependency into a strategic strength. Its mission is to boost the growth and attractiveness of the European raw materials sector via excessive innovation. (European Institute of Innovation & Technology, 2016)

The "EIT Raw Materials" initiative was created in December 2014 as a Knowledge and Innovation Community (KIC), bringing together higher education institutions, research labs and companies to form dynamic cross-border partnerships. (EIT RawMaterials e.V., 2016) This knowledge community, or consortium of European partners, is called "KIC Raw MatTERS" and is subdivided into co-location centers (CLCs) each focusing on different aspects of the resource strategy such as sustainable exploration, extraction, processing, recycling, and substitution as indicated in Figure 1.

Within the "CLC East", a Regional Innovation Center on Raw Materials in East and South-East Europe (RIC ESEE) was established and coordinated by Austria with headquarters at Montanuniversitaet Leoben. (Moser et al., 2016)



Figure 1: Map of the different CLCs in Europe (Moser et al., 2016)

The ESEE region is highly relevant for the European commodity strategy of more independence due to its unique potential on primary and secondary raw materials. The sustainable development of its raw materials sector is therefore an explicit objective of the Regional Innovation Center. Hence, the staff team consists of various experts covering the fields of mining, mineral processing, metallurgy, renaturation, and recycling. Amongst the first RIC ESEE tasks was the inventory of primary and secondary resource deposits and a collection of promising project opportunities for these materials. (RIC ESEE, 2016)

One project opportunity identified by the CDL<sup>1</sup> for Optimization and Biomass Utilization in Heavy Metal Recycling - a RIC ESEE partner at the Montanuniversitate - was the retrieval of minerals through the reprocessing of side products from industrial metal production.

Manufactures demand high performing materials for their products, which makes it necessary to segregate impurities and certain chemical elements from these materials during fabrication to enhance their physical properties. For this purification various methods can be applied (often precipitation and cementation) resulting in the unfortunate consequence of enormous amounts of residues. Slags,

<sup>&</sup>lt;sup>1</sup> The Christian Doppler Research Association promotes the cooperation between science and business in specially established research units, in which application-orientated basic research is pursued. (Christian-Doppler-Forschungsgesellschaft, 2016)

slurries or dusts have become undesired yet inevitable industrial byproducts while manufacturing many important raw materials. Though recycling of finalized substances in the form of e.g. scrap metal is already well developed all over the world and recycling rates are high, the mechanism that fuels this practice is simple. Remelting old metal is cheaper and easier than production from crude ore, but the reutilization of industrial residues in form of slags or dusts is a far greater technical, and therefore also economical challenge, rendering this praxis barely profitable. Nevertheless, steel fabricating companies like the voestalpine are determined to reuse and repurpose most of the slags and dusts that accrue during production. The feeding back and reprocessing of residues has improved greatly in recent years and now contributes to less carbon dioxide emissions, a cleaner company image, and less use of primary resources. This development again is spurred by economic considerations, however, this time more sophisticated. Decreasing expenses due to fewer costs for European CO<sub>2</sub> licenses, and significant savings on primary ore, only work in the right political framework, during high commodity prices and with advanced technical knowledge.

Although creditable efforts of recycling are made by some companies, residues generated during certain metal production processes remain extremely difficult to treat and reuse, especially when they incur as slurries. A good example is bauxite residue that accumulates during aluminum production through the Bayer process and is commonly called red mud. So far no profitable treatment or further use can be identified to match the vast tonnage arising annually.

Nevertheless, analyzing the development of European society over the last twenty-fife years permits us to see trends towards a circular economy and higher resource efficiency. More and more material is being recycled and reused and this movement is taking place within the heavy industry as well. First successes are encouraging, and an even greater potential still remains when one imagines that all residues created during metal production like aluminum, zinc, copper, steel, etc. can be converted to new resources once an adequate and economic treatment has been discovered. Millions of tons of declared waste could experience a post processing and serve as new deposits thereby lowering supply dependency and nurturing a cleaner industry. This can be achieved through research, which eventually makes a secondary treatment not only technically realizable but also economically viable.

With accordance to this mindset, the CDL detected the opportunity to retrieve minerals from a hazardous and environmentally harmful slurry residue called jarosite, an undesired byproduct of the hydrometallurgical zinc production process, seen in Figure 2. (Pappu, et al. 2006)



Figure 2: Jarosite slurry impoundments in Nordenham, Germany during filling (Galing II) and after renaturation has been completed (Galing I)

The potential of this project regarding quantities available for treatment is considerable within the EU and its southeast, due to heavy zinc production. (Graf, 2003) Taking a look at the worldwide production of zinc expands this potential even further as Figure 3 and Figure 4 illustrate. Notable, is that although Europe only mined roughly 700.000t of zinc ore in 2012 (Reichel, et al. 2014, p. 154), its zinc refineries produce more than three times as much zinc metal. This is explained by advancing globalization which gradually decoupled ore mining and ore refining, and broke the geographical and economic correspondence of these two industries.

Considering that for every ton of zinc produced, in accordance with the jarosite process, 600 to 1000kg of leaching residue is generated alongside. Globally, the amount of slurry released per year lies somewhere between 7 and 10 million tons dispersed as indicated in Figure 4.



Figure 3: Distribution of worldwide zinc production (Zinc Study, 2008)



Figure 4: Primary hydrometallurgical zinc production worldwide (Zinc Study, 2008) multiplied with a factor of 0.7 to approximate jarosite accrual

It was estimated that these residues contain metal values of several hundred million USD. (Pawlek, 1983; Reuter, 2011) Important to note are that these numbers are steadily growing and merely represent the amount of newly created jarosite every year. The jarosite process has been in use since the 1970s (Pawlek, 1983) which makes it hard to determine the true residual remains in slurry dumps or landfills throughout the world; and even harder to estimate its possible value.

Due to technological advancements, residues deposited today contain fewer desirable metals than in the past, which then supports the view that recycling old slurry dumps could prove to be extremely lucrative. This is also the reason why, within Europe, the ESEE region is of major interest. The technological delay of many countries in this area leaves a greater amount of obtainable metals in the slurry than in fully industrialized states. Revenue is mainly generated by recovering commodities like gold (Au), zinc (Zn), lead (Pb), silver (Ag), aluminum (Al), cadmium (Cd), copper (Cu), and minor metals such as Gallium (Ga), Germanium (Ge) and Indium (In). Therefore, the less technological the former production was, the easier it is to make recovery profitable.

The Elixir Group conducted exploration of jarosite residue in Šabac, Serbia in 2013 and calculated the element concentrations shown in Table 1, of which the desired valuable metals are highlighted.

	Au_ppm	Ag_ppm	Al_%	As_ppm	Cd_ppm	Cu_%	Fe_%
Number of samples	524	524	524	524	524	517	524
Min	0,11	30	0,44	439	179,5	0,146	6,63
Max	3,6	347	4,42	7330	1900	0,919	32,6
Mean	0,73	186,09	0,94	2886,04	618,32	0,51	23,16
	Ga_ppm	Ge_ppm	In_ppm	Pb_%	S_%	SiO2_%	Zn_%
Number of samples	524	524	524	524	520	56	524
Min	13,3	3,84	40,1	1,085	1,35	4,18	2,42
Max	187,5	61,5	371	9,56	10	25,2	10,9
Mean	41,94	15,71	200,09	5,38	8,04	10,02	6,17

# Table 1: Extractable high value metals present in jarosite residue at variating concentrations(Elixir Group, 2013)

Realizing this potential around 2008, the CDL in cooperation with Metso Minerals and an investor in Dubai, conducted numerous tests on how to reprocess the slurry and reclaim these valuable metals. They developed a process that is operational on a small scale (50-100kg/batch) and can extract, via a liquid lead bath, over 90% of the desired metals. A detailed description of the process is given in chapter 1.5 Extraction Process of Valuables from Jarosite. To date it has not reached full sized application. Falling commodity prices, mainly of silver, slowed down the drive to recover minerals from the zinc residue and the project was marginalized.

Nevertheless, under the new aspect of a more independent resource supply for Europe and a growing environmental conscience, the CDL revived the idea of reprocessing jarosite. Although the investigations on the treatment were thorough and successful, they predominantly focused on metallurgical aspects of the retrieval technology, neglecting questions concerning necessary preoperational steps prior to the treatment.

However, the goal of the CDL, as a partner of the RIC ESEE, is to acquire the comprehensive insight to decide, in any individual case, whether or not the recycling of a jarosite slurry impoundment can be rendered economically viable. To do so, not only the costs for the metallurgical reclamation process itself, but also all expenses linked to setting up the procedure have to be taken into account. Technical and deriving economic deliberations concerning the excavation of a residual disposal area (RDA) are not within the core expertise of the CDL. Therefore, this thesis, from a non-metallurgical viewpoint, shall address that knowledge gap. Questions of how to remobilize and extract the residue from impoundments, how transport to the treatment facilities can be undertaken, and reflections on what mineral processing possibilities exist to further enhance the recycling method, are some of the questions that will be analyzed in this work. But first, a quick review of zinc production and the origin of jarosite slurry are provided.

## **1.2 Zinc Production Process and Jarosite Formation**

This chapter will give a brief overview of the hydrometallurgical zinc production procedure, and the mechanisms that lead to the formation of jarosite. Today more than 13.5 million tons of zinc is produced annually worldwide and over 85% (Zinc Study, 2008) of this amount is obtained via a hydrometallurgical process.

Although zinc is found in various minerals, the process most commonly applied requires high grade zinc blende (ZnS). These zinc blende (Sphalerite) deposits are

almost always associated with iron and lead minerals e.g. FeS and PbS. Despite the fact that concentrated ZnS is acquired by flotation, it is inevitable to fully impede the presence of iron, lead and other elements in the feed material.

First, ZnS concentrate is roasted in a fluidized bed oven at about 900°C, where zinc sulfide reacts with oxygen to form zinc oxide (ZnO), preparing it for metal extraction. The sulfur in ZnS oxidizes as well and forms sulfur dioxide (SO<sub>2</sub>). The same oxidation occurs for iron impurities in the concentrate.

#### $2 \operatorname{ZnS} + 3 \operatorname{O}_2 \rightarrow 2 \operatorname{ZnO} + 2 \operatorname{SO}_2$ (1)

To prevent the discharge of  $SO_2$  in the exhaust emissions, a sulfuric acid plant is operated downstream using the double contact process, converting  $SO_2$  into sulfuric acid, which is used partially within the plant during the leaching processes, but is mainly sold to chemical industries.

$2 \operatorname{SO}_2 + \operatorname{O}_2 \xrightarrow{} 2 \operatorname{SO}_3$	(2)
$SO_3 + H_2O \rightarrow H_2SO_4$	(3)

Unfortunately, during the roasting of zinc blende, it also reacts with iron dioxide forming zinc ferrite ( $ZnFe_2O_4$ ), which becomes a problem later in the process.

(4)

#### $ZnS + FeO_2 + O_2 \rightarrow ZnFe_2O_4 + SO_2$

After roasting, the hydrometallurgical process can start. In the initial step (neutral leaching), calcine (ZnO) is dissolved in diluted sulfuric acid (15g  $H_2SO_4/L$ ) to liberate zinc ions.

## $ZnO + H_2SO_4 \leftrightarrow Zn^{2+} + SO_4^{2-} + H_2O$ (5)

The leaching process results in an impure liquor containing, amongst other elements, about 65g  $Zn^{2+}/L$ . This zinc enriched solution has to be separated from solid residues that did not dissolve in the weak sulfuric acid. The difficulty is determining the correct leaching conditions. If the acid is too weak, a great portion of zinc remains unsolved in the residue, if it is too strong, iron particles from the earlier mentioned zinc ferrite end up in the leachate, impeding electrolysis. After filtering out all solids, the solution is purified through cementation (adding of Zinc dust), during which copper, cadmium and cobalt, all elements nobler than zinc, successively precipitate. The purified liquor now contains only  $Zn^{2+}$  ions and metallic zinc can be won through electrolysis. (Graf, 2003; Pawlek, 1983)

To increase Zn recovery, solid residues from the neutral leaching are treated in a second step. They still contain considerable amounts of Zn (~20%) ligated in zinc ferrite, which formed during the roasting process as mentioned earlier. Zinc ferrite contains zinc as well as iron and is purposely not dissolved during neutral leaching. This is done to keep the leachate free from interfering iron ions and therefore reduce the material stream having to undergo hot acid leaching. At a temperature of 95°C and using a mixture of cell acid and sulfuric acid at a concentration of 50–150g H<sub>2</sub>SO<sub>4</sub>/L, zinc ferrite is now dispersed, bringing it and remaining elements like iron, copper, arsenic, germanium, nickel etc. into solution. Lead, and possibly present precious metals, remain solid. Afterwards, a separation of liquid solution and non-dissolving solid phases produces two fractions. The solid residue fraction contains lead and silver in guantities that depend on the feed material as well as the efficiency of the process. If feasible, this product could receive additional processing in smelters where lead and silver can be won. Although mentioned and acknowledged as best working practice in all literature, often, no further treatment of the valuable "Pb-Ag-residue" is undertaken. Low technological standards, or non-remunerative investment, are possible reasons for why it is disposed along with the jarosite. This fact is of crucial importance when it comes to feasibility estimations of recycling residue dumps. (Graf, 2003; Pawlek, 1983)

The second fraction of the solid/liquid separation is another zinc solution with concentrations of around 80g Zn<sup>2+</sup>/L, which also contain the aforementioned impurities - especially iron. "*As the iron interferes with the electrolytic process even at low concentrations, it must be precipitated from the zinc sulfate solution.*" (Graf, 2003, p. 672)

Removing iron from the solution was previously a great technical challenge. Precipitation of iron as iron hydroxide ( $Fe_2O_3*3 H_2O$ ) lead to the formation of voluminous deposits that could not be filtered properly. Only with the introduction of selective iron precipitation as jarosite mineral was the problem solved and a significant increase of zinc recovery rates achieved. With the formation of this mineral it is possible to tie iron and other impurities in jarosite slurry and easily filter it from the zinc solution. The cleaned zinc containing liquor is then returned to

the processing step of neutral leaching to close the liquor circuit. Here metallic zinc is won again through electrolysis. (Graf, 2003; Pawlek, 1983)

The simplified schematic process flowchart of a hydrometallurgical zinc winning process can be seen in Figure 5 and gives an overview of input and output streams. The precipitation process itself will be explained in more detail in the following chapter.



Figure 5: Schematic structure of hydrometallurgical zinc winning process with jarosite precipitation (Unger, 2011)

## **1.3 Iron Precipitation through Jarosite Process**

In order to achieve a higher recovery of zinc in the hydrometallurgical process, separating iron, and other elements in the liquor, is required. An easy separation method through filtration is possible once alkali metals or ammonium ions are added to the solution. The zinc sulfate solution reacts with these additives to form iron complexes (jarosite). This precipitation slurry has the additional advantage of being insoluble in sulfuric acid, being a mineral with good filtering properties, and having high iron content, limiting the amount of precipitant formed. The complex has the same composition as the naturally occurring mineral jarosite and the chemical structure is as follows:

XB3 (SO4)2(OH)6X: mostly  $NH_4^+$  &  $Na^+$  but also  $H_3O^+$ ,  $K^+$ ,  $Ag^+$ ,  $Li^+$  etc.B:  $Fe^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$  or  $Al^{3+}$  (Weiß, 2002)

The widespread use of jarosite-type compounds to eliminate impurities in the hydrometallurgical industry is due to the ability to incorporate several elements into their structures. (Patiño et al., 2013) In doing so, iron and other impurities are captured inside the jarosite slurry, which is then extracted by filter screens and ultimately deposited in slurry pits. Zinc ions remain in solution and are won by electrolysis previously explained.

The chemical reaction for removing iron through ammonium jarosite is:

#### $3 \operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3} + 2 \operatorname{NH}_{4}^{+} + 12 \operatorname{H}_{2}O \leftrightarrow 2 \operatorname{NH}_{4} [\operatorname{Fe}_{3}(\operatorname{SO}_{4})_{2}(\operatorname{OH})_{6}] + 5 \operatorname{H}_{2}\operatorname{SO}_{4} + 2\operatorname{H}^{+} (6)$

The precipitation reaction takes place at a low pH-value of 1.5. The hydrolysis liberates sulfuric acid that has to be neutralized with calcine in order to maintain the pH-level. The neutralization reaction uses sulfuric acid to dissolve zinc oxide, and with the reduction of available acid, the pH-value rises.

$$ZnO + H_2SO_4 \leftrightarrow Zn^{2+} + SO_4^{2-} + H_2O$$
(7)

Further requirements prior to the precipitation are a temperature of  $95^{\circ}$ C, and an oxidation of Fe(II) ions in the solution to Fe(III) ions, achieved through adding MnO<sub>2</sub>.

$$MnO_2(s) + 2 Fe^{2+} + 2 H^+ \leftrightarrow 2 Fe^{3+} + MnO(s) + H_2O$$
 (8)

The forming MnO can be percolated together with jarosite slurry in the liquid/solid separation. In most cases, it is sufficient to guide air as a deliverer of oxygen through the liquor to oxidize iron ions, thereby reducing costs.

Depending on the alkali metal or other substance added to the zinc sulfate solution, different types of jarosite can form. However, praxis indicates that ammonium and sodium jarosite are most commonly used for zinc production. Low costs of the chemicals  $(NH_4)_2SO_4$  and  $Na_2[CO_3]^*$  10H<sub>2</sub>O, and especially a simple control of mineral formation, are decisive factors. (Patino et al., 1998)

Although higher zinc yields are possible with the jarosite process, new challenges arise and remedies are required, which is the subject of the next chapter. (Graf, 2003; Pawlek, 1983)

### 1.4 Challenges concerning Jarosite Slurry

Considering the purpose of jarosite to tie iron in slurry and to make it filterable from zinc leachate, the mineral is suitable, but not the best available option. Theoretically it contains, amongst other elements, only 37% iron and 13% sulfur as sulfate. In reality, the iron content is even lower and ranges from 25 to 30%, which prevents its use as a secondary resource for the steel industry. The low iron content leads to massive amounts of residue to be discharged. As mentioned earlier, every ton of zinc produced by this process generates 600-1000kg of jarosite, and these residues must be transported to slurry ponds where they settle and dewater. However, due to the fact that jarosite still contains soluble zinc and other harmful heavy metals, it must be stored completely sealed off from the environment and phreatic water. As the precipitation occurs in an acidic environment, the slurry possesses a low pH-value of down to 2.7 (Pappu et al., 2006), further complicating the disposal.

Alternative processes for the removal of iron from zinc liquor exist. Iron precipitation as Goethite grants similar zinc recovery rates, but leaves far less residue since the iron content of this mineral lies at around 43%. Nevertheless, it does not find much application. The same applies to the Hematite Process - a method where the precipitated mineral contains even up to 60% iron. (Von Röpenack et al., 1994) This byproduct can be reused in the cement or steel industry, and no landfill use is required. Despite obvious benefits for the

environment, the amount of zinc produced by these two methods is negligible. The main reasons for the avoidance of these practices are the complex processes, and the costly technology necessary for operation. Another approach involves direct leaching of zinc concentrate, which is especially useful in the processing of low-grade material. Ultimately, this method fails because of the massive expenditure of time. (Haakana et al., 2007)

As indicated above, various methods for the reduction, reutilization, treatment, or prevention of jarosite slurry have been investigated - always with the goal of creating products fit for reuse in other industries. In most cases, technical implementation is possible, but more detailed analysis reveals economic obstacles. Thermal treatment to provoke a transformation of jarosite to hematite, and with it a reuse in the cement or steel industries, demands excessive energy use. The approach of adding NH<sub>3</sub> to ammonia jarosite, creating crystalline hematite, is too expensive because of the high use of chemicals, and is also limited to pure ammonia jarosite, which is rarely encountered in praxis. (Von Röpenack et al., 1991)

All efforts and realized experiments indicate that jarosite slurry, and its effects on the environment, are a well documented and recognized problem. If not handled and sealed off properly from water and atmospheric  $O_2$ , jarosite impoundments can contaminate the adjacent soil or groundwater - a phenomenon commonly described as acid mine drainage (AMD) (Akcil & Koldas, 2006) - typically emitting high concentrations of heavy metals and SO<sub>4</sub> at low pH-values into the ground. (Moncur et al., 2004)

This is a major concern not only for environmentalists and scientists, but also the zinc industry itself. Currently, the production of zinc relies heavily on the practice of depositing enormous quantities of slurry, but stricter waste dump regulations, especially in countries with high environmental awareness, pose a serious threat to the smelting industry.

Even though the degree of environmental threat posed by jarosite slurry ponds is comparable to waste-products of different industries e.g. chemical waste or certain slags, the settling pits remain a delicate topic in environmental discussions. The general public is especially sensitive towards slurry impoundments mostly because of various negative incidents which made the headlines in recent years (Aznalcollár, Spain 1998; Baia Mare, Hungary 2010; Mariana, Brazil 2015). Leaking or breaking slurry pits were covered broadly by the media and paint a devastating picture – static tailing dumps are perceived as far less dangerous then a breaking dam flooding villages and contaminating entire swaths of land is perceived more dangerous than static tailing dumps.

A growing environmental awareness by the population in general is an important driving force in this development as well. Taking the unnatural color, smell and the acidity of these slurries into consideration, one easily understands the mounting public rejection of these practices.

The main challenges facing the zinc producing industry, especially in central Europe, are:

- The great amount of residue that is generated year after year
- The growing costs and difficulty of an approval procedure for slurry pits
- Expensive maintenance, renaturation and post controlling of pits
- Low acceptance of residue impoundments in the general public
- Increasing restrictions and complex safety terms from the government
- Great dependency on the jarosite process and on depositing its residue
- Lack of economically feasible alternatives to the current process

However, despite being confronted with challenges and a poor prospective, jarosite also holds potential as a secondary resource, as mentioned earlier. Currently, it is still difficult to prevent losses of zinc, copper, lead and even silver during the iron precipitation, and these elements remain present in the disposed slurry. (Patino et al., 1998) Diminishing high grade ore deposits and long-term increasing demand for resources worldwide lead to reevaluating the potential of old residue sites. Today, secondary mining and recycling, hold important roles in the European sector of raw materials production. The post treating of jarosite slurry, and the recovery of valuable metals from it, builds the backbone of the project and this process is elaborated upon in the next chapter.

## **1.5 Extraction Process of Valuables from Jarosite**

As mentioned prior, the jarosite residue still contains metals which are present in various chemical compounds. The distribution of these compounds fluctuates from plant to plant due to different process specifications. Contrary to Table 1, where single elements were focused on, the following Table 2 states the concentrations of the desired metals in a sodium jarosite according to their actual appearance in mineral compounds.

Parameter	Value	Parameter	Value	Parameter	Value [%]
	[%]		[%]		
$2K[Fe_3(SO_4)_2(OH)_6]$	3.05	MnO	0.05	CuSO <sub>4</sub>	0.34
$2Na[Fe_3(SO_4)_2(OH)_6]$	27.94	CaSO <sub>4</sub>	17.47	$H_2SO_4$	10.79
$2H_3O[Fe_3(SO_4)_2(OH)_6]$	10.61	MgO	0.05	ZnSO4	4.24
Ag (various compounds)	0.018	Al <sub>2</sub> O <sub>3</sub>	1.20	FeS <sub>2</sub>	3.01
PbSO <sub>4</sub>	8.79	SiO <sub>2</sub>	1.80	Rest	~10.00

Table 2: Distribution of mineral compounds in sodium jarosite (Antrekowitsch, 2015)

Since jarosite is an iron precipitation residue, naturally its iron content is high and ranges around 30% Fe (Graf, 2003). Additionally, considerable amounts of lead, zinc, copper and silver can still be detected. As mentioned in chapter 1.2 Zinc Production Process and Jarosite Formation, in many processing plants, lead and silver is not extracted and not won in a parallel production line, but disposed alongside jarosite. This leads to high Ag and Pb contents in the slurry, but even if the Pb-Ag-residue was to be separated and recovered, some lead and silver together with minor metals would inevitably end up in jarosite. This is caused by accomplishing the necessary adjustment of the pH-value for the iron precipitation. Roasted material (ZnO) is added to the leachate, containing zinc, lead, silver and other metals in small quantities (Pawlek, 1983). Liberating all valuable metals in jarosite and making them recoverable is the main objective of the following process. Three major steps are necessary, which are indicated in Figure 6, and followed with a thorough description.



Figure 6: Overview of metal extraction process (Unger, 2011)

The first step in the process is optional and conduces the "cleaning" of the residue. Jarosite contains varying amounts of crystalline sulfuric acid which can be separated from the remaining residue through rinsing. Although chemical bonds of accompanying elements are being broken up as well, the main reason for this practice remains the separation of crystalline excess of  $H_2SO_4$ .

Through washing, an average of 15.7% of the original solid residue is going into solution - a significant accumulation of silver, lead and minor metals occurs. The goal is a load reduction for the second step which is the roasting plant. (Unger, 2011)

Advantages of load reduction are obvious for residues with high sulfur concentrations due to a large mass reduction (also reduction of  $Na_2SO_4$  and  $K_2SO_4$ ), and for roasting plants that operate at their maximum capacity.

A major disadvantage is that a washing process requires complex and expensive waste water treatment facilities. Also, the load reduction is not necessarily an advantage since sulfuric acid can be produced from the SO<sub>2</sub> emission during roasting and sold afterwards. Drying the washed slurry previous to roasting, also consumes high amounts of energy.

The next step is roasting/calcining the residue at 900°C. The goal is the separation of sulfur from the residue present in form of sulfates, sulfides, and also  $H_2SO_4$  if not washed previously. In doing so, the total mass of jarosite decreases by 24.37% due to evaporation of sulfur and all crystalline water. The loss of jarosite mass leads to a further enrichment of the remaining valuable metals. Further, jarosite connections are disintegrated and a change of color from yellow-brown to red can be observed. The disintegration of the jarosite forms up to 30% hematite (Fe<sub>2</sub>O<sub>3</sub>), which is responsible for the red color.

Figure 7 shows various stable compounds found in jarosite and their decreasing or increasing concentration depending on process temperature during roasting. The sulfur dioxide concentration rises, indicating  $SO_2$  formation through the dissociation of other compounds like  $ZnSO_4$  and  $PbSO_4$  at different temperatures.



Figure 7: Thermodynamic equilibrium calculation of roasting process (Unger, 2011) SO<sub>2</sub> can once again be used for the production of sulfuric acid as described earlier. The roasting has to be restrained to a temperature of 900°C or otherwise

PbO starts to evaporate, which shall remain in the roasted material for later lead extraction.

The final, and most important step of the recovery process, is the reduction of all metal oxides present in the remaining residue. This is accomplished via a molten lead bath. The roasted feeding material is introduced into a furnace with liquid lead at a temperature of 1200°C. Foundry pig iron is added to the bath and serves as reduction agent. Alternatively, carbon in form of petroleum coke could be used. Through the high density of lead, all adjoined material sits on top of the bath and a gradual reduction of ZnO, CuO, PbO, Ag<sub>2</sub>O and oxides of minor metals takes place. This only works if the oxygen affinity of these compounds is lower than the one of the reducing agent (foundry pig iron), and if the added materials establish a liquid slag on top of the bath. Maintaining a constantly liquid slag is difficult and demands the right mixture of additives.

As the valuable elements are reduced, they begin sinking through the slag layer into the lead bath where they dissolve as pure metals (Cu<sup>2+</sup>, Ag<sup>+</sup>, Pb<sup>2+</sup> etc.). Some of the occurring chemical reactions are stated below and could be expanded by various other metals present in the residue.

$ZnO + C \rightarrow CO_g + Zn_g$	(9)
PbO + C $\rightarrow$ CO <sub>g</sub> + Pb <sub>liqu</sub>	(10)
$Ag_2O + C \rightarrow CO_a + 2Ag_{liau}$	(11)

These metals dissolve in lead because it acts as a collector with high solving power for other metals. This is confirmed when investigating the binary systems of those elements that are to be extracted. The according diagrams are attached in ANNEX A.

(11)

Most show a good solubility at process temperatures (1200°C), except for pig iron which indicates the contrary. It maintains a solid state at process conditions and does not dissolve or sink into the metal bath. This fact supports the process of separating iron from the lead bath and keeping it in the slag where it remains available as reduction agent.

Besides iron, all other chemical composites that cannot be reduced through foundry pig iron remain in the process slag as well. The slag, therefore, mainly consists of various compounds of the former jarosite, the now oxidized pig iron, but also small amounts of zinc oxide. Based on a thermodynamic analysis of the feeding material at 1200°C, all metals oxides are less stable than iron oxide, which means that reduction of these metals through foundry pig iron is successful. Only zinc oxide has the same stability and remains partially in the slag.

Through this process, a slag with little to no remaining valuable metals is generated, and consequently, the lead bath is rich in the desired elements (95% recovery rate (Unger, 2011)). The volume of the lead bath and also the amount of slag on top of the lead grow steadily, hence, the slag has to be skimmed away to keep the reaction going and the bath itself has to be partially drained to prevent overflow. The binary diagrams also indicate decreasing solubility of metals dissolved in lead with sinking temperatures, which means that all present metals will liquate out of the lead bath by simply lowering its temperature.

As noted in the equations before, not all metals accrue in liquid state. Zinc, and also the minor metal Indium, evaporate during the reduction and are discharged together with the process steam. These exhaust fumes are cooled, and through precipitation, the metals, again as oxides, are collected. Reprocessing of the accruing dust in a zinc smelter can finally win pure metals.

The produced slag, with minimal remains of zinc, can find application in the cement industry, for sandblasting or as base material in road construction. Consideration also goes towards using it for steel production. With high iron content of up to 50%, it is richer than ore mined at the Styrian Erzberg and could be introduced to the sinter plant. A challenge is sodium, present in the slag, complicating the smelting process since it circulates in the process and cannot be combed out. Unfortunately, the majority of arising residue is sodium jarosite, limiting this application to few occasions.

Another limitation is found in the conditioning to jarofix. Once conditioned, the residue cannot be supplied to and benefit from the described process. The problem is, amongst other complications, the high content of alkanes (the added calcium carbonate) requiring too excessive roasting temperatures.

It can be stated, however, that considerable efforts are put into finding more and more opportunities for utilizing the accruing process slag. Even if not all slag can be conveyed to consuming industries for now, recycling leaves behind significantly less waste material, which additionally can be disposed without reservations due to its inert and environmentally neutral character.

The method was trialed at batch sizes of 50-100kg and provided good test results. Information about the process was mainly derived from the master thesis of Alois Unger, who conducted research on this matter for the Department of Non-Ferrous Metallurgy at Montanuniversitaet Leoben. (Unger, 2011)

### **1.6 Current Disposal Procedures for Jarosite**

Zinc is produced in many countries of the European Union, and although there are EU laws that dictate how to handle processing residues (EU Publications Office, 2015), the execution of these laws vary tremendously in the individual countries. While in north and central Europe high standards of environmental protection are practiced, other countries, especially of the ESEE region, concern themselves little with this issue. (Kisliakova et al. 2005, p. 51) In these countries, enormous amounts of jarosite and other industrial residues are often released into depressions or insufficiently sealed impoundments with poor environmental protection standards and little effort for improving disposal practices is found there.

Companies in different regions, however, go to great lengths and considerable expenses to minimize effects of the disposal on the surroundings. Many patents for a further use of jarosite have been issued, but possible commercial applications are, and continue to be, a major challenge.

As mentioned before, the main problem with the disposal of jarosite residue originates in the solubility of heavy metals and sulfate ions from the slurry possibly leading to AMD. According to this solubility of contaminant particles, it is rated in the graded waste class system of the EU (European Council, 1991). This system categorizes waste related to the amount of pollutants released during standardized elution experiments. The harmfulness of discharged particles is also taken into consideration. A higher waste class requires more elaborate safety standards for deposition, causing excessive and expensive containment measures.

To avoid these constraints, a method to immobilize harmful substances inside of jarosite has been sought out. The residue is converted into a stable substance,

tying ions so no elution can take place. This is achieved by means of adding cement and lime stone to jarosite in varying weight percentages, turning the slurry into a sand-like coarse grained material. Each plant has an individual recipe to accomplish this task and additives range from 10-14% cement and 2-12% calcium carbonate per ton of jarosite. (Lehtinen et al., 2015; Halle, 2016) Aggregates are mixed into the residue and released into an open bunker, where small dozers distribute the material. It remains for three days until the cement has set and jarosite has gained enough stability to be transported for disposal via trucks. (Halle, 2016)

The method creates a material uniformly referred to as jarofix and is at the moment considered best available practice in some countries. It prevents most elution of contaminating particles and makes the residue hazard-free for the environment. Therefore, the waste class drops to a level where it equals the one for construction residue. (Halle, 2016) This practice can result in more public acceptance, less requirements for the disposal and ultimately reduced costs. However, fact is also that despite the benefits of jarofix, conditioning also creates a much larger quantity (up to 20%) of material that has to be discharged. Another major disadvantage is the fact that jarofix cannot be recycled through the earlier described process. The controversy in disposal practices is reflected in the opposing philosophies of individual smelting companies. While some believe in the solution through jarofix, others doubt its inert character and rather continue deposition as jarosite slurry, counting on complete recycling in the future (Salmie<sup>2</sup>, 2016).

A growing number of plants adapting to the jarofix conditioning practice indicates that immediate advantages of disposing material under reduced environmental requirements are often considered more beneficial than increasing expenditures through additives and material transport (Halle, 2016). In the same way, it is accepted that the possibility of complete jarosite recycling is spoiled.

The following paragraphs describe some commonly practiced disposal methods for both jarosite slurry and jarofix, and describe related environmental protection measures carried out in the impoundments. The manner in which jarosite residue

Evaluation of Excavation Methods for Jarosite Disposal Areas within Europe

<sup>&</sup>lt;sup>2</sup> The name was altered to protect the identity of zinc smelting facility B

is handled and stored is not only determined by company choices, but also by governmental legislation, technical standard regulations and factors such as age of the embankment, land availability or climate. Therefore, various modifications of deposition methods are applied throughout the world.

#### 1.6.1 Disposal of Jarosite Slurry in Mono-landfill

As jarosite is a result of a precipitation process in leachate, it accrues with high water content. Being pumpable, the most common approach is to pass slurry through pipes and distribute it equally inside the residual disposal area with help of a ring line. The deposition occurs layer by layer, which accounts for an inhomogeneous composition of the residue body. When a process changes at the zinc plant, it equally affects the residue. Consequently, a RDA filled in the described fashion consists of layers with altering chemical and even physical properties. One of the physical properties of jarosite is to strongly tie water (40%) upon deposition (Halle, 2016)) in both the crystalline structure and between molecules. This characteristic has the negative effect that great portions of the settling pit's volume are taken up by water rather than jarosite, making dewatering essential. Being considered dangerous waste however, jarosite impoundments require, amongst other provisions, a combined lining. A mineralogical layer of material with extremely low permeability like clay (K =  $1 \times 10^{-9}$  m/s), and another layer with impermeable synthetics to prevent seepage (Bundesgerichtshof, 2009), are stipulated. Hence, the runoff of excess water into the ground is prevented by this bottom sealing. To still grant dewatering, and with it a maximization of the holding capacity, excess water can escape through built in drainage channels in a controlled way. This process is constantly monitored by sampling. Liquid from desorption of the dumped jarosite and from rain, collect on the top of the embankment, where they are pumped off and returned to the smelter. (Nürdeklasch, 1995)

Solid content of the jetted suspension settles in the pond and gradually consolidates under its own weight. Through this compaction, surplus water from deeper layers (where the pressure is higher) is pressed out, reducing the volume of stored slurry. Due to extremely small grain sizes and high humidity ratio, jarosite remains with a considerable water content and low stability. The lack of stability

impedes a stacking of the slurry into an inclination above 0.5% (Nürdeklasch, 1995) and disposal capacity of an impoundment is therefore confined by its dam height or by the depth of a depression.

During dry periods it is possible for the top layer of an impoundment to dehydrate completely, leading to wind erosion and deflation, carrying contaminating dust onto surrounding fields. If not caused voluntarily for construction works, dehydration has to be prevented and a certain level of humidity permanently maintained. In some cases appliance of dust agents is necessary. (Halle, 2016) This is by far the most frequent way of storing jarosite residue.

#### 1.6.2 Disposal of Jarofix in Mono-landfill

As some plants are adapting their disposal strategy, switching to the use of jarofix new disposal methods will arise. In contrast to jarosite that behaves like a suspension or slurry, jarofix is comparable to sand, and can be handled according to standard earth work aspects. Its material's properties allow that no distinction has to be made regarding machinery for transportation and mounting. Its waste class is ranked the same as construction residue, requiring equally low safety standards for the disposal. A homogenous jarofix RDA is considered nondangerous waste, and has to feature only standard mineralogical sealing and monitoring system for drainage water.

So far, no disposal site exclusively for jarofix is operated, however, to our knowledge one is in planning (Nordenham, Germany). The common method for storing jarofix at the moment is on top of the depositories previously filled with jarosite slurry. Characteristic features of these disposal sites are explained in the following chapter.

#### 1.6.3 Storing Jarofix in combined Depository

Conditioning to jarofix is accompanied by significant alterations of the waste product. In regards to chemistry, interaction with the surrounding environment has been drastically reduced, and regarding geo-mechanical aspects, jarofix possesses higher shearing strength, cohesion and loading capacity than jarosite, at lower water content. These new properties allow a profiling of the material inside the impoundments. Profiling permits mounting jarofix to heap depositories with sloped surface incline, winning considerable storage volume compared to the flat storage of jarosite. This newly usable volume is indicated dark red in the graphic "Galing II" (Annex B) and can be translated to a prolongation of the impoundment's operability. (Zöller, 2012) Profiling jarofix allows considerable amounts of additional material to be deposited, postponing the necessity of a new impoundment by several years. Stacking also meets modern environmental protection requirements that ask for a surface sealing at an incline of 5% to guarantee sufficient drainage of rain water.

Therefore, combined storage of both materials is applied by zinc producing companies instead of continuing to replenish an impoundment with jarosite and afterwards building a separate area for jarofix. The reason for applying this method lies founded in lengthy and difficult planning procedures for new RDAs. Another benefit of stacking jarofix on top of jarosite is the creation of a thick cover layer using material with immobilized pollutants. This layer serves as part of the surface sealing, which consequently can be kept comparatively simple. Despite some minor advantages, this practice is counterproductive for a future recycling process.

The main challenge of combined storage is applying high loads of sand-like solid material (jarofix) on top of soft and unstable slurry (jarosite). This practice is explained in chapter 2.2.2 Transition from Jarosite to Jarofix Deposition. Jarofix covering the slurry also strongly affects residue extraction methods. The same applies to all impoundment renaturation measures. Understanding the storage facility structure, as well as sealing concepts, is therefore important and will be mentioned in the same referenced chapter.

## **1.7 Evaluation of Jarofix Process compared to Recycling**

Recalling the main challenges of modern zinc plants provides a basis to evaluate the current trend towards conditioning the residue to jarofix. Advantages and disadvantages of the process are summarized on the next page.

#### Advantages of Jarofix:

- More material can be stored in impoundments, maximizing dumping capacity per surface
- Storage of jarofix is cheaper due to lower waste class and less stipulations

- The technique is safer for environment, resulting in lower hurdles for approving further impoundments
- The technology holds more acceptance in general public
- Changes for the adaption of the process are affordable

#### Disadvantages of Jarofix:

- Additives for the conditioning create additional costs
- The lumpy structure impedes pumping of jarofix. Transport has to be executed discontinuously by trucks in batches, increasing costs and traffic
- Additives to form jarofix increase the amount of residue to be deposited
- Dependency on disposal sites remains. No sustainable long term solution
- Once conditioned to jarofix, material cannot be applied to recycling process

The last two arguments, especially, illustrate how the overall drawbacks for this new practice weigh heavy. The general problem of disposing harmful residues is merely reduced and the solution temporary. The future approval of dump sites, even with a low waste class, will be difficult to achieve judging from the overall development in this field. Nevertheless, some countries and companies, for now, believe that jarofix represents the best opportunity to continue with zinc production by jarosite precipitation. Therefore, the method finds application accepting higher costs and additional material transport. This stems from public and resulting demanding less waste governmental pressure, dangerous and more environmentally friendly production. Desiring long-term solutions, jarofix can only be an intermediate step towards a circular production economy, where all byproducts can be reused.

A great deal further down this development line lays the previously described new recycling method researched by the CDL. Comparing its pros and cons to that of the jarofix technology, leaves little doubt about the supremacy of recycling. It recovers close to all present metals from the residue, which stands in accordance with a sustainable use of our limited resources and deposits. The process also leaves minimal residue amounts with no toxicity and even holds the option of a zero waste process. Remaining challenges posed are the economic feasibility of the method and the high investment necessary to adapt to the new technology.

Although application of recycling and recovery processes in the industry may derive from political agendas, or the necessity to protect the environment, they can only be implemented considering economical aspects as well.

Can it be profitable to expand the zinc processing line with its inevitable byproduct of jarosite slurry to a production cycle with possibly zero waste? And similarly, is it economically feasible to rework slurry ponds in order to extract the remaining commodities they still contain? In attempting an actual recycling process, the first targets need to be old retaining areas. Due to lower recovery rates in former times, their content of valuable metals is much higher than those of today. Of all existing RSAs, they are also often the facilities with lowest environmental protection measures. Consequently, they pose the most beneficial opportunity for recycling combining maximum profit, and maximum environmental threat reduction, at the same time. Jarosite in old embankments is also less likely to be blocked by overlaying jarofix, simplifying the extraction process. Gaining experience and assuring viability, the recycling process has to be applied to these impoundments first, which is why all following considerations are directed towards jarosite mining, mainly neglecting jarofix.

If recycling was to be realized, it would drastically alter cost distribution at the end of the production process. Expenses for impoundments and their maintenance would cease, whereas a necessary treatment of the slurry would generate additional costs. A calculation of financing has been conducted by the CDL which considers all aspects from investment over operational costs to profit generated through the recovered metals - with one exception. Until now, there has been no research on how to extract already deposited material from the impoundments, and what share of the overall expenses this would generate. Providing a suitable method (from now on also referred to as "mining, extraction or excavation method") and assessing its financial impact, is one objective of this work. The utmost focus is thereby turned on challenges generated by, or linked to, the structure of the impoundments and the soil mechanical properties of the residue.

## 2 Excavation Operation

In order to find an adequate, safe, and effective extraction method, it is crucial to know as much as possible about the material. General soil mechanical characteristics are equally important as disposal methods, or the initiation background, for a recycling endeavor. Possibly including an additional step of enrichment, located between the extraction procedure and the recycling process, makes investigation on mineral processing important as well. Hence, subsequent chapters will inform about the mentioned aspects including characteristics of the residue, experiences with the handling of jarosite or similar material, distinct considerations for recycling approaches and mineral processing opportunities.

## 2.1 Investigation and Characterization of Jarosite

Most important characteristic of jarosite is its extremely small grain size. The iron precipitation process leaves mainly particles ranging around 1–10 microns ( $\mu$ m) as seen in Figure 8 and can be categorized in soil mechanical terms as clayey silt.



Figure 8 : Example for grain size distribution of East Indian jarosite [1mm = 1000 μm] (Senapatia & Mishra, 2014)

The grain size significantly influences the rheological behavior of the material. Fines help to float coarser grains in slurry, generating a non-settling state and therefore granting excellent conditions for pumping. This effect is observed for sizes smaller than 20µm. Containing particles of this size however, another effect
starts occurring as well. As particles become smaller, the surface drag forces in slurries begin to dominate, in turn increasing their viscosity. (Potvin et al., 2005)

To estimate the true flow characteristics of jarosite suspensions is challenging. These suspensions may exhibit shear thinning or shear thickening, yield stress or shear banding as well as, wall slip, particle migration, or sedimentation, depending upon their particle interactions and concentration. (Hanks & Hanks, 1982; Turian et al., 1997) Conducted research indicates "pseudo-plastic" behavior and a non-newtonian flow pattern at solid concentrations of 40-60%. Increasing solid concentrations lead to higher shear stresses and a rise of the suspension viscosity. (Senapatia & Mishra, 2014)

Despite the opposing effects of rheology, it can be stated that jarosite slurry is well pumpable at solid concentrations below 50-55% and it has been transported via this practice for decades. Particle size as well as the particle shape, illustrated in Figure 9, not only impact flow characteristics, but also the sedimentation behavior and drainage process of a material. (Helms, 1988) Jarosite possesses a high specific surface area of approximately 160m<sup>2</sup>/g and shows moisture contents between 44–47%. (Romero & Rincon, 1997) Its high water holding capacity is caused by the fine texture, creating many gussets, which consequently tie water. (Patchet, 1983) Analyzing the microstructure of jarosite by a Scanning Electron Microscope (SEM) confirms this statement, showing small and irregularly sized particles. Mean density of jarosite was found to be 2.55g/cm<sup>3</sup> (Elixir Group, 2013) but literature reveals values of up to 3.7g/cm<sup>3</sup>. (Romero & Rincon, 1997)



Figure 9: Irregular and small particle sizes of jarosite residue; Scale for left picture is 5µm and for right picture 1µm (Senapatia & Mishra, 2014)

Dewatering enormously influences the soil mechanical properties of the residue. When no water is present, the material can be described as solid. With the addition of water, it starts to behave like a semi-solid and further increase of water content, changes the material to the liquid phase.

Although many substances experience these state boundaries in a similar fashion, jarosite possesses characteristics that divert greatly from those of natural soils. The greatest concerns are in regards to its strong thixotropic behavior. Thixotropy means that with the input of mechanical energy and dynamic strain, like pressure or vibrations, molecules rearrange themselves, altering the flow characteristic of a substance. Normally pointing in all different directions, the particles align under shearing stress, resulting in much lower viscosity. (Gehm, 1998) This is reflected in the fact that settled and partially dried material, already possessing some loading capacity, can suddenly return to the consistency of slurry when exposed to dynamic stress. The liquefaction of material causes stability problems and possibly slope failures. Alongside it, technical challenges for the reclamation and extraction process of retaining embankments arise.

The general moisture content in a jarosite impoundment is hard to verify and depends on various factors such as climate, filling method, top and bottom sealing or age of the impoundment. Received samples from the zinc plant in Nordenham, Germany showed a moisture ratio of 40% when leaving the plant for disposal. Through air drying, consolidation and drainage in the embankment the water content decreases but can only be exactly determined by in-situ testing. This testing was done at a RSA in Serbia, using an auger drilling rig, mounted on a truck. By means of drilling into the surface dry impoundment, producing vast amounts of samples, the average moisture was determined at 23% (Elixir Group, 2013). Examples of drill cores are displayed in Figure 10.



Figure 10: Drill cores produced from a jarosite impoundment (Elixir Group, 2013)

It is plausible to estimate the general water content of jarosite storage facilities in the same range permitted referring to surface dry embankments that are being prepared for sealing.

The topic of sampling in slurry embankments uncovers another issue when it comes to developing a well-founded excavation method. For erected retaining structures, or well established cases of filled depressions, it is easy to determine the volume of the present residue. Many times however, it is unclear how much residue is stored in a disposal area, especially for old renatured, poorly documented sites or uncontrolled disposal into the landscape. The excavation method heavily depends on the amount of material to be moved and on the dimensions of the impoundment. Fortunately, outlines and volume of a slurry pond can be measured by fast and non-invasive geophysical methods.

Testing of jarosite at the petro physical laboratory at the Chair of Applied Geoscience, revealed the elastic and electrical properties of moist residue:

- pressure wave speed in moist material:  $V_p = 1.500 1.600 \text{ m/s}$
- electrical resistance: ρ = 1 2.4 Ohm
- electrical conductivity: C = 0.42 1.15 S/m

Comparing these values to the ones of frequent bed rock formations (Schön, 2011, pp. 160,276), allows in most cases to measure depth and boundaries of residue bodies through seismic exploration, ground radar and geo-electric methods. Small limitations to these methods are caused by impoundment heights

exceeding 20 meters or if geophysical properties of the subsoil are too similar to the ones of the residue.

Another characteristic of the precipitation residue is its acidic milieu resulting in an overall low pH-value of 4-5 (ANNEX B). Although this does not influence the excavation method itself, it constitutes a relevant factor for disposal regulation (Bundesgerichtshof, 2009) and also affects mineral enrichment, which will be touched upon in chapter Mineral Processing and Enrichment.

The altering degrees of dryness across the depth of an impoundment, leaves the prediction of the material behavior in bulk, inaccurate at best. Producing samples from slurry retaining embankments disrupts the habitus of the settled residue body. Therefore, hardly any quantitative conclusions to the undisturbed in-situ material can be produced. However, this information is essential for an adequate mining operation. Investigation on the overall stability of an embanked jarosite body can only be approximated through mathematical variation of estimated material parameters and is greatly influenced by its water content. (Zöller, 2012) In summary it can be stated that ...

- Particle size and water content cause very strong thixotropic behavior
- High safety concerns due to possible liquefaction and slope failure
- Stability of embanked body is difficult to calculate or predict
- Volumes can be determined through geophysical methods
- pH value does not affect excavation method but does mineral processing

# 2.2 Experiences with thixotropic Material

In the case of jarosite, thixotropy and uncertain stability parameters of the residue body influence the mining operation by far the most. They raise the question of whether or not it is possible to operate heavy equipment on top of the residue surface, or next to a free standing face, without risking slope failure. What is known is that jarosite does possess some carrying capacity in a dried state as demonstrated in Figure 11. What is unknown, however, is to what extent the stability allows for the use of mining machinery.





Circling back to the difficulty of producing conclusive data about jarosite behavior by scientific means, a second option for testing the stability qualities of an impounded and settled jarosite body exists in that of practical experience. Knowledge gained regarding the challenges of working with thixotropic material was gathered from three different cases.

## 2.2.1 Superfine-grained Flotation Tailings

In course of a thesis for the Chair of Mineral Processing at Montanuniversitaet, Raimund Bartl conducted research on a tailings pond of the company RHI AG in Hochfilzen, Austria. Material with similar characteristics like jarosite, but without its environmental constrains, offered an opportunity for experiments on the matter. The reuse and possibilities of excavating an old tailings pond of superfine-grained magnesite flotation slurry was investigated.

Water content of the tailings was measured at 18.9% and showed a particle size distribution with a  $k_{80}$ -value of 16µm. (Bartl, 2009) The tailings showed a strong thixotropic behavior as well, which allows drawing parallels from handling experiences of this material onto the one of jarosite.

One experiment was to excavate the tailings by dredge and examine the stability of the free mining face. Slope failure of several cubic meters occurred, initiating a policy that banned all workers from working next to an extraction face.

Second trial was to remove the flotation residue layer by layer using small dozers with marsh drives. After taking off the first strata however, vibrations transmitted from the machine to the ground could be felt by anyone moving on the tailings. The time required to let the surface dry out enough to regain sufficient loading capacity is considerable, and obstructs steady and substantial extraction. After three days of drying the water content still reached 22% and due to the danger of sinking the equipment into the disturbed material, this method was rejected (Bartl, 2009).

Observations made during work on the tailings pit, and conclusions drawn from it, are applicable for jarosite excavation respectively and will find consideration in chapter <u>3.Mining Methods for Residual Jarosite</u>.

## 2.2.2 Transition from Jarosite to Jarofix Deposition

As previously indicated, transition from the disposal practice of jarosite to the one of jarofix is a process that concerns itself strongly with the thixotropic behavior and stability of the underlying residue.

Stacking high loads of lumpy jarofix on top of unstable jarosite slurry is delicate and carried out in gradual proceedings. It requires above all a gentle approach in order to not disturb the settled slurry by dynamic strain. This can be achieved, among other precautions, by equal weight distribution. First, jarofix material is carefully applied on top of the slurry until it surpasses the water surface and a dry panel for further work is created (Figure 12). The additional weight of jarofix onto jarosite slurry leads to consolidation and water is pressed out. To guarantee vibration free execution, a light long-arm excavator is used.



Figure 12: Transition from jarosite to jarofix disposal; Appliance of geo-textile (Zöller, 2012)

Once spread over the slurry, geo-synthetic reinforcement is installed in form of matting. This artificial barrier grants an equal distribution of overlaying weight and especially prevents material from locally sinking into the slurry in places where it has been disturbed, and consequently, diminished in its loading capacity. The procedure aims at creating an impermeable protective layer preventing deformation and activation of the underlying slurry body. The confinement of the slurry through the impoundment walls, and the protective layer, permits additional burdening without sudden movements and deformation. Only now can profiling with jarofix begin, paying attention to gradual application of mass and small changes in load. Material stacking has to occur step by step to permit sufficient time for subsidence. Once a solid base, and a sufficiently thick layer of jarofix have been established, trucks can be used for transport and dozers for distribution of material. Although some provisional stability measures, like reinforcing the temporary depository roads are still required, the method closely resembles regular earth works.

The undertaking can start at any containment wall and advances in a line across the entire pit. This permits flexibility according to changing amounts of arriving material and enables simultaneous work on matting, profiling, surface sealing and successive renaturation. The practice allows continuous work, and leaves little surface exposed to weathering, which can be seen in Figure 13.



Figure 13: Disposal of jarofix in Nordenham and successive revegetation (Halle, 2016)

The increased weight resting on the bottom sealing of the impoundment that initially was designed to support the load of merely jarosite slurry has to be kept in mind when profiling. A rupture of the base lining has to be prevented and is a challenge, especially in regard to the required minimum surface incline.

As mentioned before, reopening and extracting material from combined depositories poses too many difficulties in order to establish a profitable recycling process. Vast amounts of jarofix have to be relocated into another embankment, before extracting jarosite. Large quantities of jarofix will have mixed with underlying slurry, which raises the question of efficient material separation. The amount of recoverable metals is comparatively low. Therefore, finding solutions for mining these kinds of landfills should be addressed once recycling of old impoundments will have developed more know-how on that matter and more efficient technologies.

#### 2.2.3 Sealing of a Jarosite Embankment – By Example of Nordenham

Probably the most detailed information on how to cope with the challenges of thixotropy, are collected during the sealing and renaturation procedure of an

impoundment exclusively filled with jarosite slurry. Structure and execution of the re-cultivation works is the key for establishing a reversed process for mineral extraction. Closure of residual embankment Galing I in Nordenham was closely documented and serves as valuable source of information.

Through consolidation and dehydration, jarosite slurry develops shallow solidity increasing with settling time and absence of water. For areas with lower carrying capacity it is possible to enhance stability by vacuum dewatering. A thoroughly settled and drained layer of sufficient thickness (approx. 2.0m) can therefore support enough weight to allow sealing works via machinery. (Nürdeklasch, 1995) Frequent exposure of jarosite to dynamic strain through equipment movement however, can disrupt the hardened top layer, which consequently loses its loading capacity again impeding further work. To partially regain its carrying strength, excessive measures are necessary (time to settle or vacuum dewatering). Therefore, the stability of jarosite formed by natural consolidation and dehydration must be maintained at all costs. The earlier mentioned preventions for wind erosion can be temporarily suspended to allow favorable circumstances for a hardened top layer.

Regarding transport, distribution and installation of the various sealing materials, the following guidelines should be strictly enforced.

- Use of light equipment
- Driving slowly
- Reduction of all movement to a minimum
- Use of reinforced construction roads for transportation

Construction roads consist of soil or sand and tower 1.60m above the top surface of jarosite. At their base they reach a width of 10m and are covered with excavator mats for additional weight distribution. The first material to be installed permanently as part of the sealing concept is an anti-capillary gravel layer. It helps to drain water pressed out of the jarosite through the superimposed load of the sealing materials. Since the residue is mostly saturated (except for the dried out surface layer), the subsidence experienced when applying material resembles the volume of water leaving the RDA. Due to an average thickness of 2.10m of the entire top sealing system, estimations predict subsidence ranging from 30-50cm, increasing from the edges to the embankment center. It is assumed that 10% of all

discharged pore water will drain during the first six months and that after ten years no more water will leave through the anti-capillary layer. (Nürdeklasch, 1995)

For installation of the anti-capillary layer (first layer on top of jarosite), modified snow cats were used, keeping surface pressure at only 0.025 kilogram per square centimeter (0.025kg/cm<sup>2</sup> = 250kg/m<sup>2</sup>). Following layers are applied using light bull dozers. Although the overall jarosite stability increases through drainage and compaction, it is impossible to rule out the formation of water lenses inside the slurry. This makes it impossible to precisely predict slurry stability. In order not to endanger workers or provoke accidents, regulations regarding machinery operation on top of jarosite are very conservative, especially in Germany. Sound knowledge about the true behavior of settled jarosite residue under energy entry would help to establish specific guidelines, allowing more liberal and effective procedures without putting people at risk. (Nürdeklasch, 1995; Halle, 2016)

As mentioned before, a top sealing has to be installed guaranteeing the integrity of the impoundment for the future. Isolating the residue from outside weather influences also minimizes the drainage of contaminated water from the impoundment. This prevents interaction with the environment and controls erosion. To ensure a sufficient natural runoff of external water, a minimum slope of 5% at the depository surface is legally required. Possessing little shearing strength and cohesion when released into the embankment, it is impossible to achieve any bevel with jarosite. Hence, extraneous material has to be used instead. The slope creates a relief and diverts water off the impoundment. A top layer of impermeable synthetics above the chamfers is another prescribed protective measure. After completing these structural provisions, a vegetation film can be installed finalizing the renaturation.

With all these layers on top of the jarosite body, the top sealing is finally completed. Sealing off full retaining facilities is common practice in many countries although enormous differences in the execution of the prescribed measures can be witnessed. This makes it necessary to examine each site individually for detailed information on the applied disposal practice, which consequentially builds the basis for an excavation strategy. Plans of the embankment in Nordenham can be found in Annex B.

# 2.2.4 Use of Jarosite as Impoundment Walls – By Example of Facility B

Another zinc producing company practices a very opposing technology regarding jarosite storage, in comparison to the ones previously described. They use the residue itself for building and successively increasing the height of dams that define individual jarosite ponds.



Figure 14: Building a containment dam from jarosite (Sensitive source)

Jarosite slurry is disposed rotationally into different ponds (Figure 41; 1, 2, 3). After a pond has been sufficiently filled, the residue is left to dry and consolidate for about one year. In the meantime an alternative pond is charged with residue instead. Once settled and drained enough, residue material from the outer edges of a temporarily decommissioned pond is extracted (Figure 41; 1 & 2) and used to increase the dam height around said pond. As the reach of the applied equipment (excavators as displayed in Figure 14) is limited, only the outer rim of a pond can be extracted. This material is then piled onto the existing dam and compressed by machines driving on top of it. Layer by layer the dam height is increased this way until it is high enough to hold more jarosite, while another pond is decommissioned to settle and dry. The terraces are built in 50cm layers and compressed into an 80% pack density (Proctor-test). Other iron material is added to enforce the boundaries. The dams are then measured for their stability using standard tests and in accordance with the national dam safety regulations. The safety coefficient required by the authorities for long-term landfilling is  $F \ge 1.50$  and in short term situations  $F \ge 1.30$ . The results for the described dam building method exceeds these regulations by far, with a safety factor of F = 2.0-2.7. This leads to the conclusion that dried and packed jarosite does in fact possess good properties for shaping, and that it shows good shear resistance. This contradicts statements made by Nordenham.

At either visited facility, however, heavy equipment is not allowed to operate on top of the residue itself. The risk of equipment sinking is rated too high, in both cases. Reasons for why one plant uses jarosite to build dams and the other plant refuses to work with it could not be found in the physical properties of the residue. It is assumed that the driving forces behind the opposing jarosite handling are governmental restrictions. Although using the residue for building dams, a complete trust in the stability of jarosite is not displayed by facility B. For security purposes, another impoundment wall surrounds all individual residue ponds with their jarosite dams. This impoundment wall is constructed from solid material and is gradually increased in height as also the jarosite dams grow taller. Beneath all disposed material a bottom sealing prevents ground seepage in the same way as described in the previous example.

The pre-described method poses a good opportunity for re-mining due to the absence of foreign materials such as sealing foils, drainage gravel and above all earth from the dams themselves. It also grants great storage capacities without the need to expand the landfill. The massive height, however, requires impoundment walls with considerable structural stabilities. Long-term planning and starting the dams at sufficient widths are essential to ensuring the required safety factors. Constantly transporting large amounts of material is another downside to this practice; so is the lack of flexibility of this method. Once started, the disposal practice is set for the long run and opportunities to alter the technique are almost nonexistent.

The method of disposing jarosite as slurry contained in consolidated jarosite based dams is intriguing and represents a suitable subject for further investigation. Sadly, information obtained from facility B was limited and restrictions to reporting on plant operations high. With ongoing communication, however, this particular site might prove valuable to trial and develop the recycling technology on which this work is built upon.

## 2.2.5 Gathered Conclusions for Jarosite Handling

Conclusions drawn from the previously stated experiences with thixotropic material can be used as framework in the development of adequate extraction concepts. They are listed below:

- Carrying capacity of residue body and the risk of slope failure are difficult to estimate
- Impoundment height heavily influences excavation face stability
- Due to extensive consolidation and dewatering, carrying capacity of jarosite can be increased
- Jarosite stability generated naturally through consolidation and drainage should be maintained for re-mining requiring low dynamic forces
- Dimensions of embankments make full extraction impossible, if moving along the impoundment dams only
- Top sealing has to be removed before residue extraction
- Equipment used for applying top sealing can also be used to remove the sealing
- Integrity of impoundment dams has to be maintained at all times
- Base sealing has to stay intact during the excavation process
- Differing disposal philosophies require individual excavation approaches

Different circumstances regarding geo-mechanical residue properties, impoundment structure, as well as disposal philosophies, all impact on the selection of a re-mining concept. They were stated and summarized in the last chapters, but do not complete the factors to consider when choosing an excavation concept.

# 2.3 Recycling Backgrounds and their Process Impact

Rock and soil mechanical characteristics are always decision criterions for the extraction method. However, another important criterion for the excavation approach is the downstream recycling process intentions for the material. A general outline of the post depository considerations for jarosite, including mineral treatment and metallurgical processing, are indicated in Figure 15.



#### Figure 15: General outline of the recycling procedure for jarosite (Antrekowitsch, 2015)

As elaborated upon in chapter 1.5 Extraction Process of Valuables from Jarosite, the metallurgical part of zinc residue recycling starts with roasting the material at 900°C, evaporating excess water and starting the chemical reactions. Considering the vast amount of material to be processed (jarosite embankments can contain several million tons of residue) predicts enormous energy consumption, affecting financial viability of the recycling process. Two general approaches are conceivable for recycling jarosite, which subsequently influence extraction, transportation, mineral processing and the final deposition of process waste. Decisive factor of these two fundamentally different strategies is the overall background for initiating the recycling project:

# 1. Environmental Background

Ultimate goal is removal of hazardous jarosite impoundments and full use of the process products. The entire precipitation residue must pass through recycling to change its contaminating character. Extraction of valuable metals is the beneficial side effect lowering overall project costs. Profitability is questionable and external subventions likely necessary.

## 2. Economic Background

Main goal is generating a profit through reprocessing jarosite residue and winning commodities from it. Optimizing expenses requires reduction of material stream passing through the recycling process, making a mineral enrichment step inevitable. The extraction of valuables has to finance the entire project including the re-disposal of unrecycled jarosite.

The first approach demands direct processing (roasting) of the entire residue and makes it necessary to win the material in a fashion that grants lowest water contents possible. This implies the application of dry mining technologies, operating without the use of water. Heating a relatively dehydrated residue to process temperature (900°C) consumes less energy than doing the same with moist feed. Consequently, transportation of the material has to be conducted in a dry manner as well. One great disadvantage of this approach lies in the fact that minimum water content of settled jarosite is determined by its poor dewatering properties (minimum 20-25% H<sub>2</sub>O when settled for a long time). No concentration through mineral processing has to be undertaken, but dewatering through a filter is beneficial. Although applications for the by-product (slag) exist, expenses for roasting the entire jarosite residue outweigh the income from this material. The supporting argument for this practice is primarily environmental protection through complete recycling and will likely rely on government support. A schematic outline of the strategy is given on the left side of Figure 16.

The second approach puts more emphasis on economic aspects. Comparing the amount of residue stored in impoundments to the quantity of desired elements contained in it (max.10-15% valuables), reveals the need to concentrate all valuable minerals into a smaller product stream to keep energy consumption and costs at bay. Achieving this task makes a mineral enrichment process indispensable.

In order to arrive at conclusive results for the most effective concentration measure, profound experimental studies have to be conducted, which go beyond the scope of this thesis. It can be stated however that, due to brief trails on this matter with Dr. Andreas Böhm from the Department of Mineral Processing, Montanuniversitaet Leoben and due to the very fine grain size of jarosite, the most likely option for enrichment is froth flotation. Before describing the fundamentals of flotation in chapter 2.4 Mineral Processing and Enrichment, further considerations of the economic recycling strategy are elaborated.

Anticipating the fact that flotation is a wet process, leads to the important conclusion that wet (hydraulic) mining methods are suited for the economic recycling approach. These hold various advantages in regards to safety, efficiency and costs. Especially transportation of jarosite to the recycling plant which can now be carried out in a liquid state, resulting in fewer expenses for labor, equipment and fuel. Due to the pre-separation of worthless material prior to roasting, the winnowed fraction of jarosite remains for re-disposal. Although it can be conditioned to jarofix and is considerably less in quantity, the process still leaves waste material behind. A brief sketch of this approach can be found on the right side of Figure 16.

The shown contents of water and valuable metal are mere approximations to illustrate in rough outlines what the material consists of in each processing step. It is assumed that dry jarosite contains 10% of valuable metals and that flotation achieves a concentration of the factor three - both conservative estimations. Attention has to be payed to the amount of valuables in the material when starting the metallurgical recycling process.

Each approach has its justification. The first strategy is idealistic and represents the ultimate recycling goal in the long run. With currently low commodity prices however, profitable implementation is doubtful and a pilot project is unlikely to be commissioned. Although the economically induced method does not live up to the ideal of circular economy and complete disposal, it still offers a great opportunity to gain experience and gradually optimize expenses. This method is more likely to be operated economically feasible, which makes it ideal for kicking off deeper investigation. With increasing know-how in this field and higher commodity prices it will be possible to achieve economic viability for the environmental approach in the future as well.



# Figure 16: Possible schematic steps for a full recycling process; environmental background (left), economic background (right)

# 2.4 Mineral Processing and Enrichment

As mentioned, an economically focused recycling project is heavily dependent on mineral enrichment, especially under the currently low commodity prices. Flotation is the best method to complete this task and is elaborated upon in this chapter. Additional preparatory steps for an effective recycling operation are explained respectively.

# 1. Agitator

Before material can be submitted to flotation, it is important to ensure disintegration of all agglomerations of jarosite that might have formed during storage. Conventional operations use log washers or agitator devices to unscramble agglutinated material. In case of jarosite residue, such agitator aggregates are not necessary. Firstly, the use of pumps for slurry transportation acts as an agitator itself when material passes through the impeller and secondly, tests showed no tendency towards lump formation when sufficient water content is provided.

## 2. Flotation Cells

Flotation selectively separates hydrophobic materials from hydrophilic ones by exploiting differences in their surface wettability. For the method to work, the distinct minerals have to exist liberated, as physically separate grains. Therefore, the material feed is dispersed to form a suspension or a pulp and is introduced into water tanks called flotation cells. The pulp carries only 8-12 Vol% of solids. If not already by nature hydrophobic, the desired minerals are chemically conditioned to this behavior by adding surface active substances (collector chemicals), whereas the used chemicals depend on characteristics of the mineral to be recovered. The cells are constantly aerated to produce bubbles. Hydrophobic particles attach to these air bubbles which carry them to the tank surface, generating froth. This foam is permanently removed by rotating paddles, pushing it off into the overflow to allow new formation. Aiding froth stability and developing speed, so called frother chemicals are applied. (Schubert, 1975; Telle, 2007)

Hydrophilic minerals are not attracted to the air bubbles and consequently stay below the surface where they are discharged as flotation tailings. Since the process operates continuously, the quantity of water and material leaving the cell through overflow and bottom discharge is in equilibrium with the suspension feed into the tank. (Schubert, 1975; Telle, 2007) For better understanding, a schematic drawing of a flotation cell can be found in Figure 17.





Flotation is commonly undertaken in several interconnected stages to maximize recovery rates of target minerals, thus both discharge and overflow may still be subjected to further flotation steps normally arranged in a cascade connection as indicated in Figure 18.



Figure 18: Possible Rougher/Scavenger/Cleaner flotation circuit (Helal, 2002)

Additionally, a step of pre-flotation may be applied before the roughing stage to eliminate undesired particles, such as organic substances which can interfere with the downstream process. The primary objective of roughing is to recover as much valuable minerals as possible from the introduced pulp, with less emphasis on the quality of the concentrate produced. This concentrate is then passed to the cleaning stage of flotation, producing as high a grade as possible. The rougher tailings (discharge) on the other side are usually submitted to scavenger cells to recover any remaining target minerals. This is achieved by more rigorous flotation conditions than in the initial roughing. Concentrate from scavengers is returned to the rougher feed for refloating, whereas the discharge is now free of valuables and can exit the process to be disposed. An infinite number of circuit layouts exist with multiple stages of cleaning, roughing or scavenging, with interposed grinders and interconnections in various ways. Each design poses individual benefits, but further comments in regards to layouts are not part of this work. (Pease, 2007)

Amongst various other parameters, flotation efficiency is strongly determined by particle–bubble contact, which again depends on both grain size and air bubble size. Larger dimensions of both components result in lower interfacial area and therefore less probability of contact. For this reason, and because of poorer mineral liberation in bigger particles, the use of flotation cells is limited to grain sizes smaller than 0.2mm (200µm). Collision probability is also low when the material is too fine due to hydrodynamic forces. (Runge et al., 2013) For individual flotation cells the bottom and top grain sizes limits vary (usually 20–200µm), but a general qualitative tendency of operability can be seen in Figure 19.



Figure 19: Classical recovery vs. size relationship (Runge, Tabosa, & Jankovic, 2013)

Grain sizes of jarosite however, can be so fine (Figure 8 and Annex B) that they easily fall below the bottom operation limit of flotation cells in regards to separation efficiency. Hence, the use of flotation columns is preferable.

# 3. Flotation Columns

Flotation columns provide a more effective froth flotation through a countercurrent flow of air bubbles and solid particles. Injecting air at the column bottom and feed in the middle, stands in contrast to conventional cells and allows particles to descend through rising bubbles, causing more favorable head-on collisions. Further introduction of wash water at the column top forces particles downwards and increases this effect. The improved hydrodynamic conditions for flotation and the general build of the column account for a bigger collection zone, more particle-bubble contacts, higher contact efficiency, less energy consumption and smaller bubble sizes. These parameters, in variation, grant a higher flotation rate and the possibility to operate with both coarser and finer particles. Coarse particles can attach to more than one bubble, reducing the chances of the particle being torn loose and sinking again. Fine particles are more likely to collide with bubbles, since hydrodynamic forces tend to sweep small particles away from a collision with big bubbles as shown in the Figure 20. (Kawatra & Eisele, 2001)

Normally flotation is a highly effective method for concentration through mineral classification. In this case a mere enrichment by the factor three would grant major benenfits for the recycling process.



Figure 20: Smaller bubbles more effective; Greater surface area provides more attachment surface for large particles and reduces probability that hydrodynamic effects will prevent contact with small particles (Kawatra & Eisele, 2001) Froth flotation includes many inter-related components not, or only briefly, covered in this section. A thorough report should include elaborations concerning:

Chemistry components:	Collectors, frothers, activators, depressants and pH
Equipment components:	Cell design, agitation, air flow and cell bank control
Operation components:	Feed rate, mineralogy, particle size, pulp density and temperature

#### 4. Hydrocyclone

Hydrocyclones are used to separate the slurry upon arrival into a coarse grained and a fine grained material stream, generating two fractions each ideal for either cell or column flotation. Coarser particles can undergo enrichment through conventional flotation cells, whereas finer grain sizes are introduced into flotation columns. The slurry is conditioned to a volume content of 8-12% solid, which corresponds with the optimum content for operating flotation cells.

The feed enters tangentially and the slurry pressure at the inlet initiates a downward spiral in the chamber. Centrifugal forces push the coarser material outward toward the cone wall, where they displace the water toward the cone center. To counteract the crowding action as the cone diameter decreases, a secondary interior vortex is formed, which is directed counter directional and causes liquid and fine solids to be carried up and out of the overflow. The descending coarser solids will exit the cyclone through the apex at relative high solid content. Factors affecting the performance of a cyclone include, but are not limited to: geometry of the cyclone, inlet pressure, solid content, cyclone size, etc. (Schubert, 1975)

The schematic diagram of a hydrocyclone with its two opposing vertebras is illustrated in Figure 21. Upstream connecting hydrocyclones grant higher efficiency and better recovery rates. It is also likely that desired silver particles and other high value metals enrich rather in the coarse grain fraction, which leads to the possibility of generating a first concentration of valuables already through hydrocyclones, prior to flotation.



Figure 21: Schematic diagram of a hydrocyclone (AKW Apparate, 2015)

# 5. Dewatering

For both environmental and economic recycling approach, it makes sense to interpose a dewatering step prior to the recycling process. Jarosite concentrate after flotation, as well as untreated jarosite applied to recycling directly from the impoundment, still contains considerable amounts of water. Economic considerations infer that every share of moisture remaining in the feed for roasting significantly increases energy costs. Numerous types of filters, presses and other dewatering devices exist, each with individual benefits and disadvantages. Purchasing price, operating costs, throughput, degree of dewatering, size and complexity of machinery are some aspects to consider. As example, the schematic draw of a belt press is shown in Figure 22 ejecting material with about 10% water. Before applying the material stream to a filter press, further dewatering devices like thickeners or settling tanks might be needed to pre-condense the slurry to a manageable texture.

Moisture contents in the scale around 10% are acceptable for roasting. Further applicable dewatering devices are e.g. drum filters, belt filters, cloth filters, vacuum filters or chamber filter presses.



Figure 22: Schematic diagram of a continuous belt filter press (Mossweat, 2013)

# 6. Palletization

Achieving better results during roasting, pelletization of jarosite concentrate proves beneficial. This task is easily carried out by granulation systems distributed, for example, by the company Eirich. After this last mineral treatment step, the material can undergo roasting and metal extraction as described in chapter 1.5 Extraction Process of Valuables from Jarosite.

This concludes elaborations of a plausible enrichment process. That which is vital for a well operating mineral processing is, above all, a homogenous feeding stream. Only consistent material properties allow optimized enrichment. This has to be kept in mind when analyzing mining methods. In the case of rising metal prices and technological advancements, it cannot be ruled out that in the future a dry mining approach will also grant economic feasibility. This leads to contemplation of both wet and dry mining techniques in the next chapter.

# 3 Mining Methods for Residual Jarosite

The objective of residue (or tailings) retaining embankments is to provide safe storage of generated waste whilst having minimal environmental impact over the long term. Given these conditions, impoundments are built to last and subsequent excavation was not considered during their planning. Removal of these structures and their content stems from improvements in processing technology, safety concerns and/or landscape management. (Engels, 2004) Gold tailings have been reprocessed on a large scale for some years now, especially in South Africa and Australia. This practice however, is fairly new regarding jarosite and accounts for a scarcity of experience, trials or publications on that matter.

Most mining methods and equipment were developed for the extraction of material with geo-mechanical properties considerably different to the ones of jarosite. Angle of repose, cohesion, carrying capacity and consequently, the self-support of a mining face, are often essential requirements for machines to operate efficiently and safely. As mentioned in chapter 2.3 Recycling Backgrounds and their Process Impact, the different recycling backgrounds demand a classification of mining methods into "dry" and "wet" technologies. Some principal concepts are identified and explained in the following chapters, starting with dry mining approaches.

# 3.1 Excavation by Mechanical Dry Technologies

Dry mining methods can be categorized and subdivided in many ways. The distinction criterions most suitable in this case are, the operation in advance or in retreat, and excavation above or below the equipment's own position. Figure 23 illustrates an example of mining in advance and below or next to the mining face. This approach implies operation from the base of the impoundment, gradually advancing through the disposal body and slope stability is crucial for this process. Figure 24 indicates extraction in retreat with machinery standing on top of the residue and reversing while taking off material from the mining face asking for carrying capacity.



Figure 23: Mining in advance with equipment below material using face shovel (Unfallverhütungsvorschrift, 1998)



Figure 24: Dragline operating in retreat and on top of material (Unfallverhütungsvorschrift, 1998)

The following mining methods give an overview of possibilities for excavating jarosite residue. Their applicability, strengths and weaknesses are discussed in the latter part of this chapter.

## 1. Scraper winch

Scraper winches originate from underground coal mining, where space was scarce and mobility of the utmost importance. Extracting processed waste works in the same way, only using differently shaped buckets. A winch is installed on the one side of the impoundment and anchored into the dam. On the opposite side a return pulley has to be installed and anchored as well. Pulley and winch are connected by a loop cable. Attached to the wire is a bucket that can be dragged back and forth by running or reversing the winch. Pulled down by its weight, the bucket scrapes over the residue surface collecting material. The filled bucket moves to one side of the impoundment where it is unloaded. For jarosite extraction, this method removes the residue gradually layer by layer. Mining in strips makes it necessary to frequently reposition winch and pulley, accompanied by anchoring works. Further transport of the material is handled by additional equipment such as a retro excavator. Figure 25 indicates the basic schematic operation of a scraper winch in an underground setting.



Figure 25: Schematic outline of scraper winch operation (Alibaba, 2015)

# 2. Bulldozer

An operation method using dozers can be seen in the Figure 26 and is similar to the one of scraper winches. The machine navigates on top of the residue skimming away the upmost level of jarosite and pushing the material layer by layer towards the impoundment sidewalls. Dozers operate on plane surfaces, need space and cannot trench. Loading onto transportation vehicles has to be undertaken by additional machinery.



Figure 26: Dozer scraping material (Caterpillar, 2016)

# 3. Retro/Hydraulic excavator

Single bucket dredgers are very commonly used machines for the excavation of various kinds of materials. For this reason, a large assortment of different builds, drives, digging attachments, bucket sizes and actuation concepts exist. The ones most frequently used are presented, starting with retro-excavators. One common characteristic of this machine type is that excavation occurs mainly vertically. In contrast to the previously mentioned methods, layers formed upon jarosite disposal (1.6.1 Disposal of Jarosite Slurry in Mono-landfill) are transfixed by shovel or bucket, which accounts for a slight homogenization of the material.

The geometry of retro excavators makes them suitable for digs and work in confined spaces. Light weight, low costs, mobility and high flexibility make it suitable for small operations. A schematic draw of its operation radius can be seen in Figure 27, also illustrating the necessity of positioning the equipment close to the break-off edge in order to reach significant depths. In the case of digging out RDAs, mining would take place in retreat and the reach must be at least 7-8m in depth, to access the impoundment bottom. The radius requirements for this example could be met by a Liebherr R 924 Lithronic hydraulic excavator with an operating weight of 23t, burdening the ground with at least 0.45kg/cm<sup>2</sup>. (Liebherr, 2016) Size and weight of retro excavators are directly proportional to their actuation radius, shovel capacity and applied ground pressure. The use of longer booms can extend the working radius but reduces shovel size and extraction volume.



Figure 27: Schematic activity radius for retro excavator (Kovács, 1985)

## 4. Dragline

Draglines are another type of single bucket dredger and have the benefit of long winning ranges. Schematic images are given in Figure 24 and Figure 28.

Loading of the bucket occurs between I. and II., the collected material is raised afterwards. As the upper part of the dredge revolves, exploitation and loading of the material are combined in one action, making additional equipment for loading obsolete. By loosening the dragging cable the bucket turns face down (III.) for emptying and the cycle can start anew. The radius of excavation can be extended by keeping tension on the drag cable until the bucket is released and then loosening the tension at that very moment, which creates a swinging effect, making it possible to reach point IV. (Engels, 2004)

The method used with a dragline is very similar to the one of a scraper, however it is more mobile and dispenses with the pulley on the opposite embankment side. These machines are often, yet not exclusively, used in quarry ponds implying reliable operability in wet or moist milieus. Weight and jib length vary widely ranging from 35t to 7500t and from 20m to 150m. Equipment that ranges about 25m loads the floor with 0.69kg/cm<sup>2</sup>. (Liebherr, 2016; Caterpillar, 2016)

As the shorter side wall lengths of slurry pits can still reach 250-350m, a complete mining of the embankment cannot be achieved by working from the dams. Therefore equipment has to either mine in retreat (Figure 24), from on top of the residue, or operate in advance from the opposite side of the material bank (Figure

29). In this case material can first be extracted along the dams as far as the dragline reaches. For the residue remaining in the middle, an artificial working platform in the form of a dam has to be established through the impoundment. The platform grants sufficient operational height for the equipment and protects it from slope failures. The working platform does not need to be raised as high as the residue to grant sufficient protection. Because vast volumes have been extracted prior to commencement of mining, enough space is provided for sliding and liquefying material to escape into. On top of the dam, the dragline can gradually move forward to reach new material. Liquefied jarosite breaking from the mining face and running towards the excavation zone benefits the extraction.



Figure 28: Schematic outline of dragline operation range (Kovács, 1985)





For retreat mining, pontoons or planks can be used to distribute the weight onto a bigger surface, which reduces the risk of disturbing the jarosite foundation. How much load the residue body can actually support, however, remains uncertain and requires further research. Due to the extended working radius, little repositioning is necessary.

# 5. Face Shovel

An operation sketch to this piece of equipment can be seen in Figure 23. Main differences to a retro excavator are the larger size, weight and shovel capacity, and the fact that it operates next to the mining face. Generally, these machines are just used for loading the aggregated material, after having won it through drilling and blasting. For loose residue, however, face shovels can serve for mining and loading.

# 3.2 Excavation by Hydraulic Methods

An alternative to dry tailing exploitation can be found in hydraulic mining (HM) concepts. These methods exceed in areas regarding simplicity, efficiency and cost effectiveness and are far less dependent on the stability parameters of the residue. The fracturing and transport medium for these methods is water. (Roehl et al., 2007)

HM uses jets of water to move sediment or dislodge rock material. It is ideal for mining soft rock formations or placer deposits and finds wide spread application throughout the world.

# 3.2.1 Conventional Hydraulic Mining

This method involves directing high-pressure jets onto brittle and fractured rock, the material tends to crack and ravel away. When focused on soft and cohesive formations, the jet starts cutting into it. The mechanical force of impacting water is used to disintegrate solid deposits. The effects are illustrated in Figure 30.

The generated forces and the effectiveness of this method depend heavily on the jet impact angle as shown in Figure 31.



Figure 30: Effects of water jet on different rock formations (Horsley-Kozadjian, 2016)

$\begin{array}{c} V \\ \hline \\ \\ \hline \\ \\ \hline \\ \\ \hline \\ \\ \\ \\ \\ \\ \\ \\$	Wy -Vy cos/3y iin/3y
Action force when perpendicular to the front	$F_v = \rho_v \times C_v \times V_v^2$
Action force in $\beta_v$ slope angle	$F_v = \rho_v \times C_v \times V_v \times \sin \beta_v$
Action force in arc shaped slope with given angles ( $\delta_{v1}$ and $\delta_{v2})$	$F_v = \rho_v \times C_v \times V_v \times (sin\delta_{v1} + sin\delta_{v2})$

#### Figure 31: Force of water jet on surface depends on angle (Engels, 2004; Kovács, 1985)

- **ρ<sub>v</sub>:** density of water kg/m<sup>3</sup>
- V<sub>v</sub>: flow volume of water m<sup>3</sup>/s
- C<sub>v</sub>: cross section surface of water jet at the place of exploit m<sup>2</sup>

Apart from breaking down and removing deposits, water can also be used for transportation or to separate material by grain size. For example, as gold particles in placer deposits occur liberated as fine 'gold dust' particles or small 'nuggets',

they are found in the sand-like fraction of the deposit gravel. When washing the gravel by directing water beams from hydro-monitors on it, material lumps are disaggregated, forming slurry with small sized particles in suspension. While the gold containing slurry can run off for further processing, bigger rocks stay behind. (Grayson, 2013, p. 1201) Application of this practice requires far lower water jet pressures than to disintegrate rock formations. A site set up for washing tailings can be seen in Figure 32.



Figure 32: Hydraulic mining/washing of tailings/placer deposit (Horsley-Kozadjian, 2016)

The application of this method is also valid for the excavation of old tailing dumps. Advances in processing technologies make it profitable to re-work old tailings (mainly gold tailings) for a more thorough mineral recovery. This practice is commonly used around the world and is carried out by companies like Fraser Alexander Tailings Ltd. (Fraser, 2015) In an equal fashion, jarosite residue could be mined.

When a water jet impacts upon tailings (usually small grained), fine particles are detached from one another and brought into suspension. This is caused by the mechanical force of impacting water, the mechanical washing ability of downward flowing water and by rising capillary pressure. The effectiveness of slurrying settled and consolidated tailings or jarosite residue depends on the impact angle of the water beam, on its dynamic pressure, as well as on tailing properties like grain size, grain shape, density or separability.

For each operation, an ideal combination of water pressure, water jet length, and discharged water quantity exists to ensure optimum penetration into the residue pile (Figure 33) at a safe distance and to produce a good slurry density for high

production capacity. Regarding slurry density, it is important to find the equilibrium between producing an easily pumpable suspension and using the minimal amount of water for achieving this goal. Water consumption at the monitor is always a function of water pressure and nozzle diameter. Regarding safety distances, the maximum reach of water jets is most often sufficient for re-mining residue impoundments.



Figure 33: Hydraulic Mining of tailings with high pressure water jet establishing flat cutting angles (Roehl et al., 2007)

A high pressure pump station is necessary to produce sufficient force of the water jet. This station is connected to the monitor via flexible high pressure lines and does not have to be moved during excavation.

Advancing across the residue impoundment is also possible with the use of track mounted remote controlled hydro-monitors. This permits complete excavation in retreat without endangering workers. The light equipment weight of a few hundred kilograms allows the positioning on top of the residue body without sinking in.

Although jarosite slurry is pumpable at water contents above 50% (Senapatia & Mishra, 2014), hydraulic mining may generate slurry at a saturation degree of approximately 85%. The water consumption is estimated by the following calculations and visualized in Figure 34. Jarosite has a density of 1.3t/m<sup>3</sup> in the case of residue from facility B (Salmie, 2016). Since water only possesses a

density of about 1t/m<sup>3</sup>, it is important to mention that both blocks in Figure 34 merely show weight percentages (Mass%) and not Vol%.





To approximate capacities and performance of needed pressure equipment, a fictional example is given. An impoundment containing 1,000,000t of jarosite (30mass% water) is to be excavated in 10 years. The availability rate is 60% due to winter months and work time losses, which translates to about 1200 working hours per year (h/a), considering a one shift operation. The jarosite tonnage that has to be excavated in order to hold the time frame is about 83 tons per hour (t/h).

# [1,000,000t/(10 \* 1200h) = 83t/h]

A one shift operation is assumed as to allow for sufficient equipment depreciation and manageable quantities of residue to be recycled. The plant would have to handle an amount of dry jarosite in the range of 100,000t per year.

$$[83t/h * 1200 h/a = 99,600t/a]$$

As seen in Figure 34, every ton of jarosite requires about 3.7t of water to mine it. Therefore, guideline requirement for a pressure pump is to supply 300m<sup>3</sup>/h.

$$[83(t/h) * 3.7 = 307 t water/h]$$

This amount has to be provided at a pressure of around 20 bars, which is sufficient to disaggregate jarosite residue. These specifications are well within the range of standard HM equipment. Production monitors for mining china clay easily distribute between 540m<sup>3</sup>/h -780m<sup>3/</sup>h but depend on the size of the operation. Typical nozzle pressures are around 2400kPa (24bar) but can rise as high as 40 bar (Garling & Pentice, 2010).

After pulping the residue solids, the sludge accumulates in a sump and is pumped away. RDAs usually possess a slight incline at the bottom sealing to enhance drainage during storage as mentioned in chapter 1.6 Current Disposal Procedures for Jarosite. This incline now benefits the accumulation of slurry. A slurry pump station has to be installed preferably using centrifugal pumps. In Figure 34 it can be seen that of every 1,000kg of residue, 4,700kg of suspension has to be transported away. The difference between distributed water and the accruing slurry has to be taken into consideration. Consequently, the slurry pump requires a higher capacity than the pressure pump. Material now leaves the impoundment in pipelines towards the mineral processing plant, sufficient viscosity permitted. During the evacuation process the slurry pump has to be relocated only occasionally. (Garling & Pentice, 2010)

The plasticity of jarosite, its fine grain size and weak shearing strength all attest to an easy slurrying. Small scale tests with samples, and also the fact that jarosite was initially transported to the impoundment in the form of slurry, further support the adequacy of this method, which is schematically shown in Figure 35.



Figure 35: Schematical operation cycle for mining tailings (Garling & Pentice, 2010) Production water serves as transportation medium for the particles to mineral processing and can be recovered during dewatering steps. Despite circulation, in most operations water losses are unavoidable. Acknowledging however, that jarosite possesses a water content of 30% during extraction and 10% before
roasting (Figure 16) allows the assumption of a sustainable if not increasing water circuit.

A concern to address is the pH value of process water when washing through jarosite with a pH of 5.5-6.5 (Salmie, 2016). Reusing the water accumulates more and more acidic particles, constantly decreasing this value. To impede corrosion in the transportation pipe lines, counter measures have to be taken. Since a pH conditioning for process water has to be undertaken when entering flotation, the same can be done for any water accumulating at the dewatering steps. Handling this problematic is trivial, however, it must not be overlooked.





Possible approaches for hydraulically removing old tailings or residue can be seen in Figure 36 with **1** = sump/pump, **2** = direction of monitor, **3** = direction of water flow, **4** = direction of slurry flow. Exploitation with the monitor installed on top of the material (**top down method**) is seen in a) and also in Figure 33. All equipment operates on a safe and dry surface, making transitions easy. The water jet hits at a sharp angle reducing efficiency, but also establishing safe cutting angles. Caution is required not to perforate the underlying bottom sealing with the water jet. Image d) schematically represents the **bottom up** exploitation approach. This method can also be viewed in Figure 37.

For this procedure, a jet hits the settled solids perpendicular for maximum efficiency. Less equipment installation is necessary, but it has to take place inside the impoundment. A constant surveillance of the slurry flow is crucial to grant permanent access to monitor and pump.



Figure 37: Re-mining tailings in accordance with the bottom up method (Fraser, 2015)

Because of equipment exposure and the steeper cutting angles of this approach, machinery is more at risk of being flooded by sudden jarosite liquefaction and bank failures. Therefore, this method is better applied to coarse tailings or beach sand. (Garling & Pentice, 2010)

Both approaches are restricted to RDAs where the entire cross section of the residue body can be mined in one go. Mining faces of great thickness require, in case of d), considerable safety distances between face and monitor. These distances however, seldom grow too large for the beams to cut and wash away solids proficiently. Case a) is not dependent on safety distances, and despite its sharp impact angle, restrictions for the method to modest heights might only concern slope stability and not lack of impact force. Both practices (more so the bottom up approach) are only applicable if the stored jarosite can maintain a steeply inclined mining face. If material is likely to be activated and to start flowing, equipment and operators are neither safe on top of the residue nor inside the impoundment. In cases where jarosite behaves like vicouse liquid incapable of maintaining stable banks and constantly running into excavated areas, another hydraulic method would need to be undertaken, which is explained in the subsequent chapter.

HM can be infrastructure intensive, requiring considerable pipework dependent on operation size and mining capacity. Mechanical issues with pumping and pressure equipment can be high as well, but manageable with preventative measures. All hydraulic methods are sensitive to a cold climate. At temperatures close to or below freezing, excavation hast to be stopped. (Horsley-Kozadjian, 2016)

### 3.2.2 Hydraulic Mining on Floating Device

Conventional dredging uses mechanical methods to excavate material (sand, gravel, dirt, etc.) from river beds or lakes at the front end of the dredge. The material is then directly washed and sorted often by sieves and sluices on the dredge itself, winning the desired commodity. The worthless tailings are ejected at the rear end. This way the floating device always stays in a confined water body, advancing and mining continuously through a deposit body. The technology finds wide application for mining placer deposits all over the world and the schematic outline of the operation is illustrated in Figure 38.





Excavating residue from an impoundment clearly requires technological modifications to the described practice, however, the basic principle remains similar. One has to picture the dredge pond (1) as an area of jarosite in suspension and the placer deposit (2) as a zone of settled and consolidated residue. Instead of using a bucket line (3) to excavate material, jarosite is whirled up by directing water jets onto it. Dispensing the residue in this fashion makes it easy to pump towards mineral processing via flexible tubes, replacing the rear stacker (4). By no means does the dredging pond need to be as deep as indicated in Figure 38, nor the dredge as big. A small floating device big enough to support a pump and the necessary piping is sufficient. The required water depth for this operation is about 0.5m. Dragging the pontoon across the impoundment surface ensures an even residue removal with no banks or inclines. A consistent drag is ideal to avoid formation of cavities like the one of Figure 39. It also shows another

method for evacuating and removing settled bodies of mineral solids, progressing downward from the surface.



Figure 39: Hydraulically removing tailings from an impoundment (Miscovich et al., 1976)

A pressure stream of liquid is directed onto the residue in all directions forming slurry. At the slurry sump (60) the solution is pumped away creating an undercut cavity in the shape of a funnel which directs the flow of slurry towards the center. Extracting more and more material the funnel grows in size and depth with the excavation apparatus (42) sinking in deeper. New production water is supplied by an incoming line (80) and material is extracted through a discharge line (124). Both tubes should be attached to small pontoons to keep them afloat.

Picturing the depression in Figure 39 filled with slurry and imagining a swimming platform instead of a tower in the middle (42), leads to a combined method of HM and dredging. The lines for stabilization would be obsolete when using a pontoon with sufficient buoyancy and could be replaced by four winches located on each corner of the impoundment. This way, positioning the floating device anywhere in the embankment is possible. The theoretical variation of HM described in this chapter is beneficial for mining material unable to maintain a stable escarpment. Necessary development could derive from suction dredge mining.

Having considered the aforementioned excavation methods for removing settled bodies of jarosite residue, the subsequent chapter will evaluate them with accordance to various aspects.

### 3.3 Evaluation of Mining Methods

The benefits and disadvantages of the individual approaches are primarily driven by deriving costs, extraction capacities and safety. Operability is influenced by previous storage practice of jarosite, climate and transportation possibilities. Mingled into the discussion of pros and cons, is the question whether or not an accumulation of the slurry's valuable content is intended through an interposed step of mineral enrichment before roasting. The general distinction between wet and solid recuperation methods depends heavily on this downstream recycling choice for the residue.

Table 3 and Table 4 give an overview of the dry mining technologies that were described in chapter 3.1 Excavation by Mechanical Dry Technologies. Thereafter the same is done for wet excavation concepts in Table 5. Both general approaches ("wet" and "dry") are briefly discussed and it is explained for which kind of recycling projects they are best suited. Beneficial and disadvantageous aspects for the subsequent methods are limited to the most mentionable ones. Nevertheless, the tables give a good first impression of where strengths and weaknesses are present.

Dry Methods	Advantages	Disadvantages
Dragline	<ul> <li>Considerable extraction capacity</li> <li>Extensive operating range</li> <li>Working farther away from break off edge</li> <li>Extraction and loading of material possibly simultaneously</li> </ul>	<ul> <li>Expensive and heavy equipment</li> <li>Limitation to medium profound impoundments because of slope stability</li> <li>Special bucket for slurry needed</li> </ul>
<u>In Retreat</u>	Lower costs compared to method in advance	<ul> <li>Stability parameters of jarosite essential</li> <li>Imposing heavy load onto jarosite (slope failure risk)</li> <li>Additional work for weight distribution required</li> </ul>
In Advance	<ul> <li>Workers operate from safe dams at all times</li> <li>Slope failures do not impair mining</li> <li>Equipment operation from solid base at all times</li> </ul>	<ul> <li>Considerable amount of earthmoving necessary</li> <li>Cost intensive</li> </ul>

Table 3: Benefits and disadvantages of individual "dry" mining approaches 1

Dry Methods	Advantages	Disadvantages		
Scraper Winch	<ul> <li>Workers operate from safe dams at all times</li> </ul>	<ul> <li>No homogenization of material possible</li> </ul>		
	<ul> <li>Removal in layers grant stable jarosite slopes</li> </ul>	<ul> <li>Extraction capacity limited by bucket size</li> </ul>		
	<ul> <li>Reliable slurry buckets for excavation exist</li> </ul>	<ul> <li>Frequent repositioning of pulley and winch</li> </ul>		
	<ul> <li>Reduced water content through surface drying</li> </ul>	<ul> <li>Great surface is exposed to weather influences</li> </ul>		
	<ul> <li>Residue not burdened with dynamic stress</li> </ul>	<ul> <li>Excessive effort for installation &amp; anchoring</li> </ul>		
		<ul> <li>Additional loading equipment necessary</li> </ul>		
Bulldozer	Low cost and easy equipment acquisition	<ul> <li>Stability parameters of jarosite essential</li> </ul>		
	No preparatory steps required	<ul> <li>Danger of base failure through superimposed loads</li> </ul>		
	• Marsh drives available	<ul> <li>Sinking of equipment possible when reaching wet strata</li> </ul>		
		<ul> <li>No homogenization of material possible</li> </ul>		
		<ul> <li>Large surface is exposed to weather influences</li> </ul>		
		<ul> <li>Additional loading equipment necessary</li> </ul>		
Retro Excavator	Low cost and easy equipment acquisition	Stability parameters of jarosite     essential		
	<ul> <li>Extraction and loading of material simultaneously</li> </ul>	<ul> <li>Working close to the break off edge on top of residue</li> </ul>		
	<ul><li>possible</li><li>Little preparatory work</li></ul>	Bigger machines impose heavy load onto the base (possible slope		
	<ul> <li>Slight homogenization possible</li> </ul>	Limited operating range compared		
	<ul> <li>Possibility of gradual top sealing removal leaving little surface exposed to weather</li> </ul>	Restriction to shallow     impoundments		
<b>5</b>	influences			
Face Shovel	<ul> <li>Easy equipment acquisition</li> <li>Extraction and loading of material possible simultaneously</li> </ul>	<ul> <li>Equipment directly attacks mining face</li> <li>Slope failure immediately endangers workers and</li> </ul>		
	Little preparatory work required	Perforation of base sealing		
	Large capacity	Expensive equipment		

Table 4: Benefits and disadvantages of "dry" mining approaches 2

For medium sized impoundments at moderate depths, the use of draglines in advance can be considered best available practice. Worker safety and independency from material behavior outweigh higher costs. Dry material transportation however, cause excessive expenses, due to the intensive labor costs (drivers) associated with discontinuous transportation in charges. Therefore, these mining methods are generally more suitable for environmentally induced recycling projects where focus is set less on costs but on fully removing hazards.

Wet Methods	Advantages	Disadvantages
Convectional HM	<ul> <li>Proven technology</li> <li>Efficient transport to processing in pipelines</li> <li>Homogenization of material possible</li> <li>Adjustable extraction capacity, flexibility</li> <li>Excavation, loading and transportation all by the same medium</li> <li>Light equipment easy to reposition</li> <li>High productivity = low cost</li> </ul>	<ul> <li>Elaborated process-water circuit</li> <li>Excessive installation of pressure equipment and piping required</li> <li>Limitation to medium profound impoundments because of slope stability</li> <li>Not applicable in winter</li> </ul>
<u>Top Approach</u>	<ul> <li>Little exposed surface through gradual removal of top sealing</li> <li>Generates flat slopes</li> <li>Equipment operates on dry surface</li> </ul>	<ul> <li>Stability parameters of jarosite essential</li> <li>Unfavorable impact angle</li> <li>Risk of perforating bottom sealing</li> </ul>
<u>Base Approach</u>	<ul> <li>Highly efficient impact angle</li> <li>Less piping necessary</li> <li>Applicable also for jarosite unable to maintain stable mining face</li> </ul>	<ul> <li>Equipment installment inside the impoundment</li> <li>Permanent monitoring of slurry flow</li> <li>Produces steeper slopes</li> <li>Equipment is exposed and at risk of being flooded</li> </ul>
HM on floating device	<ul> <li>Independent from stability parameters of jarosite</li> <li>Only low pressure needed for excavation</li> <li>Transport to processing plant in pipelines</li> <li>Not limited by height of impoundment</li> </ul>	<ul> <li>Experimental method for tailings excavation</li> <li>Homogenization of material is limited</li> <li>Elaborate water cycle</li> <li>Not applicable in winter</li> </ul>

 Table 5: Benefits and disadvantages of "wet" mining approaches

Hydraulic mining is especially beneficial when concentrating metals from the slurry prior to roasting. Enriching the desired minerals through flotation significantly reduces the material throughput of the roasting step and is a strong argument for cost reduction. The wet treatment steps can directly use the pulped residue from hydraulic mining methods, which extends the benefits even further. HM additionally grants convincing advantages regarding workers safety and mining efficiency. In contrast to labor intense discontinuous material transportation, the use of pipe lines requires a minimum human work force. This advantage is counterweighted by high initial investment when installing the piping. Although transportation costs per ton of material are significantly lower, the fixed overheads are higher than when using dump trucks. Once a pumping system is installed, extraction costs remain about the same, regardless if capacity increases or decreases - meaning low cost flexibility.

Another major drawback of hydraulic mining is the inapplicability of this method in certain geographic locations. While in northern countries, long lasting winters with freezing temeratures can damage pipelines and mechanical equipment (Cuevas & Jansson, 2002), southern countries might experience a lack of available water. This can limit the use of this method and restrict it to certain timeframes.

It can be stated that for impoundments of medium profoundness, and jarosite with sufficient bank stability, conventional hydraulic mining is the most beneficial excavation method. In the case of very profound impoundments with viscose behaving material, hydraulic mining with floating devices is likely to provide the most benefits.

## 4 Description of visited Disposal Sites

In order to gain a better understanding of the challenges concerning jarosite/jarofix disposal, its excavation and recycling, two zinc smelting facilities in Europe were visited. Establishing a connection to companies and investigating actual disposal sites granted valuable information and helped with the evaluation of suitable mining methods. The following notations briefly describe the visited plants and state the different approaches for dealing with residue from their zinc production.

### 4.1 Nordenham Zinc Smelting Facilities

On January 29<sup>th</sup> 2016, it was possible to visit the Glencore-Xstrata owned zinc smelting facility in Nordenham, Germany. The plant was built in 1906 and produces around 140.000 tons of pure zinc annually accompanied by an estimated 175.000t of sulfuric acid, 420t Cadmium, 14,000t Lead-Silver concentrate (23%Pb, 0.1%Ag) and 1,500t copper concentrate (55%Cu). (Xstrata Zink GmbH, 2016). After changing the zinc production method from thermic to electrolytic in 1972, the amount of precipitation residue rose steadily according to the increasing zinc output. A notable achievement of the Nordenham smelter is the reduction of dry jarosite residue to 300kg per 1000kg zinc produced - which is amongst the best ratios worldwide. In 1974 the first disposal site (Galing I) was put into operation, located 7.5km driving distance away from the smelter. Geographical setting of the operation is illustrated in Figure 40.

With a surface of 105,000m<sup>2</sup> and an average filling height of 6.5m, its holding capacity calculates to ca. 680,000m<sup>3</sup>. Tankers transported jarosite slurry at a water content of 40% to the disposal area in ten to twelve runs daily where the sludge was pumped through ring pipes for equal distribution. Over the years the initial 30,000t residue per annum rose considerably and filled up Galing I by 1989. A total 730,000t of jarosite (dry weight) was transported here before environmental protection measures were initiated. Due to the toxicity of the residue, this RDA is categorized in Germany as disposal class III and 2.5m of sealing strata was applied. The underlying jarosite is estimated to contain 30% water and possibly water lenses. It is also believed that this level is maintained even after years of consolidation and drainage.



Figure 40: Geographical layout of disposal site and smelting facilities in Nordenham (Google Maps, 2016)

A reform for waste disposal made a revision of the re-cultivation concept necessary and delayed sealing to 1994. Total costs generated by the construction amounted to 20.5 million German Mark (~10 mio.€). Until 1985 the zinc smelting process did not include a hot acid leaching step, concluding that the content of valuable metals (Pb, Zn, Ag, Cu) that remained in the generated residue until then is significantly higher than in overlaying layers or newer disposal areas. (Nürdeklasch, 1995)

Ever since the old storage area reached maximum capacity (1989), Galing II is being charged with zinc residue, at first using the same technique as before. The new slurry pit extends over 135,000m<sup>3</sup> and offers a filling volume of 800,000m<sup>3</sup>. In 2011 Galing II reached its designated filling height containing 1,056,000t of jarosite. For numerous reasons, the production process at the smelter was then altered and a transition to the deposition of jarofix was made. This transition allowed profiling of the arising waste and prolonged the sited storage capacity till 2018. Jarofix was no longer transported with tankers but in containers, due to the sand like, coarse grained texture. The gradually expanding zinc production and the additional additives for the conditioning to jarofix increased the residue amount to roughly 170,000t per year. Trucks now transport material in 30 to 33 runs every day. The change in disposal method and alterations of environmental law forced a renewal of re-cultivation plans. In accordance with the German legislation (§ 31 Abs. 2 KrW/AbfG), charging and distributing jarofix is followed by immediate and successive renaturation and limits the exposed surface to one hectare at most. The top incline of the sealing layer has to be steeper than 5% to guarantee sufficient water runoff. The weight of the overlying strata however would exceed the permitted maximum load onto the synthetic sealing layers at the bottom. With additional synthetic shielding at the top it was possible for the Nordenham zinc smelter to proof same water diverting effects at a slope angle of only 3.7%. (Xstrata Zink GmbH, 2016), (Nürdeklasch, 1995)

With Galing II rapidly approaching its maximum filling capacity, the planning for yet another embankment has already been undertaken. After analyzing various locations the position best site suited for the new RDA was found adjacent to the existing ones. Significant time and effort had to be invested in planning the new containment facilities. Especially in Germany, where environmental standards are high, numerous permissions had to be granted and lengthy investigation conducted before starting the construction of the new embankment. Only after submission and approval of, amongst other documents, the regional planning procedure, federal immission control act, plan approval procedure, license application, "technical manual for clean air and waste" and the environmental impact assessment, authorities gave the go ahead for Galing BA III. (Xstrata Zink GmbH, 2016)

Besides dealing with authorities, in Germany it is very important to deal with the concerns of local residents. Environmentally related issues demand high sensitivity and have to be taken seriously. Once the general public is against a project, it can become difficult to impossible to further pursue it. In the field of public relations, the Nordenham Zinc Smelter displayed exemplary manners, taking initiatives to openly address and inform neighbors of their plans for

expanding the disposal site. This dialogue allowed most resentment and cynicism towards Galing III to be resolved and residents now generally approve of the project. (Lohe , 2016)

Principal staff within the company however still expressed their concerns regarding further RDA developments once Galing III has been filled. Although its capacities are likely to last for the coming 25 years, doubt is cast as to whether or not another disposal site would be approved. In the meantime, roughly 1.4 million euros are spent annually for the disposal of jarofix, including aggregates, its conditioning, labor costs, and maintenance of the disposal site. (Halle, 2016)

### 4.2 Zinc Smelting Facility B

On the 10<sup>th</sup> of May, 2016, the zinc plant B was visited. Established 90 years ago, the site was converted to an electrolytic plant at the end of the 1960s, commissioned with a capacity of around 100.000t per year. Production capacity was expanded to 150.000t per year 40 years ago and included new purification technologies along with other changes in the operational process. (Wood & Mackenzie, 2015) Over the years production and efficiency steadily increased and reached about 300.000t per year under the current owner. At this capacity, and employing around 500 workers, the plant ranks amongst the bigger zinc producers in the world and up to 85% of its production is exported to foreign countries.

Up until 20 years ago the plant applied ammonium jarosite precipitation, but transitioned to the sodium jarosite process afterwards. At the moment, an average 500kg of dry jarosite is generated for every ton of zinc. The latest link in the chain of development is a silver recovery process that was brought into use a few years back. After hot acid leaching Ag-Pb residue, as mentioned in chapter <u>1.2</u> Zinc Production Process and Jarosite Formation, is separated and enriched through flotation. A concentrate with up to 1.4% Ag and 30% Pb is produced and directly sold to lead smelters. The process extracts about 85% of all present silver and lead. (Salmie, 2016)

Nevertheless, the currently disposed jarosite still contains about 2-3% zinc, 3% lead, 15% iron as well as small amounts of indium and silver. The residue is pumped via tubes to an impoundment located directly next to the zinc plant itself. The layout of this storage facility can be seen in Figure 41 and its structure is very

different to the one observed in Nordenham. The plant opposes the philosophy of conditioning the residue to jarofix. Firstly, this practice obstructs later metallurgical recycling and secondly, it is assumed, that jarofix is still subject to leaching.

Currently the impoundment rises 27m above sea level and holds approximately 6-7 million tons of jarosite with a water content of 40%. (Salmie, 2016) Similar to Nordenham, facility B is also looking for ways to increase their storage capacities. By law, the landfill is limited to a height of 40 meters. Although storage capacities still last for several years, the option to expand the site is already being discussed. Disposal practices are mainly influenced by governmental laws. Concerns of local residents are rarely heard due to scarce population and limited alternative employers in the region.



Figure 41: Layout of the jarosite impoundment at facility B (Google Maps, 2016)

1, 2=Dried and partially excavated ponds to increase dam height; 3=Pond being currently filled with jarosite; 4=After seeping through residue, water accumulates; 5=Water is pumped towards zinc plant for reprocessing; 6= Neutral leaching dusts from 70s currently being recycled; 7=Stable outer dam enclosing entire disposal area

Besides structural variations and the fact that dams between individual jarosite ponds are built from jarosite, another difference to Nordenham was observed. Upon deposition, jarosite slurry is pumped into small ponds (1, 2, 3). Here excess slurry water and water from rainfalls seep through the residue body and are directed according to the arrows; first towards 4 and then to the collector (5). From this location it is pumped towards re-processing. While traversing through the settled residue, water collects metal ions from jarosite, which then can be extracted in the zinc plant. This practice can be considered a natural leaching cycle and recovers, although very slowly, small amounts of valuable metals from the residue.

On rare occasions it can happen that during warm weather periods the impoundment surface dries to the extend where wind erosion becomes a problem. In these cases dust binding agents are distributed on top of the disposal area. They prevent dusting by agglomerating fine particles and by reducing the weathering, hence impeding contamination of the surroundings.

The plant currently recycles old neutral leaching dusts from the 1970s (6). Further, the management is very open-minded towards a complete recycling strategy for jarosite residue to recover all remaining valuables and to solve disposal concerns. Samples of their residue will be sent to the CDL for detailed analysis in the upcoming months. Deposition costs are in the range of 30€ per ton of jarosite.

Grain size distribution of disposed residue averages  $5.9\mu$ m, with a density of roughly  $1.3t/m^3$  and a pH value of about 6.5. The composition of disposed jarosite in % can be seen in Table 6.

S	Ca	Mn	Fe	Cu	Zn	As	Cd	Hg	Pb
35,13%	2,91%	0,10%	14,76%	0,12%	2,83%	0,50%	0,04%	0,005%	4,87%
S(el)+S	NH4+	Na							
26,83%	1,33%	0,10%							

 Table 6: Composition of disposed jarosite at zinc facility B (Salmie, 2016)

### Evaluation concerning Jarosite Recycling

This chapter briefly states the advantages and disadvantages of the aforementioned sites concerning a possible recycling project.

### <u>Nordenham:</u>

- + Very high concentration of valuables (Galing I)
- + Possibility to completely remove an old landfill (environmental approach)
- + Impoundment structure (Galing I) suitable for most extraction methods
- + Good location for buyer's market regarding products of the recycling process
- Currently jarofix conditioning is practiced
- Difficult access of jarosite beneath jarofix (Galing II)
- Lengthy distance between impoundment and zinc plant
- Removal of sealing strata necessary
- Sensitive situation with local residents

The given circumstances describe an old, re-vegetated, small sized impoundment with high content of valuables. Against the background of removing a RDA that does not meet today's environmental standards and provides the opportunity of recovering considerable amounts of valuable metals, it is suggested that an environmental recycling approach for Galing I is the best available option. Major downside to this particular site is the limitation to the small impoundment Galing I regarding a possible recycling project. The second impoundment, as well as further disposed residue are unavailable to the metal recovery process due to jarofix conditioning. Another disadvantage is the lengthy distance between landfill and zinc plant.

Applying an environmental approach means jarosite is to be mined "dry", preferably by dragline in advance. Transportation of the material would have to be carried out by trucks, generating high labor costs. Long transportation ways make the application of hydraulic methods worth discussing. For this approach, best prospect of success is seen in conventional hydraulic mining, mainly because of the easy impoundment geometry and the small pond depth.

### Zinc Facility B:

- + Impoundment at close proximity to zinc plant
- + Disposal only as jarosite slurry
- + Open-minded plant management, secluded plant location
- + Possibility of re-disposing untreated jarosite (economic approach plausible)
- + Space available and few opposing local residents (
- + Considerable amounts of ammonium jarosite present
- + Ag-Pb residue used to be deposited (decent concentration of valuables)
- + Unsealed impoundment
- Homogenization difficult to achieve
- Challenging impoundment geometry (height)
- Limited extraction options
- Complete recycling unlikely to be profitable

The RDA at facility B possesses various layers of alternating residue. This is attributed to the fact, that since the establishment of the plant, all jarosite was disposed of in the same pond. With changing technology, the composition of residue changed respectively. Therefore, the top layers are not as rich in desirable metals (similar to Galing I) whereas further down, metal contents increase. Excavation of the impoundment is challenging, attributable to its immense height and the inhomogeneous build. A feeding stream with steady properties is of major importance, especially regarding jarosite with such greatly fluctuating composition. The best method to address these issues is believed to be hydraulic mining. Depending on slope stability either conventional HM or hydraulic mining on floating devices is conceivable. The rather low content of valuables makes an economic recycling approach most beneficial. Against the background of gradually increasing amounts of recoverable metals linked to the excavation depth, a switch from an economic to an environmental approach might be fitting after some time.

An advantage of this site in particular, lies in the likeliness to carry out disposal or excavation projects rather undisturbed from resident concerns and with less interfering governmental restrictions as in comparison to Germany.

## **5** Cost Estimation for Hydraulic Mining

Estimations for the financial impact of different excavation methods are extremely challenging. The vast number of expense-altering variables makes it absolutely mandatory to consider each recycling venture individually. Even small modifications to a mining approach significantly shift the deriving costs. Labor costs, equipment costs, energy costs, water price, maintenance expenses and sampling costs are only a few of the aspects to consider. These, again, vary according to disposal practice, country laws, regulations, transport distances, material quantities, throughput, geographical setting, recycling considerations and chosen excavation approach.

Within the scope of this thesis, it is only possible to theoretically discuss the most cost effective mining method. Removing material by dry technologies requires excavation machines as well as transportation devices such as conveyor belts or trucks. General observation indicates that operation of any dry approach is likely to be more cost intensive than HM. (Engels J. , 2012) Size and location of the operation impact heavily on the deriving costs. Installing pipelines for small impoundments that are quickly depleted is counterproductive. The situation may also arise whereby building a pipeline is not possible or effective due to dense population and citizens' initiatives. The remaining question is whether dewatering is less costly in operation than the expense difference between dry and wet material transportation. If this is the case, hydraulic mining can also be applied for an environmentally initiated recycling venture.

Most specifically, costs, generated by HM technology are highly significant for project feasibilities. Parameters and requirements change in each case, and with them, the operating expenses. Factors concerning the resource itself are tonnage, location, impoundment depth, particle size and process response. Availability of power, fuel and water are further aspects to consider. Judging from conducted research, hydraulic mining may cost about  $3-5 \in /t$  of feed and  $6-8 \in /t$  for processing (Garling, 2015), but exact prices and installation costs are subject to further research and require substantial cooperation with companies and the framework of a full-scale feasibility study.

## 6 Conclusion and Outlook

This work has given an overview of various plausible mining methods for the excavation of the precipitation residue jarosite from storage impoundments. Considering the strong thixotropic behavior of such settled residue bodies in regards to slope stability or liquefaction probability, lead to the election of hydraulic mining methods, more precisely of top-down hydraulic mining, as the best available technology. Superior safety, productivity and cost efficiency aspects, as well as availability of sound experience in the application of this method, were decisive.

The goal of approximating extraction costs for the excavation technology was only partly achieved. Since every location has its unique situational circumstances, each site has to be evaluated independently in order to produce precise financial statements. Although an in-depth cost analysis was unattainable, important expenditure generating features were indicated. In the same way, guidelines for dimensioning a hydraulic mining operation were given. For the feasibility of recycling, however, the process has to be viewed in its entirety. After excavation, the material also has to be treated and converted to useful products. The submitted research and delving deeply into the subject of metallurgical recycling, allow the statement that costs for excavation and enrichment procedure of jarosite are marginal compared to the great expenses generated by the high temperature material roasting. Therefore, costs can only be moderately optimized by the use of the most efficient mining method.

With elaborations on the hydrometallurgical zinc production process, the metallurgical jarosite recycling scheme and on a mineral processing concept for increased profitability, this thesis acts as a base line study. The largest obstruction to producing tangible statements is the contradicting perceptions of jarosite stability behavior. While one company attests good shearing strength of the material, the other restricts close to all interaction with the material in fear of stability failures. Taking stock of the gathered information reveals a severe lack of hand on real life experience and experiments in this field, which is the main source of the various uncertainties mentioned throughout the thesis. Neither in-situ excavation trials nor laboratory testing for geo-mechanical characteristics of

jarosite in bulk have been undertaken thus far. The little knowledge attained about material behavior as settled bodies was gathered by individual companies while handling the residue in the course of disposal practices. These findings are contradictory and not communicated amongst the individual plants.

Acknowledging the deficits, the focus can now be directed towards preventing them in the future. To arrive at proven facts and valid statements in the field of reexcavating jarosite, further research has to be taken. Foremost, an in-situ pilot project is essential to provide the missing data needed for establishing both an effective full sized excavation operation, as well as well-founded cost related evaluations. Data concerning jarosite slope stability parameters, true water content and elutriation ability have to be collected, as well as genuine water, energy, and fuel consumption, for the most promising mining approaches.

While a breakdown of costs for the technically viable metallurgical recycling process was possible in the laboratory, knowing also about water and energy consumption, throughput limitations and achievable mineral concentration rates associated with the enrichment technologies, is equally important. It delivers valuable cost information for this process and requires initiating a pilot mineral processing plant.

Commonly, companies are not motivated to invest in technologies where they are uncertain of subsequent provability. To calculate the economic benefit of a project however, data and experience are the most valuable assets and can, in turn, only be gathered through pilot projects. This vicious circle needs to be penetrated by either governmental support or company driven innovation initiatives. The constantly rising European demand for resources, and depleting European mineral deposits, build a strong case in favor of increasing research in this field.

Establishing, and subsequently optimizing, the metal recovery process might build the foundation for recycling concepts regarding other hydrometallurgical wastes that accrue in even greater quantities than jarosite. Significantly increasing metal recovery and subsequently using all created products, bring us closer to a circular economy, leading to increased profits and a zero-waste production in in the heavy industry. Although there are many challenges, several missing fields of research have been identified in course of this study and will have to be solved in order to enable the industry to overcoming the described shortcomings.

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## **10 List of Abbreviations**

%	Percent
а	Year
AMD	Acid Mine Drainage
CDL	Christian Doppler Labor
CLC	Co-Location Centre
cm	Centimeter
EU	European Union
€	Euro
EIT	European Institute of Innovation a
ESEE	East and South East Europe
etc.	Et cetera
F	Factor of Safety
g	Gram
h	Hour
HM	Hydraulic Mining
KIC	Knowledge and Innovation Community
kg	Kilo gram
kPa	Kilo Pascal
Mass%	Mass percent
min.	Minute
mio.	Million
m	Meter
mm	Millimeter

рН	Potentia Hydrogenii
RDA	Residue Disposal Area
RIC	Regional Innovation Center
RSA	Residual Storage Area
S	Second
SEM	Scanning Electron Microscope
t	Ton
Vol%	Volume percent
μm	Micro meter

## **Annex Table of Contents**

### A: METALLURGY:

Binary system Pb – Cu (Bolcavage et al., 1995) and Pb – Fe (Unger, 2011)

### **B: NORDENHAM**

Graphics and charts regarding the jarosite impoundment in Nordenham

## Annex

### A: METALLURGY



#### Binary system Pb – Cu (Bolcavage et al., 1995)

Binary system Pb – Fe (Unger, 2011)

## **B: NORDENHAM**





Titel der Diplomarbeit






Weser-Metall GmbH Xstrata Zink GmbH Jarositdeponie Galing I und II Jahresübersicht 2011

pH-Wert Jarosit

Anlage 3.5.2