GEOLOGICA ULTRAIECTINA

Mededelingen van de
Faculteit Aardwetenschappen
Universiteit Utrecht

No. 169

Autoclave Reduction of Jarosites and Other Metal Sulfates

A New Approach to Major Waste Problems

J.L.T. (Hans) Hage

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Cover photo: Iron oxide waste storage containing zinc ferrite (from roasted calcine) originated from past electrolytic zinc production in Sardinia, Italy. The recovery of zinc was improved by the introduction of the jarosite precipitation process in the 60's, which makes it possible to recover zinc from these zinc ferrites. The photograph was taken during the combined final meeting of the two EC - Brite Euram projects dealing with the treatment of jarosite (October 1998).

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Autoclave Reduction of Jarosites and Other Metal Sulfates

A New Approach to Major Waste Problems

Autoclaaf Reductie van Jarosieten en Andere Metaalsulfaten

Een Nieuwe Aanpak van Milieuproblemen

(met een samenvatting in het Nederlands)

PROEFSCHRIFT TER VERKRIJGING VAN DE GRAAD VAN DOCTOR AAN DE
UNIVERSITEIT UTRECHT OP GEZAG VAN DE RECTOR MAGNIFICUS,
PROF. DR. H.O. VOORMA, INGEVOLGE HET BESLUIT VAN HET
COLLEGE VOOR PROMOTIES IN HET OPENBAAR TE VERDEDIGEN OP
MAANDAG 22 MAART 1999 DES NAMIDDAGS TE 4:15 UUR

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to Marina

to Siebrand

The Idea 'autoclave reduction reactions with cellulose' was already existing;
one only had to remember...

(After the pre-existence theory of Plato, 427 - 347 BC)

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Part one of this thesis: the jarosite / sludge process

Industrial jarosite is a waste product of the zinc industry. It is considered a serious environmental problem, due to the quantity produced and the mobile hazardous metals it contains. Over 50 million tons are already stored worldwide. The jarosite sludge autoclave treatment process described in this thesis is a technically and economically feasible alternative to storage, which is only a temporary solution.

Jarosite waste

Zinc is produced from sphalerite ore (ZnS). The common production route consists of pyrometallurgical and hydrometallurgical techniques. In a roast process, sphalerite is transformed into zincite (ZnO) at 900 °C. Pyrite (FeS_2) is a mineral that is commonly associated with sphalerite. Pyrite will react with zincite to produce franklinite ($ZnFe_2O_4$). After roasting, the calcine (franklinite) is leached in sulfuric acid. In a so-called *neutral leach* zincite is dissolved, followed by a *hot acid leach* to dissolve franklinite. Iron dissolves especially in this second leach step. Before the electrowinning, iron and other impurities have to be removed from the leach liquor. A common method is the precipitation of jarosite ($NH_4Fe_3[SO_4]_2[OH]_6$) by the addition of ammonium sulfate ($[NH_4]_2SO_4$) at 95 °C. Metals such as lead, silver and arsenic are incorporated in the jarosite. Zinc, cadmium and copper are not precipitated. Undissolved minerals such as silica (SiO_2) are mixed with the jarosite. After filtration, the moisture content of the jarosite filter cake is about 40 wt%. The jarosite can be washed before storage to improve zinc recovery. Because of the hazardous metals, controlled storage is mandatory. This must be seen however as a temporary solution since leakage will inevitably occur making it necessary to collect the contaminated leachate run-off in perpetuity.

Sewage sludge

Another major waste problem of modern civilization is sewage sludge. In Western-European countries, urban waste water is treated for nearly twenty years before disposal. After settling, aeration, and fermentation, the water is ready for discharge into surface waters. The waste product of these treatment plants is sewage sludge. This material contains sand and clay minerals (from the settling tanks) and virtually non-digestable organic matter, such as cellulose (from the fermentation tanks). Sewage sludge contains about 5 wt% solids, which will not settle. Up to the 1980's the aged sludge was used as fertilizer, but this is no longer permitted as it contains deleterious metals and organics. Nowadays sewage sludge is dewatered and burned in suitable refuse-incinerators. Wet oxidation techniques appeared to be an alternative to burning. This technique is succesfully developed commercially by VarTech near Apeldoorn in the Netherlands. In a pressure vessel sewage sludge reacts with injected oxygen. The oxidation residue is dumped, while the effluent is treated by standard biological purification technology.

The jarosite/sludge process, a 'waste-to-waste' technology

Treating two waste products together in order to yield less hazardous, or even useful, products is called a 'waste-to-waste' technology. Jarosite could provide the 'oxygen' for the oxidation of sewage sludge according to the wet oxidation technique. The released acid has to be neutralized to prevent the dissolution of hazardous metals and to influence reduction reactions. At higher pH magnetite is produced, while at lower pH hematite will be produced. When the redox potential is sufficiently low to produce magnetite, some sulfate is also reduced to sulfide and galena (PbS) is formed. The overall reaction of the reduction of jarosite is shown in reaction 1.

Reaction 1 - Reduction of jarosite to magnetite

$$\tfrac{1}{2}PbFe_3[SO_4]_2[OH]_6 + [C_6H_{10}O_5]_n + NH_4OH \rightarrow Fe_3O_4 + NH_4^+ + SO_4^{2-} + H_2O + n\{TOC + C + CO_2\} + PbS + HS^-$$

A solid/liquid separation is part of the process. The effluent contains mainly ammonium sulfate. Sulfate can be precipitated as gypsum ($CaSO_4{\cdot}2H_2O$) by the addition of calcium hydroxide ($Ca[OH]_2$). Gypsum is a raw material for cement. Due to the resulting high pH ammonium can be stripped as ammonia (NH_3), which can be recycled. After standard purification the effluent can be disposed into surface waters. The solid residue contains iron and other metals compounds, sand and clay minerals. Due to the autoclave treatment the metals are immobilized and the solid may be suitable as construction material. Nevertheless, for an environmental safe option without compromises, the residue has to be treated. A possibility is melting at 1500 °C. Metals like zinc, lead and silver would be evaporated and subsequently condensated and could be recycled. The melt containing iron, sand and clay minerals could be cast into stones to be used as an alternative to the basaltic rock used for the construction of dikes. No residues will remain in this integrated jarosite/sludge treatment process.

Part two of this thesis: scientific spin off

The jarosite/sludge process yielded the more general concept: 'autoclave reduction reactions with cellulose'. Sewage sludge is a cellulose-type waste product, as are saw dust, liquid manure, and waste paper. To simulate cellulose-type waste products pure cellulose was used for the reduction of inorganic compounds. However, not all inorganic compounds are suitable for this purpose. The most important criterion for the reduction of an inorganic compound is that the compound is in solution or unstable during the break down of cellulose. The reduction of Cu^{2+} to Cu^0 and the reduction of pure jarosite to magnetite with cellulose are described.

Samenvatting (Summary in Dutch)

Deel 1 van dit proefschrift: het jarosiet / slib proces

Jarosiet is een afvalproduct van de zinkindustrie. Door de mobiele zware metalen en door de grote geproduceerde hoeveelheden wordt het gezien als een ernstig milieuprobleem. Meer dan 50 miljoen ton van dit afvalproduct ligt wereldwijd opgeslagen in bassins, waarvan alleen al in Nederland meer dan 2 miljoen ton. In dit proefschrift wordt een technisch en economisch haalbaar verwerkingsproces in een autoclaaf beschreven, dat een duurzaam alternatief biedt voor de tijdelijke opslag. Een autoclaaf is een drukreactor waarin waterige suspensies kunnnen worden verhit boven het (atmosferische) kookpunt van water.

Jarosiet

Zink kan op verschillende manieren uit sfaleriet-erts (ZnS) worden geraffineerd. Een veel gebruikte methode is via een gekombineerde pyro- en hydrometallurgische weg. Eerst wordt sfaleriet omgezet in zinkiet (ZnO) bij 900°C. Pyriet (FeS_2), een mineraal dat veel voorkomt in sfaleriet ertsen, reageert samen met zinkiet naar frankliniet ($ZnFe_2O_4$). Dit roostgoed wordt vervolgens geloogd in verdund zwavelzuur. In een eerste stap, de *neutral leach*, wordt het zinkiet opgelost en in een tweede loging, de *hot acid leach*, wordt ook de frankliniet opgelost. Met name in deze tweede loging wordt er veel ijzer opgelost. Voor de elektrolyse van zink moet de loogvloeistof worden gezuiverd. Een manier om ijzer te verwijderen is door het toevoegen van ammonium sulfaat ($[NH_4]_2SO_4$) bij 95°C. Na enkele uren slaat het ijzer neer als jarosiet ($NH_4Fe_3[SO_4]_2[OH]_6$). Metalen zoals lood, zilver en arsenicum komen eveneens in de jarosiet terecht, tesamen met niet opgeloste mineralen zoals kwarts (SiO_2). Zink, cadmium en koper zullen juist niet neerslaan, maar blijven opgelost in de loogvloeistof. Nieuw geprecipiteerd en gefiltreerd jarosiet bestaat voor ca. 40 wt% uit loogvloeistof. In sommige gevallen wordt deze loogvloeistof eerst uit de jarosiet gewassen alvorens deze wordt opgeslagen in bassins. Door de mobiele zware metalen in jarosiet is gecontroleerde opslag een vereiste. Dit is echter een tijdelijke oplossing. Hierdoor wordt jarosiet beschouwd als één van de grotere milieuproblemen.

Rioolslib

Een ander groot milieuprobleem is rioolslib. In West-Europese landen wordt sinds de jaren 70 rioolwater eerst gereinigd alvorens te worden geloosd. Na bezinkingen, beluchtingen, aerobe en anaerobe behandelingen is de waterkwaliteit voldoende om te lozen op het oppervlaktewater. Het afvalproduct van de waterzuivering is slib. Zuiveringsslib bevat zand en kleimineralen van de bezinkingsprocessen en organisch materiaal (vnl. cellulose) van de anaerobe vergisting. Dit materiaal bevat in totaal ca. 5 wt% vaste stof, die zeer moeilijk bezinkt. Tot halverwege de jaren tachtig werd dit materiaal na rijping als meststof uitgereden op landbouw- en veegronden. Omdat rioolslib relatief kleine hoeveelheden zware metalen en organische componenten bevat die schadelijk zouden kunnen zijn voor de volksgezondheid, is dit niet langer toegestaan. Tegenwoordig wordt dit restprodukt eerst ontwaterd en vervolgens verbrand. Bij VarTech te Apeldoorn wordt het slib behandeld in een zogenaamde natte verbrandingsinstallatie. In de VerTech reactor reageert het slib met de zuurstof die onder druk wordt toegevoegd. Het organisch materiaal verbrandt en na een reguliere vast/vloeistof scheiding wordt de resterende vaste stof gestort, terwijl het effluent verder biologisch wordt gereinigd.

Het jarosiet/slib proces, een ‘waste-to-waste’ technologie

Volgens het *waste-to-waste* principe worden twee afvalproducten samen behandeld met als doel minder schadelijke of zelfs bruikbare producten te produceren. Jarosiet zou in theorie de ‘zuurstof’ kunnen leveren voor de oxidatie van rioolslib volgens het natte verbrandingsprincipe. Echter, als jarosiet wordt omgezet naar ijzeroxides, komt er zuur vrij. Om te voorkomen dat door de lagere pH de zware metalen uit de jarosiet oplossen, dient er een neutralisatiemiddel te worden toegevoegd. Op deze manier kunnen tevens het verloop van de reacties en daarmee de uiteindelijke producten worden gestuurd. Magnetiet kan zich alleen bij hogere pH uit jarosiet vormen, terwijl bij een lagere pH hematiet zal ontstaan. Als de redox potentiaal laag genoeg is om magnetiet te vormen, zal ook sulfaat gedeeltelijk reduceren en wordt galeniet (PbS) gevormd. De componenten van de *overall* reductie reactie van plumbojarosiet zijn te zien in Reactie 1.

Reactie 1 - Reductie van plumbojarosiet naar magnetiet en galeniet

$$\tfrac{1}{2}PbFe_3[SO_4]_2[OH]_6 + [C_6H_{10}O_5]_n + NH_4OH \rightarrow Fe_3O_4 + NH_4^+ + SO_4^{2-} + H_2O + n\{TOC + C + CO_2\} + PbS + HS^-$$

Na de autoclaaf reactie volgt een vast/vloeistof scheiding. Het effluent bevat voornamelijk ammonium sulfaat. Door calciumhydroxide ($Ca[OH]_2$) toe te voegen ontstaat gips ($CaSO_4 \cdot 2\ H_2O$), een grondstof voor cement. Door de ontstane hoge pH kan ammonium worden gestript (destilleren) als ammoniak (NH_3) dat weer terug kan worden gevoerd in de reactor als neutraliserend agens. Na een reguliere waterzuivering is het effluent schoon genoeg om te worden geloosd. De vaste fase bevat al het ijzer, metalen, zand en kleideeltjes. In principe zijn door de autoclaaf behandeling de zware metalen geïmmobiliseerd en kan het veilig worden gebruikt als bouwmateriaal. Echter, voor een absoluut milieuveilige oplossing moet dit residu verder worden behandeld. Een mogelijkheid is het te smelten. Hierbij worden metalen zoals zink, lood, cadmium en zilver verdampt en vervolgens gecondenseerd. Dit materiaal is als secundair erts te verwerken. Het mengsel van gesmolten ijzer, zand en kleimineralen kan in blokken worden gegoten. Deze blokken kunnen een alternatief zijn voor basaltblokken, welke worden gebruikt in de dijkenbouw. In dit jarosiet/slib verwerkingsproces worden geen nieuwe afvalstoffen gevormd.

Deel 2 van dit proefschrift: overige wetenschappelijke aspecten

Het jarosiet/slib proces heeft geleid tot een meer algemeen concept: 'autoclaaf reductie reacties met cellulose'. Aan de hand van enkele voorbeelden wordt dit concept beschreven. Als reductiemiddel is telkens puur cellulose gebruikt en voor de te reduceren componenten slechts zuivere stoffen. Zuiver cellulose staat model voor cellulose houdende afvalstoffen zoals rioolslib, zaagsel en oud papier. Niet alle anorganische componenten lenen zich voor reductie. De belangrijkste randvoorwaarde is dat de anorganische component in oplossing is op het moment dat de cellulose afbreekt (zoals Cu^{2+}), of de vaste verbinding moet op dat moment instabiel zijn (zoals slecht kristallijne vormen van goethiet, FeOOH). Een ander belangrijk criterium is dat de redox potentiaal die nodig is om van de ene valentietoestand in de andere te komen niet tè laag mag zijn, in ieder geval niet lager dan de dissociatie van water. In dit tweede deel wordt de reductie van Cu^{2+} naar Cu^0 en de reductie van zuiver Na-jarosiet naar magnetiet behandeld.

Introduction

Chapter 1

New Developments in Autoclave Reduction Reactions with Cellulose-Type Material

Abstract

Industrial jarosite is formed in the hydrometallurgical processing route for zinc metal. Its chemical formula is $M\text{Fe}_3[\text{SO}_4]_2[\text{OH}]_6$ in which M stands for compounds such as NH_4^+, Na^+, $\frac{1}{2}\text{Pb}^{2+}$. Industrial jarosite is considered a hazardous waste material, due to its contained metals such as zinc and cadmium, which are easily leached. The selected disposal option at many zinc refineries is storage in lined ponds. Unfortunately, these ponds are guaranteed for a limited number of years.

Another waste material of human activities is *sewage sludge*. It is the discard product of sewage works. An economically and environmentally accepted solution for sewage sludge is oxidation in refuse-incinerators or in wet treatment plants. In this thesis, the co-treatment of jarosite and sewage sludge, a "waste-to-waste" technology, is described. This study extended into a new field of research as well. The principle of autoclave reduction reactions with cellulose is described, allowing reactions for which the kinetics are too slow under atmospheric pressure.

The Original Concept

Zinc refineries, based on hydrometallurgical processing routes, have to eliminate dissolved iron from their pregnant solutions. A widespread option is to add ammonium sulfate and roaster calcine as a neutralizing agent. As a consequence jarosite, $M\text{Fe}_3[\text{SO}_4]_2[\text{OH}]_6$, in which M stands for compounds such as NH_4^+, Na^+, $\frac{1}{2}\text{Pb}^{2+}$, is precipitated, incorporating other contaminating metals like arsenic, lead and silver. After filtration, the moisture content of the cake is about 40 wt%. The composition of this moisture is reflecting the pregnant solution, which contains zinc, cadmium and copper. Sometimes the jarosite is washed before storage, to improve the recovery of zinc. Storage in lined ponds is a commonly selected option, but is only guaranteed against leaking for a limited time. Budelco is the Dutch zinc factory located in the southern part of the Netherlands. Over the years, they have installed four ponds and at time of writing, two out of four ponds are leaking. Groundwater from within the plant perimeter is continuously pumped and cleaned in a bioreactor [1]. Alternatives for storage are many, but all fail for economic reasons [2].

Another Dutch environmental problem is also found in the southern part of the Netherlands. This area is known for its intensive pig farming. As a consequence, pig manure, a cellulose-type waste product, is produced in large tonnages. The ratio land/manure is too small for sound environmentally acceptable disposal, but alternatives are few [3]. The question was put whether it would be possible to combine both problems and to create less or non-hazardous products.

Wet oxidation is the treatment of cellulose-type waste products with oxygen in pressure vessels [4]. In the original concept jarosite instead of oxygen was added: the jarosite should be reduced to magnetite, which is easily separable from the metal oxides. Initially, this new process was to be developed for local purposes. At second thought, a more generally applicable approach was selected. Pig manure is a local problem. It was substituted as additive by commonly available sewage sludge, another cellulose-type waste product originating from sewage works. Farmland deposition of this material is no longer accepted due to its contained hazardous metals. Drying and burning in a refuse incinerator is a common treatment method, since storage is not a durable option and too expensive. Table 1 shows the production of jarosite and sludge in Europe [5]. Instead of using the pig manure, the co-treatment of jarosite and sewage sludge, based on wet oxidation technology, formed the basis for the testwork described in Part One of this thesis.

Table 1 - Availability in dry solids of jarosite and sludge in Europe (situation in 1993)

countries	sludge production (kton/year)	jarosite production (kton/year)	stored jarosite (kton)
the Netherlands	323	100-150	2300
Belgium	59	0	0
Germany	2681	50-60	1000
Denmark	170	0	0
France	852	0	570
Spain	350	100-150	2000
Norway	(unknown)	50-60	500
Finland	(unknown)	70-100	1800

First results

The initial aim was to transform jarosite waste into a 'secondary ore'. The hypothesis was that under reducing conditions, a part of the iron from the jarosite would be reduced and form magnetite. Magnetic separation would then yield an iron residue, leaving a metal concentrate. However, it appeared to be impossible to create magnetite by just autoclaving a mixture of sewage sludge and jarosite. Several reaction parameters were changed. The importance of a neutralizing agent became clear; it is only possible to produce magnetite in a certain pH range and at a certain redox potential. Finally the reduction of jarosite into magnetite with sewage sludge by the addition of a neutralizing agent was demonstrated. It was not possible to separate the iron phase from the minerals containing the base metal values by magnetic separation. The particles were either too small or were intergrown, which prevented their separation. Due to the dissolution of sulfate and ammonia, the concentrations of metals such as lead and zinc in the autoclave residue were slightly increased [6]. These results were the basis for a request to the European Community for a grant to continue the research.

Project number BE-7673-93 of the Brite Euram Program of the European Community

Introduction

A consortium of research institutes and industrial partners was put together. Geochem Research B.V. (Utrecht, the Netherlands) was the coordinator and the principal investigator of the autoclave reaction. As a Ph.D. student, I was contracted at the faculty of Earth Sciences at the University of Utrecht. The faculty of Minerals Processing and Environmental Engineering of the INPL-LEM (Nancy, France) was involved as they are specializing in pyrometallurgical treatment methods. The faculty for Chemical Engineering and Metallurgy of the University of Barcelona (Spain) took care of the advanced analyses. Industrial contributions came from VarTech Treatment Systems (Apeldoorn, the Netherlands) and Asturiana de Zinc S.A. (Oviedo, Spain). VarTech utilizes a wet oxidation plant for sewage sludge treatment and Asturiana de Zinc owns a zinc factory, producing jarosite waste. Academic process engineering contributions came from the Raw Materials Department of the Applied Earth Sciences faculty of Delft University of Technology (the Netherlands). The grant was awarded, not only for the new approach for waste treatment processes, but also because jarosite treatment had a very high political priority at that time [7]. On the first of July, 1994, the project started with an initial duration of 36 months. This period was extended for another 12 months non-contract [8]. The autoclave treatment method for industrial waste products containing metals and/or cellulose-type waste products was applied for patent application in October 1995 [9].

The co-treatment of jarosite and sludge *(Part One of this thesis)*

The process of treating jarosite waste and sewage sludge is centered around a pressure vessel. In chapter 2 jarosites of two factories, using different jarosite precipitation conditions, were compared, but showed no significant differences [chapter 2]. This indicates that the jarosite source has limited impact on the reactions. Sewage sludge is not only used to generate energy, but appears to be a very useful reagent. Table 2 shows the advantages of using sewage sludge in this process.

Table 2 - Advantages of using sewage sludge in the jarosite/slduge process

- Energy production inside the autoclave
- Creating reducing conditions
- Buffering capacity reduces the amount of neutralizing agent
- TOC in the effluent is a carbon source for bacteria
- Carbon in the solid residue benefits further thermal treatment
- Sand and clay minerals benefit the production of slags in thermal treatment
- Gate fee of around US$ 400,- per ton dry solids for treating the sewage sludge
- Elimination of an environmental problem

At a temperature of 250 °C (40 bar total pressure) and a retention time of about 10 minutes, which are common conditions in wet oxidation processes, iron- and metal oxides are produced [chapter 3]. A neutralizing agent, such as MgO or NH_4OH, is to be added to prevent the dissolution of metals and to influence reduction reactions. For the jarosite/sludge process basically 3 processing units are needed: an autoclave, a washing column and a filter press (Figure 1). The shown pressure vessel is a four compartment, horizontal autoclave. A VerTech reactor, which consists of two concentric pipes of more than one kilometer length placed vertically into the ground [10], is a good alternative. The washing column could be of a multi stage, counter current type. After solid/liquid separation a liquid containing no deleterious metals and an immobilized solid remain [chapter 4]. Differential thermometric analysis (DTA) shows that this autoclave reaction is able to maintain itself by the addition of a short measure of oxygen [chapter 5].

When using MgO as a neutralizing agent, the major compounds in the effluent are magnesium, iron, ammonium, calcium, sulfate and 'total dissolved organic carbon' (TOC). In a marine environment, ammonia and TOC are quickly transformed to respectively nitrate (NO_3^-) and carbon dioxide (CO_2). Such an effluent could, in theory, safely be discharged into the sea or, more safely, seawater basins could be used to achieve this breakdown prior to discharge. Table 3 shows the average composition of the major components in ocean water [11] and a typical composition of the effluent. If necessary a small part of the sulfate may be precipitated as gypsum, incorporating iron and trace metals (such as zinc) left in the effluent before discharging. After the filter press the solid contents will be around 60 wt%, which can be further dried if required. Almost all metal oxides in the residue are stable and can be recycled as construction material, such as filler material in cement. Nevertheless, Dutch and international environmental legislation do not allow these geochemical approaches of dilution and immobilization, thus additional procedures were developed.

First, another neutralizing agent was selected: ammonia. Ammonia is not a strange compound to the system, since it is already present in both jarosite and sewage sludge in significant quantities. It can be recycled by stripping, contrary to MgO. The first investigated option to remove sulfate was bio-treatment. The high sulfate concentration of the effluent appeared to be toxic to the bacteria and had to be diluted from about 40 g/l to 10 g/l. This would increase the water balance of the effluent treatment system dramatically. New testwork was performed, but it turned out that the high ammonia content was toxic as well [12]. Another sulfate removal method was selected: gypsum precipitation. After gypsum precipitation the pH value of the liquid was around 10, which made stripping of ammonia a technically feasible option. In a water contact process 25 wt% ammonia can be produced, which will be recycled over the autoclave [13]. After regular waste water treatment to remove dissolved organics, the purified water can be discharged onto surface waters.

Due to the complexity of the solid, hydrometallurgical options are not feasible; there are too many metals in too low a concentration. Magnetic separation was ruled out in an early stage of the research, thus pyrometallurgical routes were explored. The carbon content of around 5 wt%, originating from the sewage sludge in the solid is a benefit for pyrometallurgical processes. One option investigated was to produce a so-called high density stone and a metal oxide concentrate [14]. For this option, the temperature of melting has to be around 1500 °C. Sand and clay minerals originating from the sewage sludge end up in the stone. Additional silica and other minerals would need to be added. Another investigated option is chlorination at temperatures between 800 °C and 1000 °C [15]. Metals are evaporated and precipitated as chlorides, leaving an iron residue. PVC waste can be used as a chloride and carbon source

[16]. Chlorination requires less energy, but the high density stones have an added value in comparison with the iron residue. The high density stone can be casted and could be an alternative to basaltic rock, which is used to cover sea dikes. In the chlorination process the metals are condensed as chlorides, which carries a penalty to the value of the metal concentrate. The choice between these options is as always a matter of yet unexplored and economical considerations.

Table 3- Average composition of major components in ocean water versus the typical composition of the effluent of the jarosite/sludge treatment process, using MgO as a neutralizing agent, in g/l.

element	ocean water	effluent
Na^+	11	0.4
Cl^-	20	1.2
Mg^{2+}	1.3	8.5
SO_4^{2-}	8.1	37
$Fe^{2+/3+}$	5.6e^{-8}	0.5
NH_4^+	n.d.	3.0
NO_3^-	1.9e^{-3}	0.1
Ca^{2+}	0.4	0.6
C (as TOC)*	6.4e^{-5}	0.8

* = TOC is total (dissolved) organic carbon
n.d. = not detected

Political Issues

After five years of research an integrated jarosite/sludge treatment process was developed in which no residues remain. Due to the gate fee for the sludge, the overall process economics are drastically enhanced. At this stage the laboratory tests are completed and the process is ready to enter the pilot scale stage. Nevertheless, the priority for waste treatment has changed. It has been four years since the EC-project started, and jarosite waste is at present no longer considered as an urgent problem. The attitude towards jarosite waste at this moment is to leave it in place or to improve current storages by capping or groundwater control. Since 1998 Electrolytic Zinc (Valleyfield, Canada) is using its Jar-O-Fix option on a full scale basis [17]. Jarosite is mixed with Portland cement and stored again in capped silo's. Although these methods improve the long term stability of the jarosite waste and its contained metals, they are still not permanent solutions.

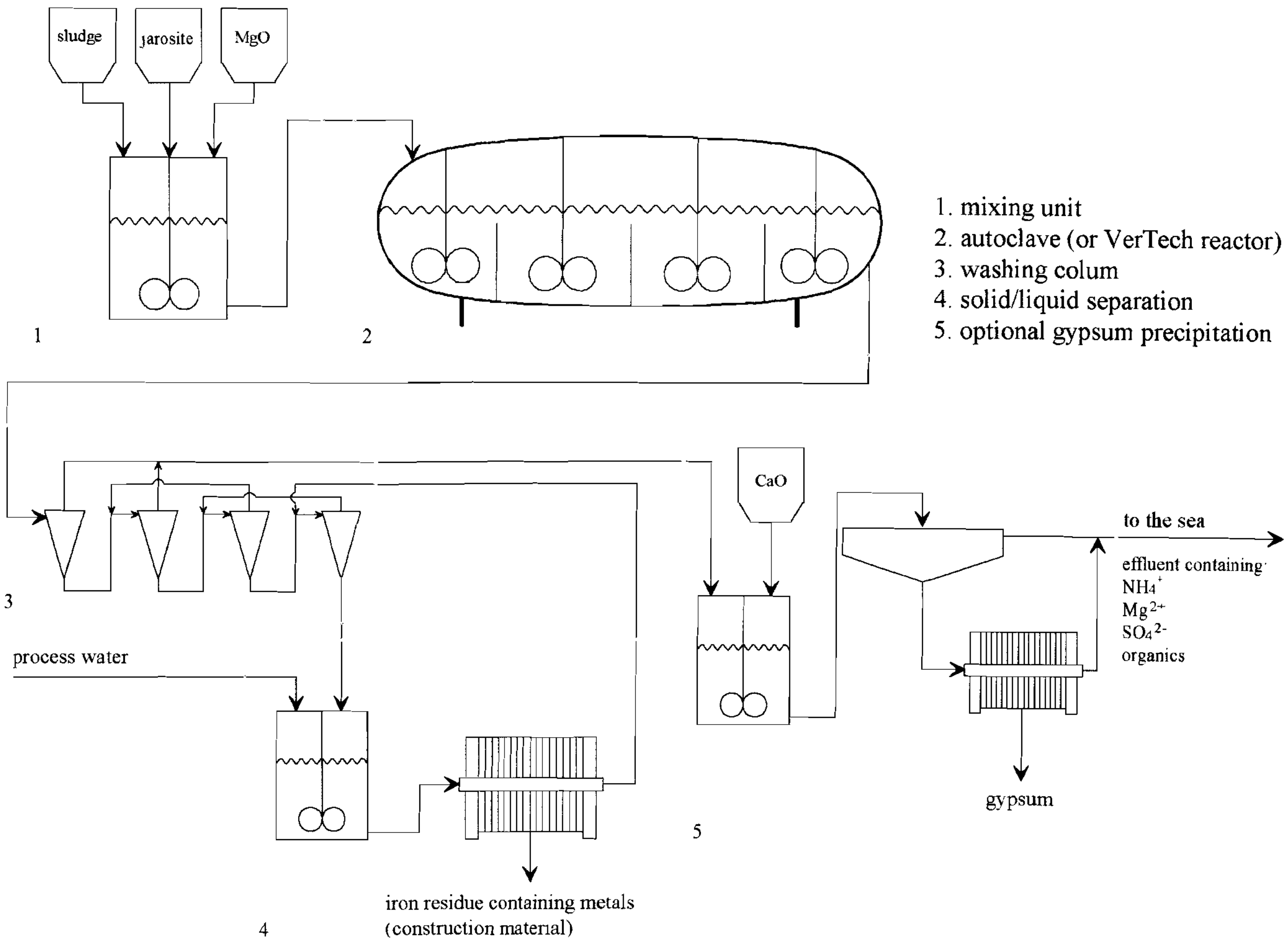

Fig. 1. Overall flowsheet of the process without additional treatment of the residue or the effluent

Scientific Spin Off *(Part Two of this thesis)*

Introduction

During the development of the jarosite/sludge treatment process, the idea of the transformation of jarosite into magnetite has evolved into a new field of research. The reduction of inorganic compounds in autoclaves with cellulose-type material may be an alternative for existing processes or the solution for certain problems [chapter 6]. There are a few restrictions for compounds to be reduced. First, these compounds must occur in several valences. The transition state has to be above the lower limit of water dissociation in a Pourbaix diagram. The compound to be reduced must be in solution during the breakdown of cellulose or be unstable enough to be affected by the reducing conditions. Hematite (Fe_2O_3), for example, is too stable, while under similar conditions goethite (FeOOH) can be reduced to magnetite (Fe_3O_4). In the 1950's Shauffelberger et al reported the precipitation of nickel in ammoniacal solution with hydrogen gas. They succesfully reduced 'autoclave reduction reactions' to practice [18]. During the research three types of reduction reactions were investigated: the reduction of iron(III), the reduction of copper(II) and the reduction of sulfate.

Reduction of Fe^{3+} to Fe^{2+}

The reaction mechanism of the reduction of synthetic Na-jarosite with pure, acid washed cellulose was studied [chapter 7]. The first step is the transformation of Na-jarosite to goethite. Next, a part of the iron is reduced and magnetite is formed. This reaction was tried with other iron hydroxides. The reduction of iron hydroxide sludges ($Fe_2O_3 \cdot n\ H_2O$), originating from waste water treatment plants, was investigated [19]. Storage of these sludges is recommended, but dewatering of is a costly and difficult procedure. Early results showed that treatment in an autoclave results in a crystalline, black magnetite powder. The addition of cellulose is not necessary since the carbon content of the dry solid is about 10 wt%; the reducing agent is already present. After autoclaving the physical properties are drastically improved. Recycling of the magnetite as pigment or as tape coating are to be investigated.

Reduction of Cu^{2+} to Cu^0 (chapter 8)

This reaction has potential as an alternative to electrolysis. Regular electrolysis requires a purification step of the pregnant solution. A benefit of this reaction is the selectivity with respect to copper. This quality makes this reaction also suitable for purification of waste waters, such as effluents from galvanic industries. Metallic copper can selectively be precipitated, leaving other impurities like iron and zinc in solution. This process applied for patent application in November 1997 [20].

Reduction of SO_4^{2-} to S^{2-}

High sulfate concentrations are an environmental problem for which (bio)processes are used to purify effluents. Not infrequently, sulfate is accompanied by metals such as copper and zinc. At this stage of the research, the autoclave reduction of sulfate to sulfide is not yet fully under control. The reduction of plumbo-jarosite ($\frac{1}{2}PbFe_3[SO_4]_2[OH]_6$) to galena (PbS) and magnetite (Fe_3O_4) has been demonstrated [21]. Based on this observation the reduction of sulfate, starting with a zinc sulfate solution was studied. Unfortunately only traces of sphalerite (ZnS) were produced. It is postulated that a solid zinc oxide/hydroxide/sulfate type material was produced at high temperature and pressure, which prevented the reduction to zinc sulfide [22]. Further research is required.

Final remarks

The *aim of this thesis* is to demonstrate the autoclave reduction of metals with cellulose, an orientation on a new and promising concept. Pure cellulose can be substituted by cellulose-type waste materials such as sewage sludge, manure, waste paper, wood chips, saw dust or straw. Probably one of the break down products of cellulose is causing the actual reduction. Generated gas and effluent are analyzed [Appendix 1 and 2]. To yield a reduced inorganic product without organic contamination, the use of one specific organic reagent other than cellulose is to be preferred.

This thesis is divided in two parts. In the first part, relevant work of the jarosite/sludge treatment process is presented; in the second part other aspects are discussed. The *structure of this thesis* is outlined in Figure 2. All chapter are, or will be published, except the introduction.

Introduction	Part One The Jarosite/Sludge Process	Part Two Scientific Spin Off
New developments in Autoclave Reduction Reactions with Cellulose-Type Material	Quantitative Analysis of Industrial Jarosites	Reduction of Inorganic Compounds in Autoclaves by using Suspended Cellulose
	An Integrated Jarosite and Sludge Treatment Process	Production of Magnetite from Sodiumjarosite under Reducing Hydrothermal Conditions; the Reduction of Fe(III) to Fe(II) with Cellulose
	Comparative Column Elution of Jarosite Waste and its Autoclaved Product; Evidence for the Immobilization of Deleterious Elements in Jarosite	Reduction of Copper with Cellulose in an Autoclave; an Alternative to Electrolysis?
	Differential Thermometric Analysis of Autoclave Reactions, with the co-Treatment of Industrial Jarosite and Sewage Sludge as an Example	

Fig. 2. Structure of this thesis

References

1. Scheeren, P.J.H., Koch, R.O., Buisman, C.J.N., 'Geohydrological Containment System and Microbial Water Treatment Plant for Metal-Contaminated Groundwater at Budelco', paper presented at World Zinc '93, International Symposium, Hobart, 10-13 October 1993, pp

2. Peacey, J.G., Hancock, P.J., 'Review of pyrometallurgical processes for treating iron residues from electrolytic zinc plants', In: Dutrizac, J.E., Harris, G.B. (Eds.), Iron control and disposal (Proc.), CIM, Ottawa, 1996, pp. 17-35.

3. Groen, M. (red.), 'Milieu: kiezen of verliezen', SDU uitgeverij, 's Gravenhage, ISBN 901206158 X, 1989, pp. 67-82, in Dutch.

4. Tessel, P., De Bekker, P., Bowers, D., 'The VerTech aqueous phase oxidation system meets Veluwe, Holland's long term sludge management requirements', presented as a poster session at the 1991 WPCF/AWWA joint residual management conference research triangle park, August 1991, North Carolina, USA.

5. Gaucherand M., Picot, P., 'Jarmest process opportunity analysis', IXAS Conseil, December 1994 (internal report, Geochem Research, the Netherlands).

6. Hage, J.L.T., 'Transformation of jarosite under moderately elevated temperature and pressure; a solution for an environmental and commercial problem?', M.Sc. Thesis, Utrecht University, faculty of Earth Sciences, Februari 1994.

7. Meijer, P.J., 'Informatiedocumenten afvalstoffen: jarosiet', RIVM, rapport nr. 738902009, August 1990, Bilthoven (the Netherlands), in Dutch.

8. 'A new method for the recycling and immobilization of metals in jarosite', Final Technical Report, Brite Euram Program, Contract no. BRE2-CT94-0975, Geochem Research BV, VarTech Treatment Systems, INPL-LEM (France), University of Barcelona, Asturiana de Zinc, November 1998.

9. Request for patent application No. 1001390, October 10, 1995, Geochem Research B.V., the Netherlands.

10. Opatken, E.J., e.a., 'Aqueous phase oxidation of sludge using the vertical reaction vessel system', EPA/600/2-87/022, PB87-170320/AS, 1987.

11. Broecker, W.S., Peng, T.-H., 'Tracers in the sea', a publication of the Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York 10964, 1982, pp. 26-27.

12. Periodic progress report, Brite Euram Program, contract no. BRE2-CT94-0975, project no. BE-7673-93, Geochem Research BV, VarTech Treatment Systems, INPL-LEM (France), University of Barcelona, Asturiana de Zinc, July 16, 1996, contribution of Paques.

13. Kolk, H.J., Sijbesma, J.J., 'Feasibility study of the Geochem jarosite treatment process. Design and economic evaluation', Procede Twente BV, December 1997 (internal report, Geochem Research, the Netherlands).

14. Periodic progress report, Brite Euram Program, contract no. BRE2-CT94-0975, project no. BE-7673-93, Geochem Research BV, VarTech Treatment Systems, INPL-LEM (France), University of Barcelona, Asturiana de Zinc, 20-07-1995, contribution of TechnoInvent VOF.

15. Periodic progress report, Brite Euram Program, contract no. BRE2-CT94-0975, project no. BE-7673-93, Geochem Research BV, VarTech Treatment Systems, INPL-LEM (France), University of Barcelona, Asturiana de Zinc, 20-07-1995, contribution of INPL-LEM.

16. Fray, D.J., 'Low-temperature treatment of dust from electric-arc furnaces', *Transactions of Institute of Mining and Metallurgy, Section C*, 1985, 95: C55-C57

17. Rosato, L.I., Agnew, M.J., 'Iron disposal options at Canadian Electrolytic Zinc', in: Dutrizac, J.E., Harris, G.B. (Eds.), Iron control and disposal (Proc.), CIM, Ottawa, 1996, pp. 77-89.

18. Shauffelberger, F.A., 'Precipitation of metal from salt solution by reduction with hydrogen, *Journal of Metals*, Transactions AIME, May 1956.

19. Bergsma, H., 'Thermal recrystallization of iron hydroxide sludges', internal report, Geochem Research BV (in cooperation with Iwaco, under assignment of Kiwa), the Netherlands, 1997.

20. Request for Patent application No. 97202904.5-2309, November 22, 1997, Geochem Research, Delft Technical University, CES B.V.

21. Periodic progress report, Brite Euram Program, contract no. BRE2-CT94-0975, project no. BE-7673-93, Geochem Research BV, VarTech Treatment Systems, INPL-LEM (France), University of Barcelona, Asturiana de Zinc, July 16, 1996, contribution of the University of Barcelona.

22. Kuyvenhoven, R., 'Autoclave reduction of metal sulfates with cellulose to yield insoluble metal sulfides', M.Sc thesis, TU Delft (in cooperation with Utrecht University), August 1997.

Part One

The Jarosite/Sludge Process

Chapter 2

Quantitative Analysis of Industrial Jarosites

Abstract

Jarosite occurs as a mineral, as well as a waste product in metallurgical processes. Jarosite is produced in the zinc industry, using hydrometallurgical processing routes in order to remove iron and other impurities from pregnant solutions. This material is usually disposed off in drainage controlled storages. Its chemical and mineral composition reflects characteristics of the original ore and its processing. In this paper two industrial jarosites derived from two different jarosite precipitation processes are compared. The first is from Budelco (Budel, the Netherlands), using the so-called Dor jarosite precipitation process. The second is from Asturiana de Zinc (Oviedo, Spain), using the conventional jarosite precipitation process. The samples were analysed by XRD, ICP-AES and flame AAS. Differences in ore composition and ore concentration are mainly reflected in the element analyses; differences in processing are reflected in the mineral composition.

Introduction

'Natural' jarosite

'Natural' jarosite is a secondary mineral with the formula ($M\mathrm{Fe_3[SO_4]_2[OH]_6}$), in which M stands for compounds such as K^+, Na^+, $\frac{1}{2}Pb^{2+}$ or H_3O^+. The color may vary from yellow to dark brown. Potassium-jarosite is a common mineral which can be found anywhere in the world; other jarosites like natro-jarosite or plumbo-jarosite are rare [1]. Crystals are trigonal; rhombohedral looking crystals are actually a combination of two trigonal pyramids. Macroscopically visible crystals are rare and small. The specific gravity is approximately 2.9-3.3 kg/l and the hardness is between 2.5-3.5. Jarosite is named after its discovery location in 1852, 'Baranco Jaroso', a small town in the Sierra Almagrera in the south of Spain. Jarosite is a secondary mineral and is the product of the oxidation of pyrite [2]. Argento-jarosite was used in the pre-Roman episode to produce silver [3].

'Industrial' jarosite, or jarosite waste

Producing zinc according to roast/leach/electrowin is still one of the most cost effective methods [4]. To remove iron from the leach liquor, the jarosite precipitation process is an effective possibility [5]. The composition of industrial jarosite depends on all aspects of refining zinc. It starts with the zinc ore itself, of which the principal component is sphalerite (ZnS), which may strongly vary in composition. The iron concentration in sphalerite, for example, is in the range of 0.1-17.4 wt% [6] After crushing and milling, the ore is upgraded by a flotation, in which the sulfide minerals (sphalerite, pyrite, galena) are separated from the oxide minerals (quartz, calcite). The flotation process is used to concentrate the sphalerite before transporting it to the zinc refineries. Table 1 shows the analysis of common elements and minerals of such a zinc concentrate, processed at the Kidd Creek zinc refinery (Timmens, Canada) [7]. The concentrate differs from day to day. Most zinc refineries use concentrates from more than one mine, mixing them before processing.

The first process step at the zinc plant is roasting at about 900 °C. During this process sulphide ore is oxidized and the sulfur is removed as sulfur dioxide. After washing steps of the gaseous phase to remove contaminants, sulfuric acid is produced in a water contact process. During the roasting, sphalerite (ZnS) is transformed to zincite (ZnO). During roasting, pyrite (FeS_2) from the concentrate reacts with zincite to franklinite (Fe_2ZnO_4). This roasted material is called 'calcine' and is transported to a temporary storage, waiting to be leached. The next process step (neutral leach) is a sulfuric acid leach, which dissolves most of the zincite. This process is called 'neutral leach' because a stoichiometric amount of sulfuric acid is added. After the neutral leach the liquid is transported to the electrolysis and the remaining solids are leached again. The second (hot acid leach) and third leach step (super hot acid leach) are needed to dissolve the franklinite. Metals like iron, copper and cadmium are dissolved as well during the leaching processes. Iron is precipitated as jarosite ($M\mathrm{Fe}_3[\mathrm{SO}_4]_2[\mathrm{OH}]_6$, $M = \mathrm{NH}_4^+$, K^+, Na^+, $\frac{1}{2}Pb^{2+}$ or H_3O^+) by adding ammonium sulphate and calcine. The effect of adding calcine is to increase the pH, needed to precipitate jarosite. Compounds which are not dissolved during the leach processes, like silica, also end up in the solid phase. Zinc is reported to precipitate in jarosite only in very small quantities [8]. After solid/liquid separation, usually with drum filters, the moisture content of the jarosite is about 40 wt%. Dissolved compounds like zinc, copper and cadmium are trapped in this moisture content. Due to these mobile elements and to other potentially leachable elements like lead and copper, jarosite is considered as an environmental hazardous waste. For this reason jarosite is usually stored in drainage controlled storage. The most common storages are in lined ponds, but there are alternatives. Norzinc (Odda, Norway), for example, uses excavated mountains, bordering the fjord to store their jarosite [9]. MetalEurop (Nordenham, Germany) even capped a jarosite pond to prevent interaction with the atmosphere [10]. Sometimes the jarosite is washed at the zinc refinery before storage; among them are Outokumpu (Kokkola, Finland) [11], and Kidd Creek [7]. Asturiana de Zinc (Oviedo, Spain) recycles water from the jarosite pond to wash the jarosite [12].

Table 1 - Analyses of a zinc concentrate treated at Kidd Creed after flotation

minerals (in wt%):	
Sphalerite (ZnS)	89.5
Pyrite (FeS_2)	8.6
Chalcopyrite ($CuFeS_2$)	1.7
Galena (PbS)	0.04
Silicates (SiO2)	0.2
major elements (in wt%):	
Zn	**53.9**
Fe	9.2
Cu	**0.6**
Cd	**0.27**
S	**32.7**
minor elements (in mg/kg):	
Ag	36
Co	**218**
In	322
Se	163
As	330
Pb	400
Hg	10
Bi	14
Sb	12
Ni	7

Commercially recovered elements are printed in **bold**

The liquid enters cementation cells to remove cadmium and copper, which are still present in the pregnant solution. Finally, the latter, containing up to 150 g/l Zn^{2+} [13], enters the electrowinning. Every zinc plant has developed its own option for the precipitation of jarosite; in this paper only two flowsheets are discussed. The first type is the Dor process, used by Budelco in Budel, the Netherlands (Figure 1, [14]) [15]. Their efficiency for recovery of zinc is high (more than 95 %). The second type is based on the conventional jarosite process. A simplified flowsheet is shown in Figure 2 [14]. In this process, the dissolution of franklinite and the precipitation of jarosite occur simultaneously [16]. The efficiency for zinc recovery is about 95 wt%. Asturiana de Zinc is using a flowsheet based on this option [12]. Although this flowsheet allows the separate production of a Pb/Ag concentrate, Asturiana de Zinc combines the jarosite and the Pb/Ag-residue and stores them together in lined ponds, since the profit for the recovery of lead and silver is too low. A third type of jarosite precipitation processes is not mentioned here: the low-contaminant jarosite process. The aim of this process is to reduce the impurity content of jarosite. In a pre-neutralization step most of the contaminants are precipitated; jarosite is precipitated in a second step. The contaminants end up in the Pb/Ag-residue [17]. This option is adopted by MetalEurop, Nordenham.This paper deals with the analyses of samples of jarosite waste from Budelco and from Asturiana de Zinc. Jarosite reflects the whole zinc refining process. In previous studies mainly qualitative analyses of mineral phases were reported [18], [19], [10].

Materials and Methods

Only random samples of the jarosite from Budelco (summer 1993) as well as Asturiana de Zinc (summer 1995) were available. The granulometry of Budelco jarosite has a D_{50} of 4.5 µm [20], and the grain size of Asturiana jarosite is similar. The samples were dried at 60 °C for 48 hours and the moisture content was determined by weighing. After drying the solids were gently crushed in an agate mortar. A small amount was used for XRD-analyses. About 100 mg of the sample is dissolved in a $HF/HClO_4/HNO_3$ mixture in a small, closed teflon vessel for at least 12 hours at 90 °C. After cooling, the vessels were opened and placed on a sandbath with a temperature of 120 °C; the gaseous phase was soaked up and neutralized. After evaporating the acids, the residue was dissolved in 1 M HNO_3 and analysed by ICP-AES for most of the elements; silver and cadmium were analysed by flame AAS. This acid destruction technique is not suitable to analyse Si; this element forms a gaseous fluorine compound and escapes from the decomposition vessel.

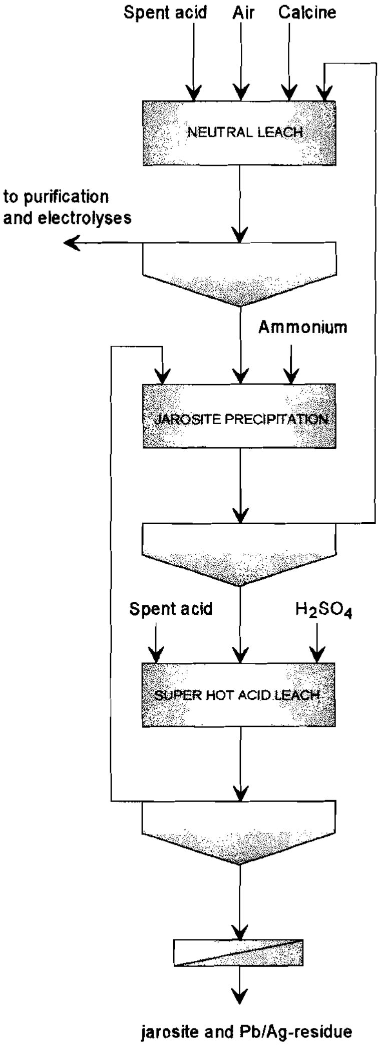

Fig. 1. Flowsheet of the Dor jarosite process (Budelco, the Netherlands)

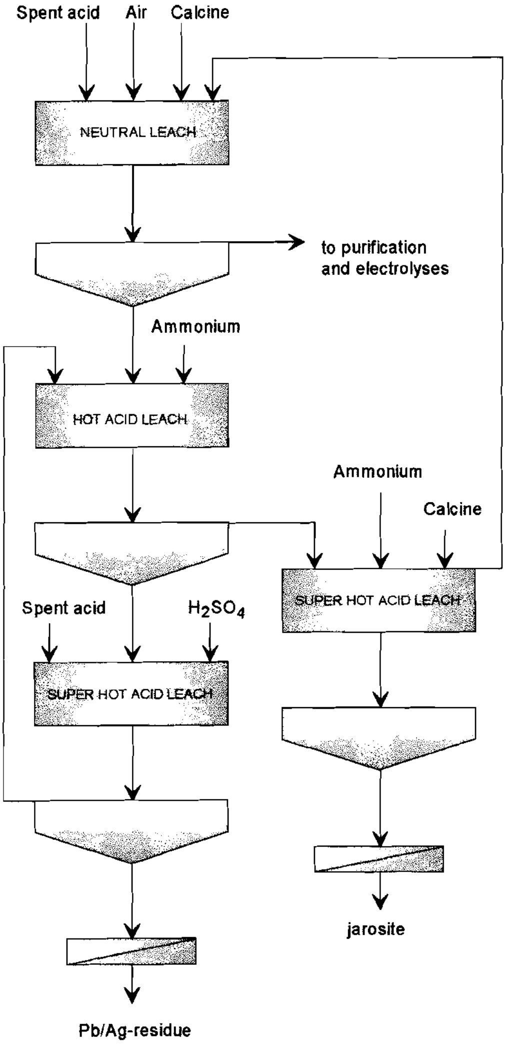

Fig. 2. Flowsheet of the 'conventional' jarosite process (Asturiana de Zinc S.A., Spain)

For this element, 50 mg of the jarosites were melted with $LiBO_2$. After cooling, the beads were dissolved in 1 M HNO_3 and analyzed by ICP-AES. Nitrogen was analyzed with an NCS analyser. Although the accuracy of XRD analyses is no better than ± 4 %, which is of the same order as the accuracy of ICP-analyses, the XRD powder patterns are crucial for quantitative analyses, as the detected minerals are the starting point for the calculations. A number of elements are confined by a single mineral phase, like Si for quartz or N for ammonium jarosite. In some cases iterations were necessary to make an estimation of the contribution of certain compounds.

Results

The results of the ICP-AES and AAS analyses are shown in Table 2. The theoretical composition of pure ammonium jarosite is shown as well. The Budelco jarosite contains more contaminants such as cadmium, silver and lead than the jarosite of Asturiana de Zinc. Silicon and calcium levels are also higher in case of the Budelco jarosite. The X-ray powder patterns are shown in Figure 3. In both cases jarosite is the most abundant mineral. Quartz (SiO_2) peaks are absent in both graphs. Gypsum ($CaSO_4 \cdot 2\ H_2O$) is only observed in Budelco jarosite; the jarosite from Asturiana de Zinc contains traces of bassanite ($CaSO_4 \cdot \frac{1}{2}\ H_2O$). It is not surprising therefor that Budelco jarosite contains much more calcium than Asturiana jarosite. Franklinite is found in both jarosites. Other minerals which could be expected are sphalerite (due to incomplete roasting) and anglesite ($PbSO_4$), but these are not present in the XRD powder patterns. In case of the flowsheet of Budelco, jarosite is precipitated after the neutral leach and leached again in the super hot acid leach. In case of the flowsheet of Asturiana de Zinc, jarosite is precipitated after the hot acid leach and removed from the system. Evidently, the moisture in the jarosites contains zinc sulfate, reflecting the concentration of the leach liquors.

To verify this statement, samples of Budelco jarosite, a second sample of Asturiana jarosite ànd Outokumpu jarosite were washed two times by washing/filtering/resuspension/washing with doubly distilled water. The most relevant elements in the solids of this procedure are listed in Table 3. The second Asturiana sample is precipitated in summer 1994. More than 60 wt% of Zn, about 70 wt% Ca and 11 wt% of S was washed out. The amounts of Pb, Fe and K in the solid increase about 20 wt% in concentration.The zinc content in the moisture of Budelco jarosite based on these results is 43 g/l Zn^{2+}. The rest of the zinc is thought to be associated with 3.9 wt% of franklinite, which agrees with the relatively small peak heights in the XRD powder pattern. Asturiana jarosite contains less mobile zinc: the zinc concentration in the moisture is about 14 g/l. The washing step at Outokumpu is even more effective.

Table 2 - Analyses of Budelco jarosite and Asturiana de Zinc jarosite in wt%, except were noted.

element	Budelco jarosite	Asturiana jarosite	pure NH_4-jarosite
Na	0.11	1.02	
Mg	0.31	0.01	
Al	0.33	0.15	
Si[1]	8.54	2.71	
S	12.0	11.2	13.4
K	0.24	0.08	
Ca	1.30	0.25	
Cr	< b.g.	0.30	
Mn	0.09	0.07	
Fe	22.6	26.7	34.9
Ni	< b.g.	0.10	
Cu	0.25	0.17	
Zn	2.80	2.65	
Ba	< b.g.	0.20	
As[1]	0.29	0.14	
Pb	5.70	3.50	
N	1.0	0.9	2.9
Ag[2] (mg/kg)	170	80	
Cd[2] (mg/kg)	360	79	
Dried solids	60	64	

[1] with $LiBO_2$ destruction

[2] AAS analyses

< b.g. = below detection limit

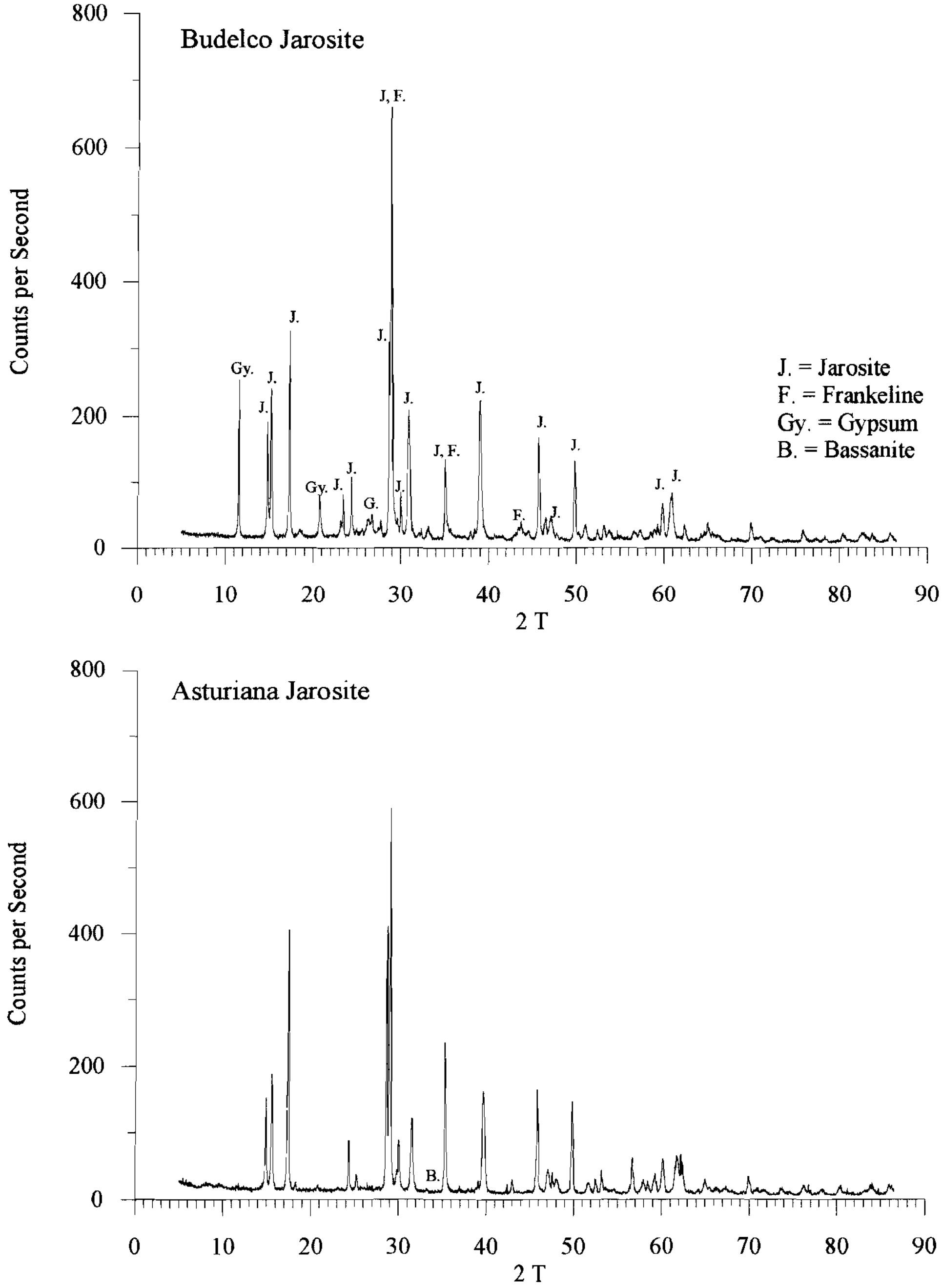

Fig. 3. XRD analyses of Budelco and Asturiana jarosite

Table 3 - Washing of jarosite; the most relevant elements (in wt%)

Budelco

element	before Washing	after Washing	difference (%)
S	12.0	10.6	-11.4
K	0.19	0.24	26.3
Ca	1.30	0.40	-69.0
Fe	22.6	26.8	18.6
Zn	2.80	1.09	-60.9
Pb	5.70	6.90	21.0

Asturiana (second sample)

element	before Washing	after Washing	difference (%)
S	11.7	11.5	- 2.4
K	0.05	0.06	15.4
Ca	< b.g.	< b.g.	
Fe	31.1	33.1	6.7
Zn	3.74	3.25	- 13.2
Pb	3.35	3.47	3.6

Outokumpu

element	before Washing	after Washing	difference (%)
S	12.1	11.6	-4.1
K	0.18	0.20	6.9
Ca	3.56	1.91	-46.4
Fe	24.4	26.2	7.3
Zn	2.33	2.14	-8.3
Pb	5.14	5.46	6.2

The computed mineral compositions are listed in Table 4, respectively Table 5. The calculated total amount of iron and sulfur is summarized and compared with the ICP-AES results. In case of Budelco jarosite, the amount of hydronium jarosite is tuned on both the iron and the sulfur content. Aluminium and copper (as beaverite, $PbCuFe_2[SO_4]_2[OH]_6$) may replace iron in jarosite [21]. These metals were included in the iron content. In both cases ammonium jarosite is not the only jarosite compound present; one may expect a mixture of several jarosite end-members, probably in a solid solution series.

Table 4 - Calculated mineral composition of Budelco Jarosite (in wt%)

Unique element	Mineral	
Zn	$ZnSO_4 \cdot ?H_2O$ (moisture content)	≥4.2
N	$NH_4Fe_3(SO_4)_2(OH)_6$	34.2
Na	$NaFe_3(SO_4)_2(OH)_6$	3.5
K	$KFe_3(SO_4)_2(OH)_6$	2.6
Pb	$½PbFe_3(SO_4)_2(OH)_6$	18.4
Zn	$ZnFe_2O_4$	3.9
Si	SiO_2 (amorphous)	18.2
Ca	$CaSO_4 \cdot 2\,H_2O$	5.6
H_3O^+	$H_3OFe_3(SO_4)_2(OH)_6$ (tuned on Fe and S)	7.6
Total:		98.2 wt%
Fe (+Al +Cu) is present in: (ICP-AES = 22.6 wt%)	$NH_4Fe_3(SO_4)_2(OH)_6$	12.0
	$NaFe_3(SO_4)_2(OH)_6$	1.2
	$KFe_3(SO_4)_2(OH)_6$	0.9
	$½PbFe_3(SO_4)_2(OH)_6$	4.6
	$ZnFe_2O_4$	1.7
	$H_3OFe_3(SO_4)_2(OH)_6$ (tuned on Fe and S)	2.6
Total:		22.9 wt%
S is present in: (ICP-AES = 12.0 wt%)	$NH_4Fe_3(SO_4)_2(OH)_6$	4.6
	$NaFe_3(SO_4)_2(OH)_6$	0.5
	$KFe_3(SO_4)_2(OH)_6$	0.3
	$½PbFe_3(SO_4)_2(OH)_6$	1.8
	$CaSO_4 \cdot 2\,H_2O$	1.0
	ZnSO4	1.0
	$H_3OFe_3(SO_4)_2(OH)_6$ (tuned on Fe and S)	1.0
Total:		10.0 wt%

Table 5 - Calculated mineral composition of Asturiana Jarosite (in wt%)

Unique element	Mineral	
Zn	$ZnSO_4 \cdot ?H_2O$ (based on a second sample)	≥1.2
N	$NH_4Fe_3(SO_4)_2(OH)_6$	30.8
Na	$NaFe_3(SO_4)_2(OH)_6$	34.6
K	$KFe_3(SO_4)_2(OH)_6$	1.3
Pb	$\frac{1}{2}PbFe_3(SO_4)_2(OH)_6$	11.3
Zn	$ZnFe_2O_4$ (estimation)	7.9
Si	SiO_2 (amorphous)	5.8
Ca	$CaSO_4 \cdot \frac{1}{2} H_2O$	1.1
Total:		94.0 wt%
Fe (+Al + Cu) is present in:	$NH_4Fe_3(SO_4)_2(OH)_6$	10.8
(ICP-AES = 27.1 wt%)	$NaFe_3(SO_4)_2(OH)_6$	12.0
	$KFe_3(SO_4)_2(OH)_6$	0.4
	$\frac{1}{2}PbFe_3(SO_4)_2(OH)_6$	2.8
	$ZnFe_2O_4$ (estimation)	3.7
Total:		29.7 wt%
S is present in:	$NH_4Fe_3(SO_4)_2(OH)_6$	4.1
(ICP-AES = 11.2 wt%)	$NaFe_3(SO_4)_2(OH)_6$	4.6
	$KFe_3(SO_4)_2(OH)_6$	0.2
	$\frac{1}{2}PbFe_3(SO_4)_2(OH)_6$	1.1
	$CaSO_4 \cdot \frac{1}{2} H_2O$	0.2
	$ZnSO_4$ (estimation)	0.2
Total:		10.4 wt%

4. Discussion

Differences in the element composition of jarosites are mainly caused by the original ore, while process parameters mainly influence the mineral composition. The lower concentrations of metal impurities in case of Asturiana de Zinc reflects a more pure sphalerite concentrate. The lower silicon (silica) content indicates that the flotation process (to concentrate the milled ore) is more efficient, or the original ore itself is of a better quality in terms of deleterious elements. Calcium (gypsum) is not such a good indicator since it can stem from the process water as well. Relatively high amounts of lead and sodium are a benefit for jarosite precipitation; it saves on the amount of added ammonium sulfate. It is noteworthy that anglesite ($PbSO_4$) was not detected. The moisture content of these particular samples was about 40 wt%, containing high zinc concentrations. Components like zincsulfate are easily washed out. Although jarosite is a waste product, it still contains valuable metals like lead, zinc and silver [22] (Table 6). Looking at those three metals, the contained metal value of Budelco jarosite would be around 100 million US-dollars. On the same basis, the jarosite from Asturiana de Zinc would contain 70 million US dollars. Nevertheless, these values are far too low to cover the recycle expenses.

Table 6 - The value of metals in one million ton of jarosite

Element	Metal value (Aug. '96)	value in Budelco jarosite	value in Asturiana jarosite
Zn	US$ 1000.0 /ton	US$ 28,000,000	US$ 28,000,000
Pb	US$ 801.5 /ton	US$ 45,685,500	US$ 28,052,500
Ag	US$ 183.0 /kg	US$ 31,100,000	US$ 14,640,000
		--------------------	-------------------
Total:		US$ 100,000,000	US$ 70,000,000

5. Conclusions

Some aspects of the original sphalerite ore and the zinc processing are reflected in the jarosite waste composition and mineralogy. The qualitative analysis is a derivative of the quality of the zinc concentrate, which in turn depends on the original ore composition and the efficiency of the flotation process. On the other hand, differences in mineral composition usually indicate differences in process parameters. The quantitative analyses show different types of jarosite minerals. Other aspects such as the efficiency of the roasting are also reflected in the quantitative analyses. The differences in jarosite composition between the Budelco and Asturiana de Zinc samples mainly reflected the original ore composition. Differences in process parameters between both jarosites were harder to define. Most of the zinc was trapped as zinc sulfate in the (filter cake) moisture content of the jarosite. Not or insufficient washing of the jarosite filtercake results in a major loss of zinc in jarosite. Although the jarosite still contains valuable elements, their value is far too low for recycling.

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References

1. Ďud'a, R., Rejl, L., Slivka, D., 'Grote Mineralen Encyclopedie', Rebo Productions, Lisse, 1987, pp. 206-207 in Dutch. (Original titel 'La Grande Encyclopedie des Minéraux', Praag, 1986).

2. Bisshop, A.C., Woolley, A.R., Hamilton, W.R., 'Elsevier's Stenengids', 1978, in Dutch. (Original titel: 'The Hamlyn Guide to Minerals, Rocks and Fossils', The Hamlyn Publishing Group, 1954).

3. Dutrizac, J.E., Jambor, J.L., O'Reilly, J.B., 'Man's first use of jarosite: the pre-Roman mining-metallurgical operations at Rio Tinto, Spain', CIM Bulletin, November 1983, pp. 78-82.

4. Ashman, D.W., 'An industrial perspective of electrolytic zinc processing', in: Hiskey, J.B., Warren, G.W. (Eds.) Proc. Int. Symp. On Hydrometallurgy, Salt Lake City, Utah, August 1-5, 1993, pp. 63-81.

5. Dutrizac, J.E., 'The physical chemistry of iron precipitation in the zinc industry', in: Cigan, J.M., Mackey, T.S., O'Keefe, T.J. (Eds.) Proc. Lead-Zinc-Tin '80, Warrendale, Pennsylvania, pp. 532-564.

6. Chen, T.T., Cabri, L.J., 'Mineralogical overview of iron control in hydrometallurgical processing', In: Dutrizac, J.E., Monhemius, A.J. (Eds.) Proc. Int. Symp. on Iron Control in Hydrometallurgy, CIM, Toronto, 1989, pp. 22.

7. Scott, J.D., Donyina, D.K.A., Mouland, J.E., 'Iron -the good with the bad- Kidd Creek zinc plant experience', In: Dutrizac, J.E., Monhemius, A.J. (Eds.) Proc. Int. Symp. on Iron Control in Hydrometallurgy, CIM, Toronto, 1989, pp. 657-675.

8. Elgersma, F., Witkamp, G.J., Van Rosmalen, G.M., 'Incorporation of zinc in continuous jarosite precipitation', *Hydrometallurgy*, 33, 1993, Elsevier Science Publisher B.V., Amsterdam, pp. 313-339.

9. Berg, D., Børve, K., 'The disposal of iron residue at Norzinc and its impact on the environment', in: Dutrizac, J.E., Harris, G.B. (Eds.), Iron control and disposal (Proc.), CIM, Ottawa, 1996, pp. 627-642.

10. Pophanken, H., 'Constructing, operating and capping of the jarosite pond, Galing 1', in: Dutrizac, J.E., Harris, G.B. (Eds.), Iron control and disposal (Proc.), CIM, Ottawa, 1996, pp. 613-626.

11. Uusipaavalniemi, E., Karlman, S.-G., 'Handling of iron at the zinc plant in Kokkola', in: Dutrizac, J.E., Harris, G.B. (Eds.), Iron control and disposal (Proc.), CIM, Ottawa, 1996, pp. 101-115.

12. Tamargo, F.J., San Martin, F., Valcarcel, M.R., 'Asturiana de Zinc: more than thirty years of experience with the jarosite process', in: Dutrizac, J.E., Harris, G.B. (Eds.), Iron control and disposal (Proc.), CIM, Ottawa, 1996, pp. 93-100.

13. G. Van Weert, 'Hydrometallurgie deel B', lecture notes, TU Delft, Faculteit der Mijnbouwkunde en Petroleumwinning, January 1994, MP3310, Chp. 1, pp. 3.

14. Elgersma, F., 'Integrated hydrometallurgical jarosite treatment', Ph.D. thesis TU Delft, The Netherlands, 1992, pp.1-24.

15. Kreuzenkamp, A., 'Preparation process for an aqueous solution of zinc sulfate intended for zinc winning, by leaching calcine', Dutch patent no. 7705,374, 1977, in Dutch.

17. Pammenter, R.V., Kershaw, M.G., Horsham, T.R., 'The low-contaminant jarosite process - further developments, and the implementation of the process, In: Dutrizac, J.E., Monhemius, A.J. (Eds.) Proc. Int. Symp. on Iron Control in Hydrometallurgy, CIM, Toronto, 1989, pp. 603-617.

18. Dutrizac, J.E., Chen, T.T., 'A mineralogical study of the jarosite phase formed during the autoclave leaching of zinc concentrate', *Canadian Metallurgical Quarterly*, Vol. 23, No. 2, CIM, pp. 147-157, 1984.

19. Lastra, R.Q., 'Characterization of residues from a zinc plant', in Romig, A.D., Chambers, W.F. (Eds.), *Microbeam Analysis*, 1986, pp. 307-311.

20. Ding., M., 'Self-sealing/healing isolation and immobilization caused by chemical discontinuities in porous media', Ph.D. thesis, Utrecht University, The Netherlands, 1997, pp. 24.

21. Dutrizac, J.E., 'The behavior of impurities during jarosite precipitation', in Bautista, R.G. (Ed.), *Hydrometallurgical Process Fundamentals*, NATO conference series, VI Material Science, published in cooperation with NATO scientific affairs division, Plenum press, pp. 125-169.

22. 'Lime Prices & Stocks', 'London Prices', *Mining Journal*, 30 August 1996, pp. 169.

Chapter 3

An Integrated Jarosite- and Sludge Treatment Process

(published in 1996)

Abstract

Jarosite, a waste product of the zinc industry, contains high concentrations of heavy metals, such as lead and zinc. Usually this synthetic jarosite is stored near the refinery. Concern for the environment has led to the search for alternatives, still not very successful. This paper describes the research on the development of a reliable, integrated and efficient treatment process for jarosite waste. Sewage sludge and an alkaline are added to jarosite, and reacted under moderately elevated temperature and pressure. The sewage sludge creates reducing conditions. Solid products comprise magnetite, hematite and galena, whereas most of the sulfate and ammonia go into solution. The residual organics in the solids, containing the heavy metals and iron, are a benefit for their pyrometallurgical treatment, of which the final products are a metal concentrate and a high density slag. The non- or partially-oxidized organics in solution play an essential role in the subsequent biological reduction of sulfate and ammonia. The sulfate will be reduced to sulfur, creating an alkaline liquor which can be recycled in this jarosite/sludge-process. The ammonia will be reduced to nitrogen gas. The process costs of this waste-to-waste technology are compensated for by the gate fees for jarosite and sewage sludge.

Introduction

Jarosite

Many minerals contain zinc as a major component, but sphalerite (ZnS) is, by far, the most important ore mineral [1]. In general zinc ores contain 5 to 10 wt% sphalerite [2]. After milling and flotation the concentration of sphalerite is between 48 and 60 wt-% sphalerite. This concentrate is sold to zinc refineries [3]. Sphalerite concentrates usually contain also about 5 wt% iron, as an isomorphous substitution in sphalerite, and as pyrite (FeS_2) or arsenopyrite (AsFeS). Moreover, all concentrates contain impurities like lead, silver, zinc and copper. At the refinery concentrates are first roasted at 900 °C. During the roasting two major reactions occur simultaneously (1, 2).

$$2\,ZnS + 3\,O_2 \rightarrow 2\,ZnO + 2\,SO_2 \tag{1}$$

$$ZnS + 2\,FeS_2 + 7\,O_2 \rightarrow ZnO.Fe_2O_3 + 5\,SO_2 \tag{2}$$

Only the zincite (ZnO) is easily leachable in a neutral leach, dilute sulfuric acid at pH 3 to 5 and 70 °C (3). In order to maintain zinc recovery, nowadays franklinite ($ZnO.Fe_2O_3$) is leached in a hot acid leach, a pH of about 1 and a temperature of 95 °C. In this leach step iron will dissolve as well (4).

$$ZnO + 2\,H^+ \rightarrow Zn^{2+} + H_2O \tag{3}$$

$$ZnO.Fe_2O_3 + 8\,H^+ \rightarrow Zn^{2+} + 2\,Fe^{3+} + H_2O \tag{4}$$

For the electrowinning of zinc, iron has to be removed from the pregnant solution. Several processes have been developed in order to precipitate iron [4]. Jarosite-precipitation is in general use (5).

$$3\,Fe^{3+} + M^+ + 2\,SO_4^{2-} + 6\,H_2O \rightarrow MFe_3(SO_4)_2(OH)_6 + 6\,H^+ \tag{5}$$

M represents ions like NH_4^+, Na^+ [3]. The jarosite process is easy and low cost. Impurities like lead and silver are incorporated within jarosite; *M* can also be Ag^+ or ½ Pb^{2+}. Moreover, jarosite is an easily filterable solid. The major disadvantage is that it is chemical waste and has to be treated or stored. The jarosite process was developed in the 1960's and rapidly introduced in many zinc plants. In 1979 the world production of jarosite was about 2 million tons per year [5]. The amount of jarosite stored worldwide today is estimated at 50 million tons. In either pyrometallurgical- or hydrometallurgical techniques for the treatment of jarosite, sulfate is the major problem. Until now the developed techniques have been too expensive. The conversion of jarosite residues into compact hematite products at moderately elevated temperature has been investigated using autoclaves [6,7]. Pulp densities as high as 140 g/l of jarosite can be used. At a temperature of 225 °C the conversion is completed after two hours. Sulfuric acid and hematite seed can be added to enhance this reaction [8].

Sludge

Sewage systems collect waste water from homes and industries. Until a few years ago, it was common use to flush this water directly into surface waters This is no longer accepted. Sewage streams contains both organic and inorganic compounds, partly suspended and partly dissolved. Due to these different types of impurities, the purification of sewage sludge is rather complex. In general the suspended material is first separated from the liquid in a settling tank. Next, the effluent is treated by aerobic bacteria, removing the dissolved organic compounds. After a second settler, this water is flushed back into surface waters. Other purifying units, such as a phosphate-removal step or an ammonia removal step, are added when required. The suspended matter is usually treated by anaerobic bacteria, mainly to reduce the total amount of solids. Organics like proteins and fatty acids are transformed into carbon dioxide and water, while other organics like cellulose remain almost intact. Most of the solid inorganic compounds can be found in the solid as well [9]. To use this sludge as a fertiliser is no longer accepted for environmental reasons: it contains metals such as zinc and copper. In densely populated areas, such as Central Europe storage has become even more expensive than burning. An order of magnitude for costs for burning is US$ 400,- per ton dry matter.

For sludge treatment not only incineration furnaces are available, wet-oxidation processes have been developed as well. One of the processes is called the 'Porteous Process' [10]. The sludge is heated to a temperature of about 200 °C in an autoclave for one hour. This technique improves dehydrating properties of the sludge, but decreases the total mass of sludge only by about 10 %. The 'Zimmermann Process' [11] operates at a temperature between 200 °C and 300 °C, adding oxygen into the system. A process based on this technique has been operated near the City of Longmont, Colorado [10]. This system does not use an autoclave, but a long double tube with a length of 1200 m. This tube is placed vertically into the ground. The fluid column creates a pressure of 120 bar at the bottom. At this pressure the sludge will not boil, even at 280 °C, and the process operates in the liquid phase. The plant near Longmont is shut down in 1985, since it was a demonstration plant. A plant based on this technology is operational near Apeldoorn, the Netherlands, and is called VerTech® (Vertical Technology) [12, 13].

Aim

The aim of this work is to develop a reliable, integrated and efficient process dealing with historical as well as newly formed jarosite, using sewage sludge or any other organic waste-product containing cellulose. Using organic material is not only an innovative approach by changing the possibilities and products in jarosite treatment, it also contributes to the cost effectiveness of the process. Using sewage sludge as organic material could solve two problems simultaneously.

Materials and Methods

Procedure

Jarosite and sewage sludge were suspended in water in different ratios. Bases like MgO were added in order to influence the reactions, which took place in a pressure vessel.

Analysis of jarosite

Synthetic jarosite can be sais to be a kind of chemical sponge in which not only iron, but all kinds of metals precipitate. This behaviour is perfect to purify the pregnant solution before electrowinning of zinc, because this precipitation process is highly selective against zinc. Table 1 shows the chemical analyses of the major elements of Dutch (Budelco) and Spanish (Asturiana de Zinc) samples of jarosite. "Spanish" jarosite is used for most of the experiments. The composition varies with the composition of the ore and process-conditions. For analyses, the solids were standard dissolved in HF and diluted in 1 M HCl. Most elements were measured by ICP, except Ag and Cd, which were analysed by AAS. For the analyses of Si and As a borate-melt was prepared and the residue dissolved in 1 M HCl.

Analysis of sewage sludge

Sewage sludge is the waste product from sewage treatment. The sludge used during these experiments is representative of that treated at the VerTech plant. The solids were ground and the solid content was fixed at 5 weight percent. The composition varies from day to day, so a sample of 25 liter was taken. The analysis of this sludge is shown in Table 1. The sludge was stored at 2 °C to prevent biodegradation.

Other chemicals

To control the acidity of the reaction mixture a base was needed. In the early studies, industrial pure MgO was used, later ammonia. Demineralized water was used for diluting the suspensions.

The laboratory autoclave

The process requires a pressure vessel for the co-treatment of jarosite and sludge. A stirred Parr Mini Reactor, model 4563, consisting of an alloy 20 Cb bomb of 600 ml. was used. The reactor was equipped with a double, six-bladed turbine type impeller, connected with the motor by a magnet coupling, spinning at 480 rpm. The diameter of the impeller was 5 cm. A glass-liner, with a volume of 500 ml, was placed inside this reactor and standard filled for 70 vol%. A tube inserted in the liquid, in combination with a sampling chamber, made it possible

Table 1 - Analyses of Jarosites and Sewage Sludge in wt%, unless indicated

element	Dutch jarosite (Budelco)	Spanish jarosite (Asturiana de Zinc)	sewage sludge (VarTech)
C	n.d.	n.d.	27.8
N	1.0	0.9	5.9
Na	0.1	1.3	0.5
Mg	0.3	0.0	0.8
Si	8.5	2.7	4.9
P	n.d.	n.d.	3.1
S	15.0	11.2	0.8
Ca	1.3	0.3	2.6
Fe	22.6	26.7	1.3
Zn	2.8	2.7	0.1
Pb	5.7	3.5	< b.g.
dry-weight	61	60	95
Ag (ppm)	170	80	
Cd (ppm)	360	79	

n.d. = not detected

< b.g. = below detection limit

to take samples during the reaction. Valves on top of the reactor made it possible to flush the reactor with nitrogen gas. The starting pressure was 5 bar. The time needed for the autoclave to reach its setpoint was linear with the temperature: 20 minutes to reach 175 °C and 48 minutes to reach 300 °C. After the reaction the pressure vessel was quenched in water. As the process will be initially designed for a VerTech reactor the pulp density is fixed 20 wt-% at maximum.

Analyses

The liquid was separated from the solid by filtering over a 0.45 μm filter. The solid was washed twice with water and subsequently dried at 50 °C. It was then destructed in HF. Both the liquid and the destructed solid were diluted in 1 M HCl and measured by ICP-ES. Trace elements like silver and cadmium were analyzed by AAS. Ammonia, Chemical Oxygen Demand (COD) and Total organic Carbon (TOC) were analyzed by spectrophotometric techniques. Carbon and nitrogen in the solid phase were analyzed by a NCS-analyzer.

Minerals were determined by XRD-, SEM- and microprobe techniques. Total suspended tolids (TSS) and total dissolved solids TDS were analysed by weighing. Gases were analyzed by a gaschromatograph.

Results

Pulp density

To study the products and the reaction mechanisms, the first series of experiments was carried out at a temperature of 280 °C and a retention time of one hour. The pulp density was 20 wt-% at maximum. The theoretical over-all reduction reaction shows that 59 gram jarosite reacts with 1 gram cellulose (6). If all carbon present in sewage sludge is present as cellulose ($C_6H_{10}O_6$), then sludge contains 20.6 g cellulose per liter. So, in theory 1.2 liter of sludge contains enough cellulose to treat 1 kg jarosite. Since the maximum pulp density may not exceed 20 wt-%, in general 125 g jarosite was suspended in 500 ml sludge, which is an excess of 330 %. Water was used to fill up one liter. The total solid content was 15 wt%, leaving some capacity for the addition of chemicals.

$$44\, M\mathrm{Fe_3(SO_4)_2(OH)_6} + 2\, \mathrm{C_6H_{10}O_6} \rightarrow 44\, M^+ + 88\, \mathrm{SO_4^{2-}} + 44\, \mathrm{Fe_3O_4} + 132\, \mathrm{H^+} + 12\, \mathrm{CO_2} + 76\, \mathrm{H_2O} \qquad (6)$$

Influence of acidity

When the reaction between jarosite and sludge takes place without the addition of a base, the resulting acidity will dissolve part of the metals. When adding a base such as MgO or NH_4OH, the metals remain in the solid. Magnesium-ammonium-sulfate or ammonium-sulfate dissolves. Magnesium is an added compound, but a good neutralizing agent. Ammonia is already present. The reaction between jarosite, sludge and magnesiumoxide is shown in (7).

$$44\, M\mathrm{Fe_3(SO_4)_2(OH)_6} + 2\, \mathrm{C_6H_{10}O_6} + 66\, \mathrm{MgO} \rightarrow 44\, M^+ + 88\, \mathrm{SO_4^{2-}} + 44\, \mathrm{Fe_3O_4} + 66\, \mathrm{Mg^{2+}} + 12\, \mathrm{CO_2} + 142\, \mathrm{H_2O} \qquad (7)$$

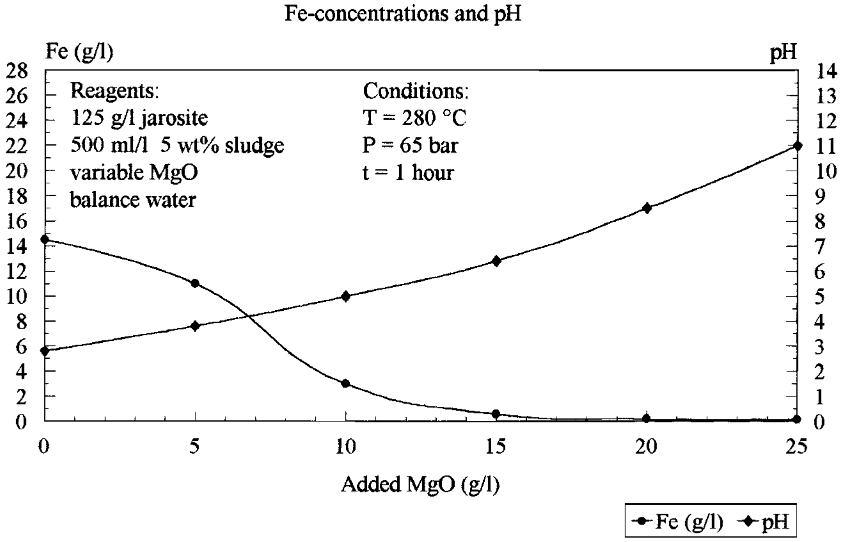

Fig. 1. Influence of the acidity; the effect of the amount of MgO added.

In six experiments increasing amounts of MgO were added, in seven other experiments increasing amounts of NH4OH. The graph of the results of the iron concentration and pH are shown as Figure 1 and Figure 2. When 15 g/l or more MgO is added, most of the iron remains in the solid. The same effect is shown when the concentration of ammonia is 13 g/l or more. The concentration of iron will not reach zero, since ammonia forms complexes with the iron. In contact with air these ferrous ammine ions are oxidized to the ferric state (8) [14].

$$4\ Fe(NH_3)_2^{2+} + O_2 + 8\ OH^- + 10\ H_2O \quad \rightarrow \quad 4\ Fe(OH)_3 + 8\ NH_4OH \qquad (8)$$

All the solid products were analysed by XRD. With acid conditions, the major components are hematite and anglesite. Under neutral and basic conditions however, the major products are magnetite and galena. The conclusion is that reducing conditions must be controlled by the acidity. SEM-analyses show that the minerals are completely intergrown and not suitable for magnetic separation techniques.

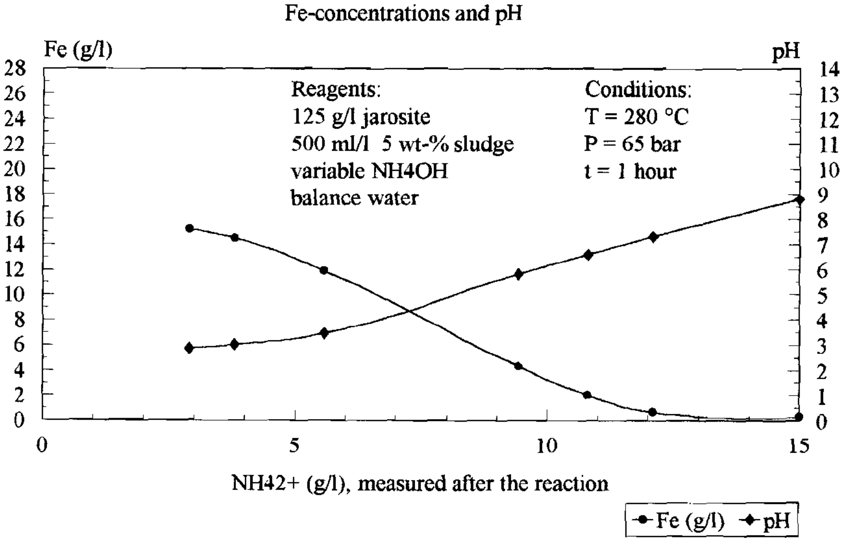

Fig. 2. Influence of the acidity; the effect of the amount of NH_4OH added.

Mass-balance of the reaction with MgO

125 g dry jarosite, 15 g MgO and 500 ml 5 wt% sewage sludge and water were mixed to give one liter. After a retention time of one hour at 280 °C, the reactor was quenched and the reaction products sampled and analyzed. The input was compared with the output and the deviation and the balance calculated. Table 2 shows the general analyses. The gases contained about 5 vol% not combusted organic compounds, such as methane, ethane and ethene. Table 3 shows the distribution of compounds in the liquid and the solid phase. The input of the most important compounds is compared with the output after the reaction. The calculated deviations show the analytical and experimental error. The deviations do not exceed an error of 5 wt%, except for carbon. Part of the carbon is oxidized and transformed into carbondioxide, which is released when opening the autoclave. This mass-balance also makes clear that most of the sulfur is transformed from the solid into the liquid. The sulfur remaining in the solid is bounded as galena and gypsum. Ammonia as well is removed from the solid, however, most of the ammonia originates from the sludge, not from the jarosite. Magnesium and potassium are for the greater part dissolved; the other metals remain in the solid.

Table 2 - Other Analyses of a Characteristic Reaction With MgO as a Base

TSS (Total Suspended Solids):	87 g/l
TDS (Total dissolved Solids):	67 g/l
Eh_{end}, against H_2:	0.48 V
pH_{end}:	6.5
Minerals detected by XRD:	major: magnetite/franklinite/magnesioferrite, hematite minor: galena, anglesite, gypsum
SEM-analyses:	minerals are intergrown
Particle size:	1-5 μm
Off gas:	> 95 vol-% carbondioxide. The rest is a mixture of different gasses like methane, ethane, hydrogen etc.
Residue, $\%H_2O$ after filtration:	50 wt%

Retention time and temperature

To study the kinetics, three liters of 'standard-reaction fluid' were prepared, containing 125 g/l dry jarosite, 500 ml/l 5 wt-% sludge, 15 g/l MgO and water and stored at 2 °C. Each experiment, using 335 ml reaction fluid, was sampled 5 times. In total six experiments were performed at six different temperatures, varying from 175 °C till 300 °C. One method to follow the kinetics is to measure the sulfate concentration. Sulfate is the only component in jarosite that dissolves during the reaction and which is present in all jarosite structures. Reduction of sulfate is neglectable compared to the sulfate concentration. The graph of the results is shown in Figure 3.

At $t = 0$ the autoclave has reached its adjusted temperature, its setpoint. When interpreting these results, it must be noted that under the conditions used, some reaction already occurred during the heating-up period. After reaching the setpoint of 250 °C, the conversion is completed within a few minutes. Increase of the setpoint of the autoclave beyond 250 °C is therefor of limited value for kinetic studies; above this temperature the reaction is probably diffusion limited at the conditions as described.

Table 3 - Mass-Balance of a Characteristic Reaction With MgO as a Base

	INPUT			OUTPUT			deviation
element	500 ml/l sludge (g/l)	125 g/l jarosite (wt-%)	total TS (g/l)	liquid (g/l)	solid (wt-%)	total TS (g/l)	(%)
S (total)	0.4	11.2	14.2	12.3	2.1	14	-1.3
Fe	0.1	22.6	28.3	0.5	33.9	29.7	5.0
Zn	0	2.8	3.5	0	4.2	3.6	3.4
Pb	0	3.5	4.4	0	5.2	4.5	2.8
Mg	0.4	0	9.2*	8.5	1	9.4	1.7
NH4	3.8	1.2	3.4	3	0.5	3.4	0.4
Ca	1.3	0.9	1.8	0.6	1.6	1.9	5.0
C	27.8	0	14	0.8	3.5	3.8	-72.6

	INPUT-BALANCE		OUTPUT-BALANCE	
element	liquid (wt-%)	solid (wt-%)	liquid (wt-%)	solid (wt-%)
S (total)	2	98	86	14
Fe	0	100	1	99
Zn	0	100	0	100
Pb	0	100	0	100
Mg	100	0	89	11
NH4	56	44	86	14
Ca	35	65	26	74
C	100	0	5	22

* 15 g/l MgO added

Heat balance

The difference in Chemical Oxygen Demand (COD) between the suspension before and after the reaction is a measure for the heat released from an exothermal reaction. Recent research shows that 13 MJ heat can be released per kg COD, within a margin of 10 % [14]. So, a way to calculate the heat balance is to measure the difference in COD. The COD of the 'standard reaction fluid' was 20 g O_2/l; after the reaction the COD of the slurry was 7.5 g O_2/l. During this reaction 160 KJ/l heat was assumed released. VerTech's experience in wet oxidation shows that when the decrease in COD is 10 g/l or more, the reaction is able to maintain itself [16].

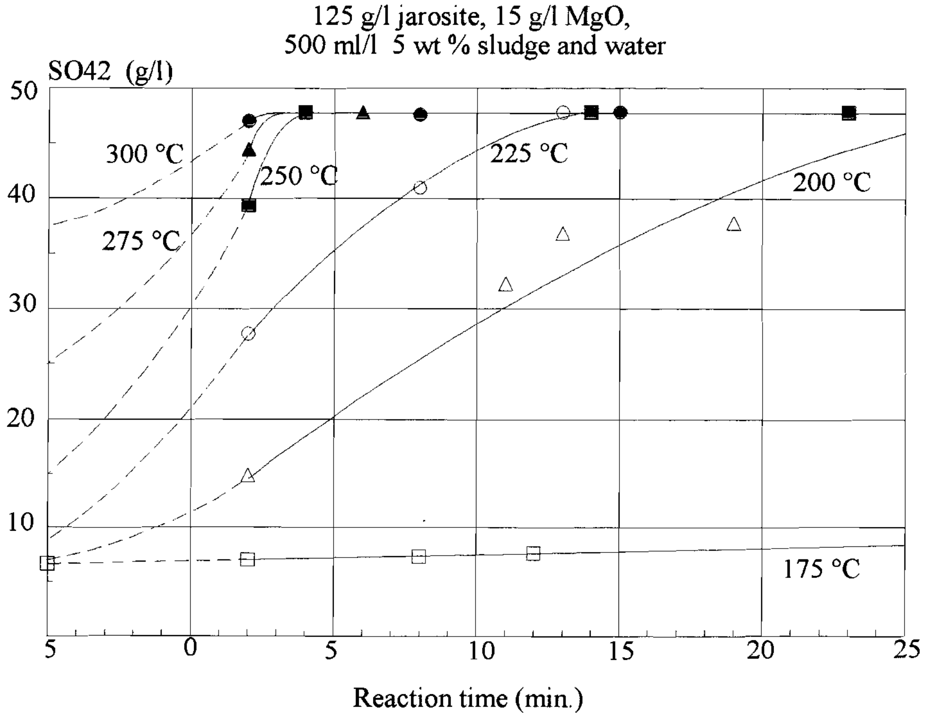

Fig. 3. Sulphate formation as indicator of reaction kinetics. Time 0 is the attainment of reaction temperature.

Discussion of the testwork and conclusions

Jarosite is broken down under reductive conditions created by the partial hydrolysis and oxidation of organic waste. The heat released from this oxidation is probably enough for the reaction to maintain itself in a countercurrent i.e. VerTech reator. The reducing conditions can be controlled by the acidity and the amount of sewage sludge. Due to the low acidity the minerals change in composition. Magnetite instead of hematite and galena instead of anglesite are produced. Organics are transformed into carbondioxide, carbon and dissolved products. These minerals and the non oxidized organics in the solid are of benefit to further pyrometallurgical solid residue treatment. The organics remaining in the liquid play an essential role in the biological effluent treatment.

Further processing

Preamble

Hypothetically it should be possible to separate ammonia and sulfate from the metals. Ammonia and sulfate can be processed in a second and third reaction step. All metals are concentrated in the remaining solid and thereby the possibilities for further processing are highly increased. Dutrizac et al [6,7] realised this partly, starting from a laboratorium-made, pure ammoniumjarosite. A liquid from a waste jarosite would still contain measurable amounts of zinc in addition to ammonium and sulfate.

Process step 1; treatment of jarosite and sludge

Since the aim of this study is the development of an integrated jarosite- and sludge-treatment process, a preliminary flowsheet is presented. After autoclaving the solid is separated from the liquid. The solid, containing 50 wt-% effluent has to be washed. After filtering, the residue is ready for further treatment (see step 3). The effluent contains ferrous ammine complexes, so it has to be oxygenated. After a second solid/liquid separation the effluent is ready for further processing by existing technologies. The gases contain too much organic carbon, so they have to be burnt. The process of co-treatment of metallurgical wastes with organic sludges is patented by Geochem Research BV [17].

Process step 2; removal of sulfate from the effluent

The effluent contains about 35 g/l sulfate, 15 g/l ammonia and 1 g/l dissolved organic compounds. It is not allowed to discharge this liquid into surface waters, so it has to be treated. Sulfate can be removed from the system by the addition of $Ca(OH)_2$, producing gypsum. Limestone has to be boughed. Another option is the reduction of sulfate to sulfur by bacteria is a new technology. It is a two-step reaction. In the first, anaerobic step sulfate is reduced to hydrogen sulfide and in the second, aerobic step hydrogen sulfide is oxidized to elementary sulfur (9, 10)

$$2\,NH_4^+ + SO_4^{2-} + 4[H_2] \rightarrow 2\,NH_4^+ + HS^- + OH^- + 3\,H_2O \qquad (9)$$

$$2\,NH_4^+ + 2\,HS^- + O2 \rightarrow 2\,NH_4^+ + 2\,S^0 + 2\,OH^- \qquad (10)$$

Instead of having to buy ammonia or ammoniumhydroxide, the system permits in process recovery. The residual organics in the liquid are a nutrient in this biological process; a small, additional carbon source can be added if required. A desulphating reactor is operational at

Budelco (the Netherlands) for sulfate-concentrations up to 500 mg/l. Ethanol is added in this system. [18]. Kennecott (USA) runs a pilot plant handling about 10 g/l sulfate, using newer technology involving the use of H_2/CO_2 gas mixture as reductant. In order to use this process, the effluent of this jarosite-sludge treatment process has to be diluted four times.

Process step 3; thermal treatment of the solid residue

To treat the solid residue, several options are available. One option is reductive melting at 1400 °C, whereby the metals are separated from the solid into the vapour phase (Table 4) [19]. The final product is a high density slag, containing those oxides which are difficult to reduce such as silica, alumina and calcium- and magnesiumoxide. The iron ends up in this slag. A similar process has recently been developed for the treatment of goethite [20]. A useful slag product would be one that is close to basalt-type material in composition. To achieve this composition (Table 5) about 70 kg sand per ton residue has to be added. A second option is thermal treatment at temperatures below 1000 °C using chlorination to remove the metals. In both cases the metals like lead, silver and zinc are concentrated and a grannular product with acceptable environmental qualities is produced.

Table 4 -	Composition of the vapour concensate in wt%
Zn	31
Pb	34
Ag	0.1
Cd	0.4

Table 5 -	Composition of the slag with iron reduction and sand addition in wt%
SiO_2	42
Al_2O_3	23
CaO	11
MgO	10
FeO	14

A number of smelting systems exists for the reductive smelting, examples are the Outokumpu flash furnace and KHD's cyclone reactor. They form part of existing metallurgical operations and are considered proven technology.

Process step 4; removal of ammonium from the effluent

The water, originating from the jarosite and the sludge has to be purified and released into surface waters. The main component is ammonia, which can be bacterially transformed into nitrogen. Again this is a two-step reaction. First ammonia is oxidized to nitrate (11) and the nitrate is subsequently reduced to nitrogen gas (12), which can be released to the atmosphere [21]. A preliminary flowsheet of the complete process is shown in Figure 4, including a mass balance.

$$2\ NH_4^{2-} + 5\ O_2 \rightarrow 2\ NO_3^- + 4\ H_2O \qquad (11)$$

$$2\ NO_3^- + 12\ H^+ \rightarrow N_2 + 6\ H_2O \qquad (12)$$

Acknowledgments

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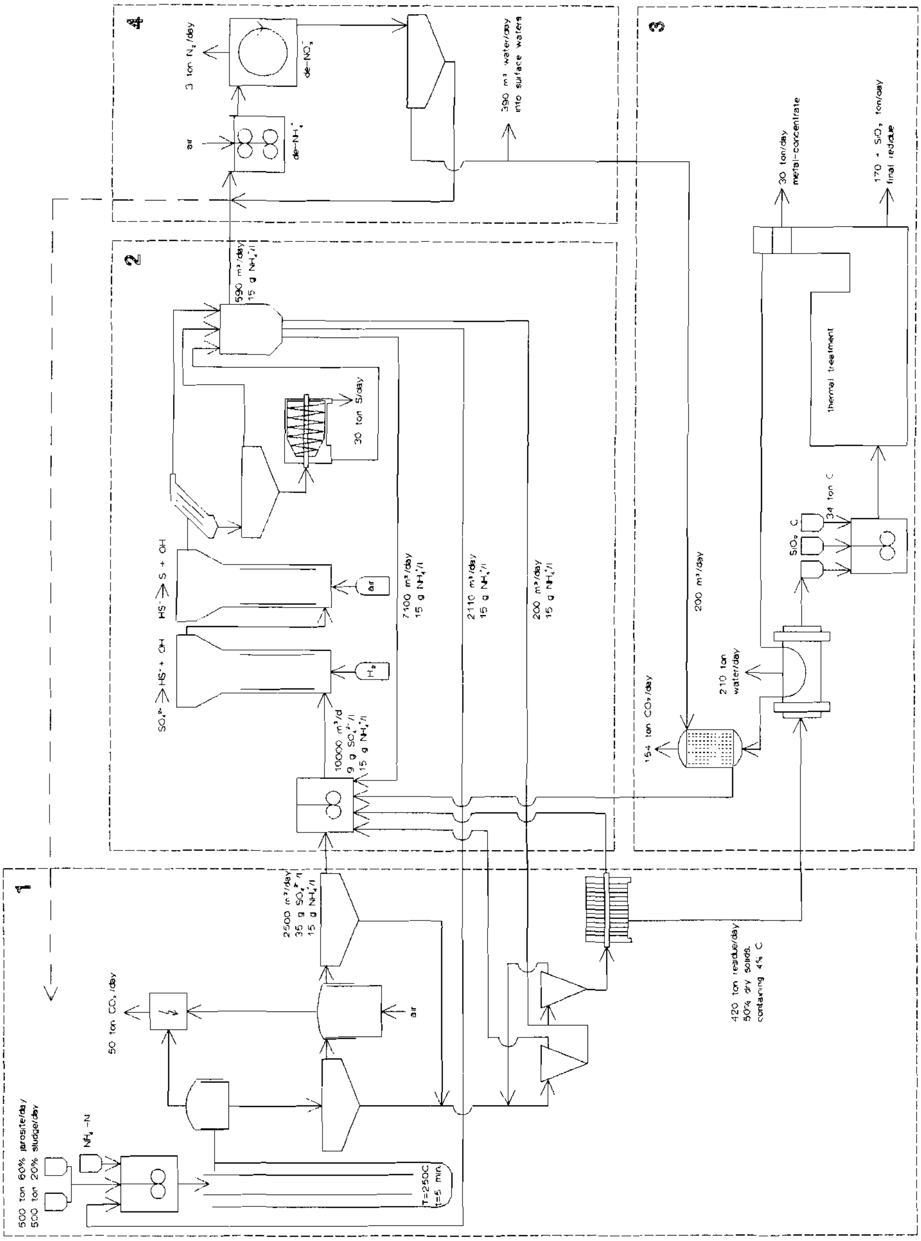


Fig. 4. - Preliminair flowsheet of an integrated jarosite- and sludge treatment process on a daily scale, based on a capacity of 100 Kton jarosite per year.

References

1. Jolly, J.H., 'Zinc', Mineral Facts and Problems, 1985 edition, Bureau of Mines Bulletin 675, 923-940.

2. Rodier, D.D., 'An overview of silver and trace metal recovery strategies in the zinc industry', in: Mackey T.S. and Prengaman R.D. (Eds.) Proc. Lead-Zinc'90, Conf. Proc. of the TMS-AIME World Symp. on Pb, Zn, TMS-Warrendale, 1990, pp. 57-85.

3. Elgersma, F., 'Integrated Hydrometallurgical Jarosite Treatment', Ph.D. Thesis, University of Delft, 1992, the Netherlands, pp. 1-13.

4. Dutrizac, J.E., 'The physical chemistry of iron precipitation in the zinc industry', in: T.S. Mackey and R.D. Prengaman (Eds.) Proc. Lead-Zinc'90, Conf. Proc. of the TMS-AIME World Symp. on Pb, Zn, TMS-Warrendale, 1990, pp. 532-564.

5. Arregui, V., Gordon, A.R., Steintveit, G., 'The Jarosite Process - Past, Present and Future', in: Mackey T.S. and Prengaman R.D. (Eds.) Proc. Lead-Zinc'90, Conf. Proc. of the TMS-AIME World Symp. on Pb, Zn, TMS-Warrendale, 1990, pp. 97-123.

6. Dutrizac, J.E., 'Converting Jarosite Residues into Compact Hematite Products', *JOM*, January 1990, pp. 36-39.

7. Dutrizac, J.E., 'The Hydrothermal Conversion of Jarosite-Type Compounds to Hematite', in: Koch, M., Taylor, J.C. (Eds.), Productivity and Technology in the Metallurgical Industries, Warrendale, PA:TMS, 1989, pp. 587-612.

8. Dutrizac, J.E., 'The effect of seeding on the rate of precipitation of ammonium jarosite and sodium jarosite', *Hydrometallurgy*, Vol. 42, 1996, pp. 293-312.

9. Koot, A.C., Behandeling van Afvalwater, second edition, 1980, ISBN 9021231727, 88-106.

10. Koot, A.C., Behandeling van Afvalwater, second edition, 1980, ISBN 9021231727, 308-335.

11. Opatken, E.J., 'Aqueous-Phase Oxidation of Sludge Using the Vertical Reaction Vessel System', EPA/600/2-87/022, PB87-170320/AS, 1987.

12. Tessel, P., De Bekker, P., Bowers, D., 'The VerTech Aqueous Phase Oxidation System Meets Veluwe, Holland's Long Term Sludge Management Requirements', presented as a poster session at the 1991 WPCF/AWWA Joint Residual Management Conference Research Triangle Park, North Carolina, USA, August 1991.

13. De Bekker, P., Van den Berg, J., Heerema, K., 'Het VerTech slibverwerkingsproces', *H_2O*, 21, 1988, 94-98, the Netherlands, in Dutch.

14. Van Weert, G., 'Hydrometallurgy', part B, January 1994, lecture notes, University of Delft, the Netherlands.

15. Wouda, T.W.M., Boleij, F.M., 'Het CZV als maat voor de stookwaarde van zuiveringsslib', *H_2O*, Vol. 22, pp. 54-58, 1989, the Netherlands.

16. Tessel, P., Private communication with the author, VerTech treatment systems BV, February 1996, the Netherlands.

17. Request for patent application No. 1001390, October 10, 1995, Geochem Research B.V., the Netherlands.

18. De Vegt, A.L., Buisman, C.J.N., 'Full Scale Biological Treatment of Heavy Metal Contaminated Groundwater', Treatment and Minimization of Heavy Metal-Containing Wastes, a publication of TMS, 1995, pp. 69-79.

19. Roorda, H.J., Hermans, J.M.A., Van Weert, G., 'Extractive Metallurgy I', September 1991, lecture notes, University of Delft, the Netherlands

20. Plescia, P., Maccari, D., 'Recovering Metals from Red Mud by Thermal Treatment and Magnetic Separation', *JOM*, January 1996.

21. Koot, A.C., Behandeling van Afvalwater, second edition, 1980, ISBN 9021231727, 165-174.

Chapter 4

Comparative Column Elution of Jarosite Waste and its Autoclaved Product

Evidence for the Immobilization of Deleterious Elements in Jarosite

Abstract

Jarosite waste, originating from the zinc industry using hydrometallurgical processing routes, is considered hazardous. Metals such as zinc, cadmium and copper are present in an environmentally mobile form, thus the jarosite waste is usually stored in lined ponds. Autoclaving of this material with a cellulose type waste material, such as sewage sludge, with the addition of a neutralizing agent will transform most of the metals into oxides, which are immobile under neutral conditions. Jarosite waste and its treated product were tested in standard column tests, as prescribed by Dutch legislation if the material is to be used as construction material. In three weeks time an amount of simulated rainwater, equal to ten times the weight of the solid, was percolated through the samples. The moisture content of jarosite waste is about 40 wt%, reflecting the leach liquor from the zinc refining process; its solutes are easily leached out. This leach liquor initially contained high concentrations of Zn, Cu and Cd, but when a liquid/solid ratio of two (L/S=2) was reached, most of these metals were removed from the jarosite waste. Co-treatment of jarosite with sewage sludge yields a product which is far more acceptable. Even so, the leached amounts of zinc and cadmium do not match the Dutch criteria for second-grade construction material. Counter current washing of the residue improves its properties as a construction material, although the best environmental option for the solid residue is further (thermal) treatment [1].

Introduction

Jarosite ($M\text{Fe}_3[\text{SO}_4]_2[\text{OH}]_6$ in which M stands for cations such as NH_4^+, Na^+, $\frac{1}{2}Pb^{2+}$) is formed in hydrometallurgical processing routes of the zinc industry. The jarosite is precipitated to purify the pregnant leach liquors. On account of leachable metals, this material is considered as hazardous waste, therefore jarosite is usually stored in lined ponds close to the zinc refinery [2]. With or without liners, pollution of the subsurface and groundwater with metals is only a matter of time, because these liners are only guaranteed for a limited number of years. A zinc plant in the Netherlands, Budelco, has four jarosite ponds, of which two are already leaking. The plant must control the groundwater and currently treats it biochemically [2]. Lined ponds are a temporary option and the search for alternatives continues. Washing of jarosite is a possibility to decrease the environmental threat of jarosite and to improve the recovery of zinc. Nevertheless, this is an expensive operation and will have unwanted impact on the water balance of a zinc plant. Besides, the jarosite still has to be stored in lined ponds.

The new treatment process of jarosite with sewage sludge is a promising and more permanent waste treatment technology, which was developed in the Brite Euram Program of the European Community under project number BE-7673-93 [4]. Sewage sludge is the waste product of sewage treatment plants, which is usually dried and subsequently burned in suitable incinerators. The main technical reasons of this new approach to use sewage sludge are to gain energy and to create reducing conditions. Acid is generated during the reaction and a neutralizing agent is required to influence the reduction, and to prevent the dissolution of metals. In an autoclave at a temperature of 250 °C and a retention time of 10 minutes, jarosite breaks down to a solid containing iron- and metal oxides; sulfate and ammonium are dissolved. A solid/liquid separation step is part of the process. Since the concentrations of sulfate and ammonia in the effluent are too high to be discharged into surface waters, further treatment is required. The sulfate from the solution is precipitated as gypsum and the ammonium is subsequently stripped from the liquid. In a water contact process, a 25 wt% NH_4OH is produced, which is recycled as a neutralizing agent over the pressure vessel.

The reduction of jarosite critically depends on several parameters [5]. Usually a combination of hematite (Fe_2O_3) / magnetite (Fe_3O_4) and anglesite ($PbSO_4$) / galena (PbS) is produced. The XRD powder pattern of a typical, well reduced product is shown in figure 1. Major compounds are magnetite, galena and quartz. Figure 2 shows a few photographs made with a scanning electron microscope (SEM) of some typical minerals present in the residue. Amorphous silica and franklinite particles are already present in the jarosite. Crystalline quartz particles are originating from the sewage sludge. In theory, the hazardous metals are immobilized during the reaction. Immobilized waste has potential as construction material. Cement, for example, contains 3-5 wt% iron oxides [6], [7]. Nevertheless, the restrictions for this application are high. In the Netherlands, a leach test is part of the common procedures for these materials. If this autoclaved material is to be used as construction material, it should at least be tested in a leach experiment. In the research described here, the leaching behavior of jarosite is compared to that of treated jarosite.

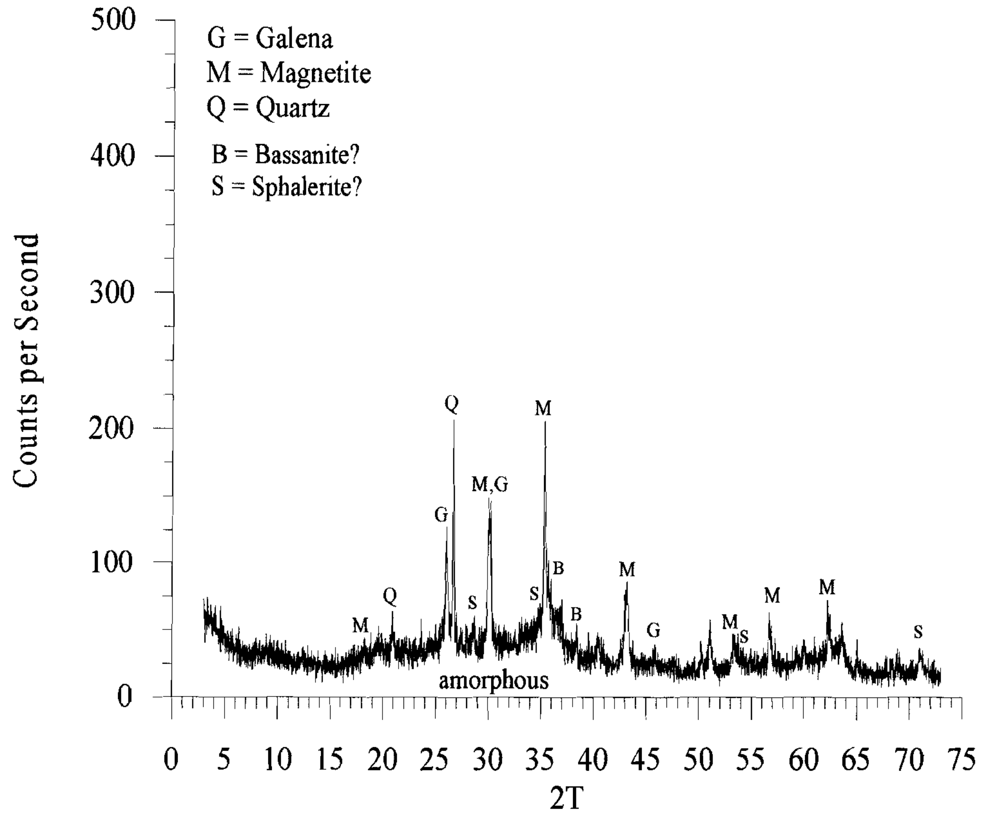
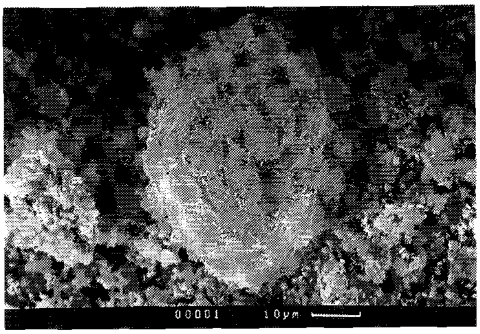


Fig. 1. Typical XRD powder pattern of well reduced jarosite waste with sewage sludge. 'Amorphous' defines material which shows up as a bulge in the powder pattern.

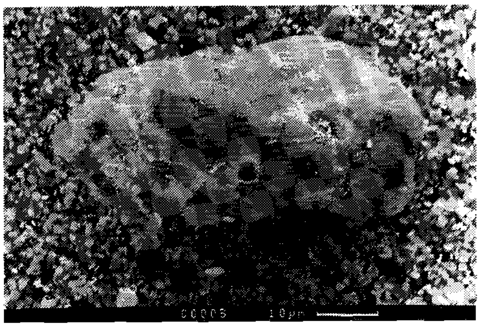
Table 1 - Recipe for jarosite treatment with sewage sludge in an autoclave

sewage sludge á 5 wt% solids:	5 liter
jarosite:	1250 gr.
ammonia:	400 ml.
water:	≈ 4 liter
	----------
total:	10 liter

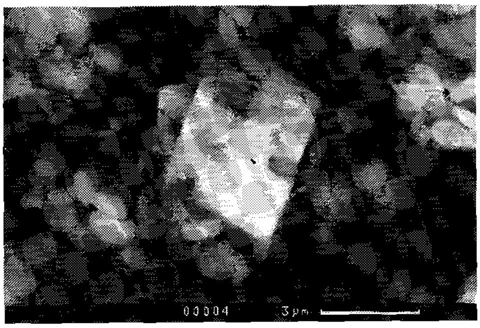
t = 1 hour
T = 250 °C



Silica (SiO_2) particle, not attaked during autoclaving



Franklinite ($ZnFe_2O_4$) particle, not attaked during autoclaving



Anglesite ($PbSO_4$) crystal, produced during autoclaving. Jarosite skeletals of iron oxides are spread around

Fig. 2. Typical particles in treated jarosite waste material, determined by SEM analyses

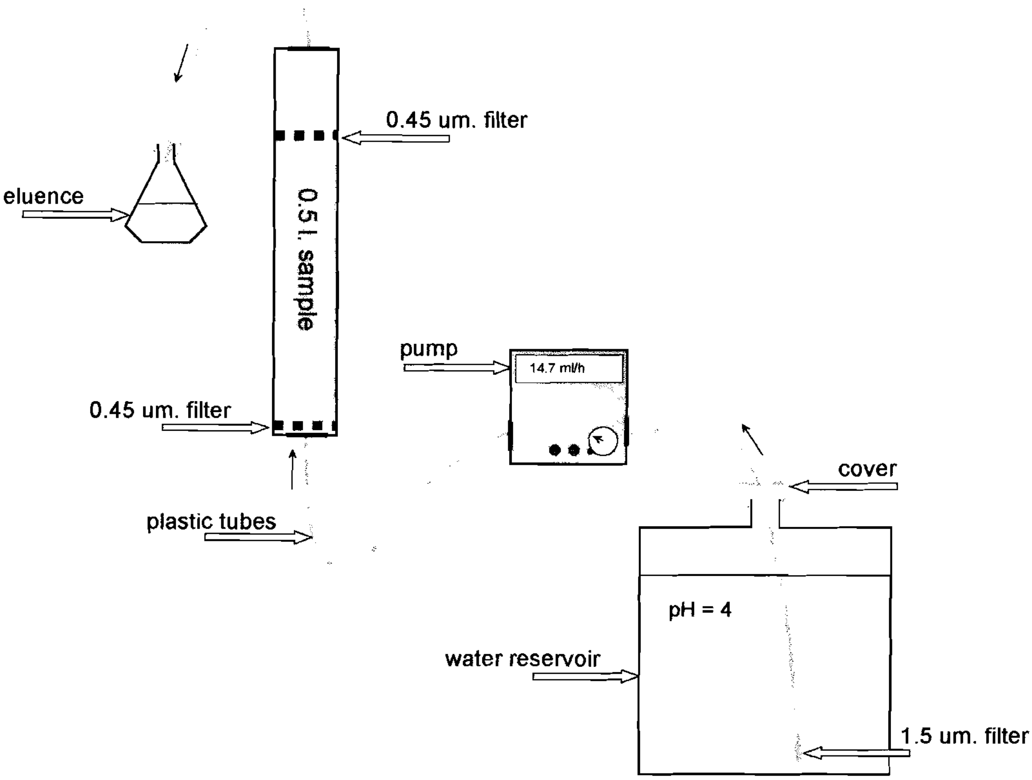


Fig. 3. Schematical view of the column set up used during the leach expermients

Methods

First, a sample of autoclaved jarosite waste was prepared. The composition of the reaction fluid and the reaction conditions are shown in Table 1; the composition of jarosite and sludge are shown in Table 5. The jarosite was not washed before the preparation of the reaction fluid, thus it still includes soluble zinc compounds. In total 10 liter material is to be prepared. As the size of the used autoclave was 1.7 liter (filled with 1.2 liter reaction fluid), several batches had to be prepared, which were mixed afterwards. After separating the solid from the liquid, the treated jarosite was washed three times in a parallel system. The product was suspended in 1 liter doubly distilled water, filtered under 6 bar pressure air, resuspended in 1 liter water, filtered, resuspended and filtered again. After this treatment, the moisture content of the sample is about 45 wt%. To prevent chemical reactions or the evaporation of certain compounds, the jarosite sample as well as the residue sample were dried at 40 °C for 48 hours. After drying, the samples were gently crushed and sieved. Exactly 0.5 liter material with a particle conglomerate size between 1 and 2 millimeter (or less) was prepared for the leach tests. The leach columns had a diameter of 5 cm and a length of 70 cm. Membrane filters with a pore size of 0.45 μm were used at the bottom and the top of the column. About 20 liter doubly distilled water was prepared for pumping through the solids. The pH was set at 4 with HNO_3, which is a common way to simulate (acid) rain water. All solutions were transported through poly-ethylene tubes. The simulated rain water was filtered over a filter with a pore size of 1.5 μm, which was placed at the beginning of the tube system. A peristaltic pump was used with a maximum capacity of 50 ml/h. All equipment was washed in dilute HNO_3 prior to usage. A schematical view of the set up for a leach experiment is shown in Figure 3. The flow of the pump is set according to Formula 1. After a certain L/S ratio was used, the sampling bottle was replaced. At normal use it takes at least 3 weeks to pump an amount of liquid through the sample which is ten times the mass of it. The mass of the liquid divided by the mass of the solid is called the L/S ratio. The tests were performed at room temperature. The liquids were analysed by ICP-AES and spectroscopic methods; after destruction, the solids were analysed by ICP-AES as well. This leach test is conform Dutch legislation [8].

Formula 1 - Calculation of the flow of the leach liquor through the samples

$$q \leq a * m_0$$

q = flow of the pump (l/h); the minimal leach time up to and including L/S=10 is three weeks
a = 0.025 l/kg·h
m_0 = mass of the original sample in kg

Results

In Table 2 the analyses of detectable elements in the effluent and the results of the three washing steps are shown. The results of the effluent show that even after autoclaving, a significant part of the zinc is still leachable. Washing of the residue removes mainly sulfate and zinc.

Table 2 - Analyses of the effluent and the washing liquids of the autoclaved jarosite in mg/l

element	effluent	wash I	wash II	wash III
S	13,300	3200	925	395
Zn	825	82.0	6.4	1.0
Mn	9.4	6.4	1.9	1.1
Fe	2.0	0.3	< 0.05	< 0.05
Mg	183	85	17	7.1
Ca	521	121	64	92
NH_4	13,700	n.d.	n.d.	n.d.
TOC	900	n.d.	n.d.	n.d.
pH	8.9	8.6	8.5	8.3

n.d. not determined

The jarosite and its autoclaved product were both leached in column experiments. Table 3 shows the conditions of the performed leach tests. After three weeks of leaching a liquid/solid ratio of ten (L/S=10) was reached; the calculated water flows are also given in table 3. The leached water was sampled in bottles, which are replaced after a certain L/S ratio was reached. The pH values of the leached fractions (L/S ratio's) are shown in Figure 4. These fractions were analysed by ICP-AES; the most relevant graphs are shown in figure 5. The cumulative leach of each component was calculated and shown in table 4. The leach liquor of the jarosite waste contains mainly S (as sulfate), Fe and Ca with Zn, Cu, As and Cd, the major deleterious elements. Zinc sulfate is present in the free moisture of jarosite and is easily washed out, as are cadmium- and copper sulfate. The high release of iron is due to the low pH (figure 4). Bassanite ($CaSO_4 \cdot ½H_2O$) is slowly dissolved. Al and Mg follows the same trend as most of the elements such as sulfate and zinc: at L/S=2 the major part of these elements are leached out. After the jarosite is treated at 250 °C, most of the elements are immobilized. Nevertheless, elements like sulfate and calcium are leached out for a large part from the treated jarosite. Fe, Al, As, P, Co, Cr, Ti, Pb and Sb are almost completely immobilized. The unwanted metals Cu, Cd, B, Sn and Ni are leached slowly, while Zn is of more serious concern. Si and Mg are leached out partly, but are no threat to the environment. Table 5 shows the analyses of the solids before and after leaching. This table confirms the results of the cumulative analyses.

Table 3 - Leach test data of jarosite waste and its autoclaved product

sample	weight (in 0.5 liter)	water flow	L/S=1	L/S=10
jarosite	558 gram	11.2 ml/h	50 hour	500 hour (~21 days)
product	260 gram	5.2 ml/h	50 hour	500 hour (~21 days)

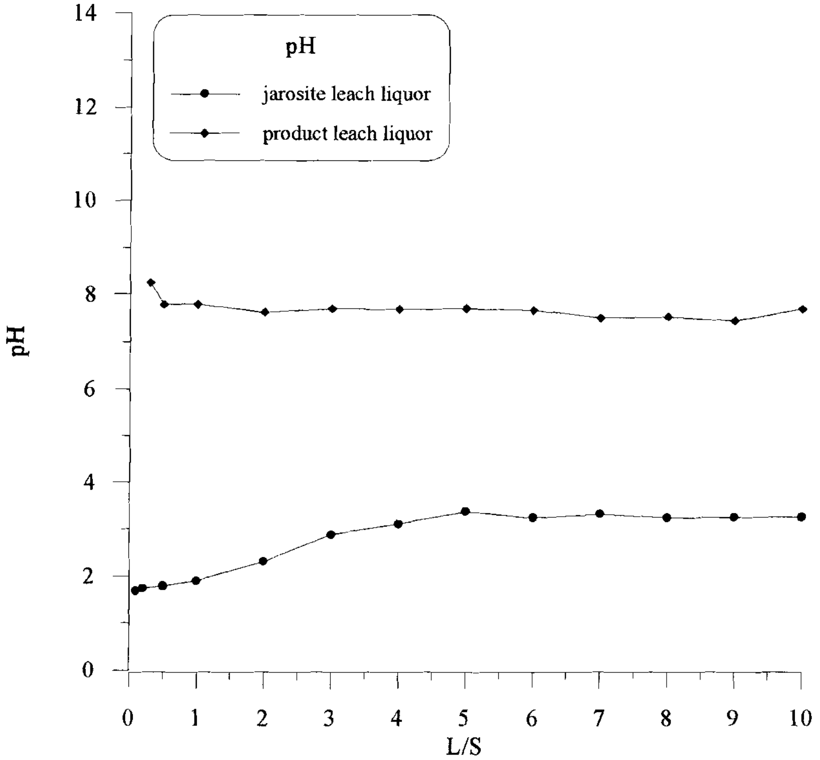


Fig. 4. pH values of the leach liquors from jarosite and its autoclaved product

Table 4 - The measured elements were multiplied with the water fraction and summarized. The cumulative leached amounts are shown in (mg/kg) and are up to and including L/S=10.Included in this table are the DutchU1 and U2 standards for building material.

element	jarosite	product	U1	U2
SO_4	150,000	24,000	750	10,000
Zn	42,000	68	3.8	15
Fe (0.05)*	11,000	< 0.46	n.r.	n.r.
Ca	4,800	5,650	n.r.	n.r.
Mg	4,100	103	n.r.	n.r.
Cu	1,750	1.8	0.72	3.5
Mn	1,375	118	n.r.	n.r.
Al (0.15)	1,200	< 1.38	n.r.	n.r.
As (0.2)	402	< 1.84	0.88	7.0
Cd	203	0.89	0.03	0.07
Si	113	64	n.r.	n.r.
P (0.25)	107	< 3.67	n.r.	n.r.
Co (0.05)	14	< 0.46	0.42	2.5
B	13	1.5	n.r.	n.r.
Sn	11	8.7	n.r.	n.r.
Ni	6.8	1.7	1.1	3.7
Cr (0.05)	6.8	< 0.46	1.3	12
Ti (0.1)	6.4	< 0.92	n.r.	n.r.
Pb (0.25)	5.5	< 2.29	0.8	8
Sb (0.1)	3.6	< 0.92	1.9	8.7
NH_4 #	23	430	n.r.	n.r.

*	The numbers between brackets are the determination limits of the ICP-AES apparatus.
#	analysed by spectroscopic techniques
U1	Dutch standard for building material without restrictions.
U2	Dutch standard for building material with restrictions.
n.r.	no restrictions

Table 5 - Analyses of the solids in wt% of jarosite and its autoclaved product before and after leaching and sludge.

element	jarosite	sludge	jarosite after leaching	product	product after leaching
Fe	21.1	1.30	27.2	30.9	34.9
S	12.4	0.81	11.0	1.25	1.29
Zn	6.00	0.08	1.66	8.17	8.66
Pb	3.54	n.d.	4.72	4.97	5.70
Al	0.57	n.d.	0.61	1.74	2.00
Ca	0.61	2.59	0.06	1.65	0.56
Cu	0.42	n.d.	0.35	0.57	0.66
P (0.25) *	< 0.02	3.07	< 0.03	0.89	0.99
Cd (0.1)	< 0.003	n.d.	< 0.005	< 0.006	< 0.007
B	0.06	n.d.	0.09	0.08	0.13
Ba	0.06	n.d.	0.08	0.22	0.26
K	0.08	n.d.	0.12	0.11	0.12
Mg	0.40	0.79	0.01	0.38	0.32
Mn	0.10	n.d.	< 0.01	0.15	0.10
Na	0.12	n.d.	0.16	0.26	0.13
Sb	0.04	n.d.	0.05	0.06	0.06
Sn	0.01	n.d.	0.01	0.02	0.01
Sr	0.01	n.d.	0.01	0.02	0.02
Ti	0.02	n.d.	0.03	0.06	0.07
As	0.20	n.d.	0.25	0.27	0.31
Si	2.7	4.88	n.d.	n.d.	n.d.
C #	0.05	27.8	n.d.	4.1	n.d.
N #	0.9	5.6	n.d.	0.3	n.d.
Dry weight	60	5	n.d.	n.d.	n.d.

* The numbers between brackets are the determination limits of the ICP-AES apparatus

analysed with a NCS analysing apparatus

n.d. not determined

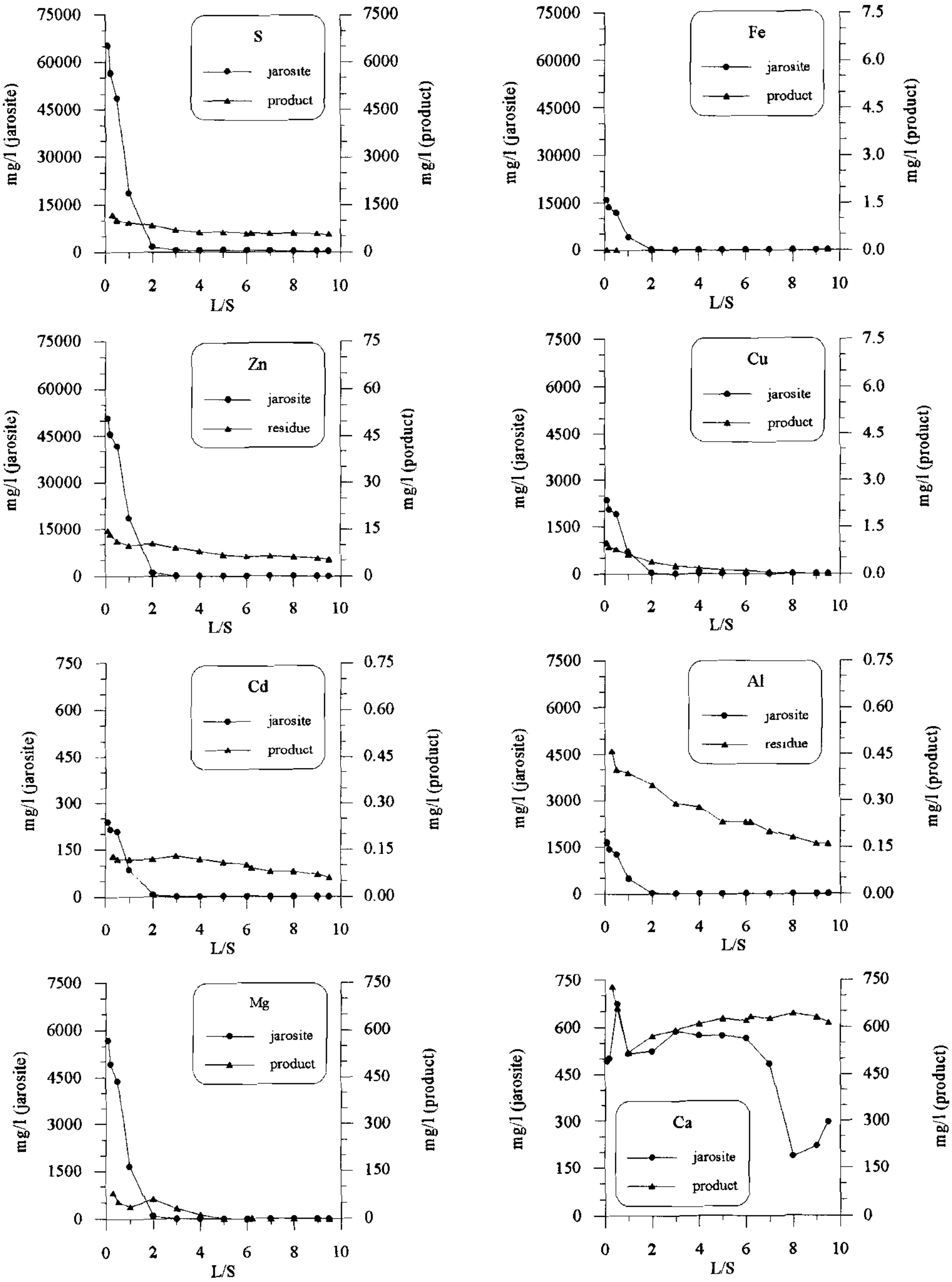


Fig. 5. Leach characteristics of most relevant elements from jarosite waste and its autoclaved product. For weights see table 4.

Discussion

Autoclave treatment of jarosite with sewage sludge and a neutralizing agent yields a product which contains minerals which are much more stable than the minerals in the original jarosite. Most of the metals are transformed to oxides or even sulfides, which are not leached by the simulated rainwater. Washing improves the quality of the product, especially where S (as sulfate) and Zn are concerned. A multi-stage counter-current washing system is recommended. In table 4 the restrictions for the use of materials as construction materials are shown as well. Construction materials which leach less metals than the limits for the U1 standard can be used without any restriction. Construction materials which satisfy the U2 standard can only be used with restrictions. Non complying materials are considered hazardous waste and storage or further treatment is necessary. Even after autoclaving, the treated jarosite/sludge mixture leaches too much zinc and cadmium, but all other elements leach within the limits of the U2 standard Recycling of treated jarosite as a construction material, such as cement filler, is chemically possible.

The autoclaved product can also be impounded in lined ponds instead of jarosite itself. Even if the liners are leaking, the immobilized product will not be a threat to the environment. Metals such as lead, zinc and silver are not lost; they are even concentrated and recycling is still a future possibility.

Conclusions

A new waste-to-waste technology was explored under the Brite Euram program of the European Community: Pressure reduction of jarosite waste with sewage sludge in an autoclave. The mobile components of the jarosite waste, are for a large part immobilized. The immobilizing capacity of an autoclave system is quite impressive. The role of sewage sludge is to generate energy, its buffering capacity saves on the neutralizing agent and the created reducing conditions will yield even more stable minerals. The leachabilty of almost all metals is decreased by a factor 1000 or more. Even so, zinc and cadmium leach in quantities which still exceed the Dutch U2 standard for building materials with restrictions. The role of sewage sludge is limited to its buffering capacity and the addition of sand and clay minerals to the solid. A counter current washing step will decrease the leachability of the solid, thus increase the possibilities for the product to be used as a construction material. Especially sulfate and zinc will benefit from such a treatment. Recycling as a construction material is possible, but faces strict restrictions. For an absolutely environmentally safe option, further treatment is recommended. An affordable environmentally safe option would be to impound the autoclave residue instead of jarosite.

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References

1. Hage, J.L.T., Schuiling, R.D., Van Enk, R. 'An Integrated Jarosite and Sludge Treatment Process', in: Dutrizac, J.E., Harris, J. (Eds.), Second International Meeting on Iron Control and Disposal, Ottawa, CIM, October 20-23, 1996, pp. 581-593.

2. Hage, J.L.T., Van Weert, G., Vriend, S.P., 'Quantitative Analysis of Jarosite Waste', to be presented at Lead & Zinc 2000.

3. Scheeren, P.J.H., Koch, R.O., Buisman, C.J.N., 'Geohydrological Containment System and Microbial Water Treatment Plant for Metal-Contaminated Groundwater at Budelco', World Zinc '93, International Symposium, Hobart, 10-13 October 1993.

4. 'A new method for the recycling and immobilization of metals in jarosite', final technical report, Brite Euram Program, Contract no. BRE2-CT94-0975, Geochem Research BV, VarTech Treatment Systems, INPL-LEM (France), University of Barcelona, Asturiana de Zinc, November 1998.

5. Hage, J.L.T., Schuiling, R.D., Vriend. S.P., 'Production of Magnetite from Sodiumjarosite under Reducing Hydrothermal Conditions', submitted for publication to Canadian Metallurgtical Quarterly, November 1998.

6. Encyclopedia Britannica, 15th Edition, Macropeadia, Vol. 21, pp. 295-296, 'Composition and properties of Portland cement'.

7. 'CBR, usine de Lixhe', une édition de CBR Ciment, Chaussée de la Hulpe 185, 1170 Bruxelles, Agence Mac & Co - 065/33.70.70, in French.

8. NEN 7343, Nederlands Normalisatie-instituut, 1995

Chapter 5

Sequential Differential Thermal Analysis (S-DTA) of Autoclave Reactions,

with the co-treatment of industrial jarosite and sewage sludge as an example

Abstract

The energy budget is an important parameter in process design. A common way to obtain the net energy transfer of reactions occurring at atmospheric pressure is to obtain the differential thermal analyses (DTA) signal by using a 'joule measuring device'. Obtaining the reaction energy at higher pressures is more complicated. Indirect information was obtained by measuring the temperature rise produced by the ongoing reaction in an autoclave during heating, compared to the temperature profile of the same autoclave during a blank experiment. This method is called here 'Sequential Differential Thermal Analyses', (S-DTA). The disadvantage of such a system is the energy loss to the environment, since the autoclave is not perfectly isolated. It has been shown that for limited energy increases this effect is negligible, and for stronger exothermic reactions the autoclave should be used with lesser quantities of reagents. The wet oxidation of cellulose with varying amounts of oxygen has been used to demonstrate the possibilities and the accuracy of this method.

Jarosite is a waste product of most zinc factories using hydrometallurgical processing routes. A proposed new process for treating this jarosite is the co-treatment with sewage sludge. This process was initially designed for a so called VerTech reactor. Only one such reactor is in full scale operation (Apeldoorn, the Netherlands). It is used for the wet oxidation of sewage sludge. The energy budget for the co-treatment of jarosite and sludge is compared with that for the wet oxidation of sewage sludge only. Influences of certain parameters, such as the addition of sub-stoichiometric oxygen, were tested as well. If a relatively small amount of oxygen is added to the jarosite/sludge reaction, the energy budgets of both reactions are of the same order.

Introduction

The energy budget of a reaction is required for its process design. If the exact reaction mechanism is known the reaction energy may be calculated, otherwise a measurement is a good alternative. For reactions under atmospheric pressure a 'joule measuring device' [1] is commonly used to determine this parameter. More complicated methods are needed for reactions under higher pressures. The technique described here is based on differential thermal analysis (DTA) and is called sequential differential thermal analysis (S-DTA).

Sewage sludge is the final product of sewage works. Usually this material is dried and burned in a refuse-incinerator. An alternative to this technique is wet oxidation in an autoclave with oxygen, eliminating the need to dry the sludge. VerTech Treatment Systems (Apeldoorn, the Netherlands) uses a double tube of more than one kilometer length, which is placed vertically into the ground as a pressure vessel. The hydrostatic pressure allows reactions to proceed in the liquid phase at temperatures of around 250 °C at the bottom of the tube [2]. Sewage sludge with ~5 wt% dry solids is treated in the VerTech process; about 60 wt% of these solids are organics. The organic phase in sewage sludge is mainly cellulose, and cellulose in this work has been used as a model for the wet oxidation of sludge. The wet oxidation of pure cellulose is easily carried out in an autoclave and a significant increase in temperature can be expected, as the reaction is exothermic [3]. The reaction equation is shown in Equation 1.Without oxygen the cellulose is cracked into smaller organic compounds and carbon. The wet oxidation of cellulose at varying amounts of stoichiometric oxygen has been used to illustrate the accuracy of using a regular autoclave for DTA analyses.

Equation 1 - Reaction between cellulose and oxygen

$$[C_6H_{10}O_5]_n \quad + \quad 6n\,O_2 \quad \rightarrow \quad 6n\,CO_2 \quad + \quad 5n\,H_2O$$

The co-treatment of industrial jarosite (MFe$_3$[SO$_4$]$_2$[OH]$_6$, in which M stands for compounds like NH_4^+, Na^+, $\frac{1}{2}Pb^{2+}$) and sewage sludge is a new process developed under project number BE-7673-93 of the BriteEuram program of the European Community [4]. Jarosite is a hazardous waste product from the zinc industry, usually stored in lined ponds near the refinery. A neutralizing agent is added to influence the reduction process. The reaction is shown in Equation 2. The energy release of this reaction is discussed in this chapter and compared with the energy budget of the wet oxidation of sludge in the VerTech reactor. By adding additional sewage sludge and a short measure of oxygen, extra energy can be generated without influencing the reduction of jarosite.

Equation 2 - Overall reaction between jarosite and cellulose. The exact reaction mechanism is not known, since the organic products are not fully identified.

$$\mathrm{NaFe_3[SO_4]_2[OH]_6 + [C_6H_{10}O_5]_n + 1\tfrac{1}{2}\,MgO \rightarrow Fe_3O_4 + n\{C + CO_2 + TOC\} + Na^+ + 1\tfrac{1}{2}\,Mg^{2+} + 2\,SO_4^{2-} + H_2O}$$

Methods

A common procedure to determine the energy budget is by using small pressure vessels in a perfectly isolated heating chamber. In the first series of experiments, tiny autoclaves made of pure gold were used. Their size was about 1 by 0.5 cm. After adding the solids and a small amount of water these cups were sealed through melting. Two of those cups were placed inside a pressure chamber; one of them was filled with the reagents and the other with a blanc, usually quartz powder. The pressure chamber was closed and heated till 300 °C. The temperature of both cups were measured continuously. The differential thermal analysis (DTA) signal is the difference between the temperature of the blanc and the temperature of the reaction. Unfortunately, the results were disappointing. It appears to be very difficult to prepare a reaction fluid inside these tiny cups, knowing the exact concentrations. This is due to the fact that a very small amount of water must be added to the solids, which partly evaporates during the sealing. Moreover, it was impossible to flush the gaseous phase or to add extra oxygen. Mixing of the contents of the cups is not possible and not matching a practical situation. Nevertheless, the experience of this first series of experiments was important for the development of a more suitable method for DTA analyses under pressure; the autoclave itself was used as a DTA measuring device. This apparatus is less well isolated than a 'joule measuring device' was, but thought to be a satisfactory alternative. Instead of heating both the blank and the reagents at the same time, the blank and the reaction fluid were heated sequentially. The oven was put on a constant power output. Water was chosen for the blank, since this is an inert material and it is the major component of the reaction fluid. The temperature was measured continuously. After cooling and draining off the autoclave, the same amount of reaction fluid as the blank was added to the system. The power output of the oven was exactly the same. Again the temperature was measured continuously. If both graphs are plotted in the same figure, the sequential differential thermal analysis (S-DTA) signal is the difference between both graphs.

Table 1 - The general gas law

$$n = \frac{P * V * Gr}{R * T * 100}$$

P = gas pressure in Pa (1 bar = $1 \cdot 10^5$ Pa)
V = volume (m^3)
n = number of moles of gas
R = 8.314 J/K/mol
T = temperature in degrees Kelvin (K)
Gr = grade of the oxygen gas (%)

For the experiments, a Parr 600 ml. Bench top mini reactor, type 4563 was used. Glass liners with a volume of 500 ml. were used inside the autoclave, which were filled with 250 ml. reaction fluid. Before the reaction took place, the head space of the autoclave was flushed and filled with nitrogen gas or oxygen gas. The amount of oxygen gas used in the autoclave was calculated using the general gas law (Table 1). The capacity of the heater was fixed at 100% power output of 780 Watt. The temperature was monitored constantly with a K-type thermocouple. When the system reached a temperature of around 300 °C, the heater was turned off and the autoclave was quenched with water.

The thermocouple/controller- and manometer system was tested for its accuracy. The temperature was plotted against the vapor pressure, together with the theoretical values for water pressure [5] (Figure 1). The measured curve was not corrected for partial pressures of oxygen and nitrogen gas, since these amounts are negligible compared to water. The maximum deviation of the thermocouple/controller and the manometer is 1.7 °C. To exclude a combined failure of the thermocouple/controller and the manometer system, the thermocouple was placed in boiling water; the display shows 101 °C. According to the manual, the accuracy of the system is ± 2 °C [6]. Although another type of thermocouple and another type of temperature controller may yield a more accurate system, a deviation of around 2 °C is considered to be within limits of a useful estimation of the energy budget. In earlier studies the accuracy of this DTA measuring method was determined.Based on three blanc experiments the maximum deviation is estimated at ± 3 °C [7].

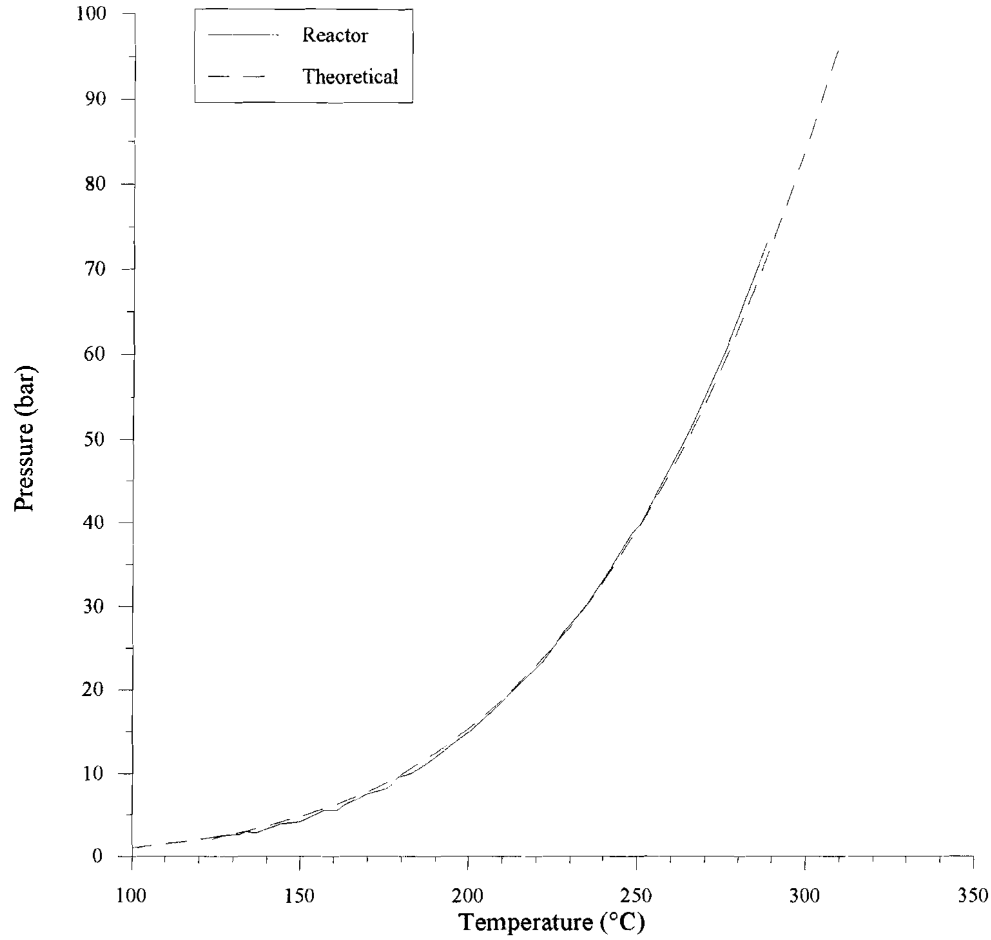

Fig. 1. Measured and theoretical values of the vapor pressure of water. The measured values were obtained with a Parr 600 ml. pressure vessel, type 4563.

Results

Two series of experiments were carried out. The first series was based on the wet oxidation of pure cellulose, to demonstrate the possibilities and accuracy of this energy measuring method. The list of experiments of the first series are given in Table 2; the graphs are shown in Figure 2. The amount of cellulose was kept constant during the reactions at 20 g/l in

250 ml. The amount of oxygen added to this system varied from 0.00 to 1.31 mol/l in the head space, also 250 ml. The first graph (C1) shows the temperature profile without the addition of oxygen. As can be expected, the energy production is lower than with the addition of oxygen; cracking of cellulose yields less energy than oxidizing. In the next three experiments increasing amounts of oxygen were added. The stoichiometric oxidation of 20 g/l cellulose in 250 ml liquid requires 0.74 mol/l oxygen in 250 ml gaseous phase. Since the heat loss to the environment will increase as well, the heat production is not a straight function of oxygen added. The graph of dT_{max} against the added amount of oxygen is slightly parabolic (Figure 3). Till dT_{max}=35 °C the heat loss to the environment is negligible. The sudden drop after this point is probably due to a short measure of cellulose, indicating that for a complete oxidation of cellulose more oxygen is required than stoichiometrically is calculated..

In the second series the energy budget of the co-treatment of jarosite and sewage sludge is determined. In Table 3 a selection of about 20 experiments of sewage sludge and jarosite is listed; the graphs are shown in Figure 4. The first two experiments show again the effect of adding extra oxygen to a cellulose-type system: the energy production dramatically increases. The conditions of the second graph (J2) are matching the conditions of the VerTech system: a comparable oxygen/sludge ratio was used. The transformation of jarosite to hematite [8] is shown in the third graph (J3). This reaction is exothermic and yielded a maximum temperature rise of 12 °C over the blank experiment. Adding sewage sludge and a neutralizing agent (25% NH_4OH) yielded extra energy (J4). This fourth graph shows a dotted line, which is the real course of the temperature. The dip is due to water left in the tube of the thermocouple. After evaporating the water the thermocouple was acting normal again. When sewage sludge, a neutralizing agent (25 wt% NH_4OH) and a relatively small amount of oxygen are added, the temperature rise is comparable to the temperature rise of the VerTech system (J5 versus J2). Adding another neutralizing agent (MgO) does not influence the energy production (J6), but NH_4^+ oxidation might (see difference between J3 and J4).

Table 2 - Tested wet oxidation reactions of cellulose, in order to illustrate a method to measure the energy budget with a regular autoclave.

No.	reagent (in 250 ml)	gaseous phase	P_0 (bar)	O_2 (in 250 ml)
blanc	demi water	nitrogen gas	4	0.00 mol/l
C1	20 g/l cellulose	nitrogen gas	4	0.00 mol/l
C2	20 g/l cellulose	20 vol% oxygen	10	0.08 mol/l
C3	20 g/l cellulose	100 vol% oxygen	4.8	0.20 mol/l
C4	20 g/l cellulose	20 vol% oxygen	28	0.23 mol/l
C5	20 g/l cellulose	80 vol% oxygen	20	0.66 mol/l
C6	20 g/l cellulose	80 vol% oxygen	40	1.31 mol/l

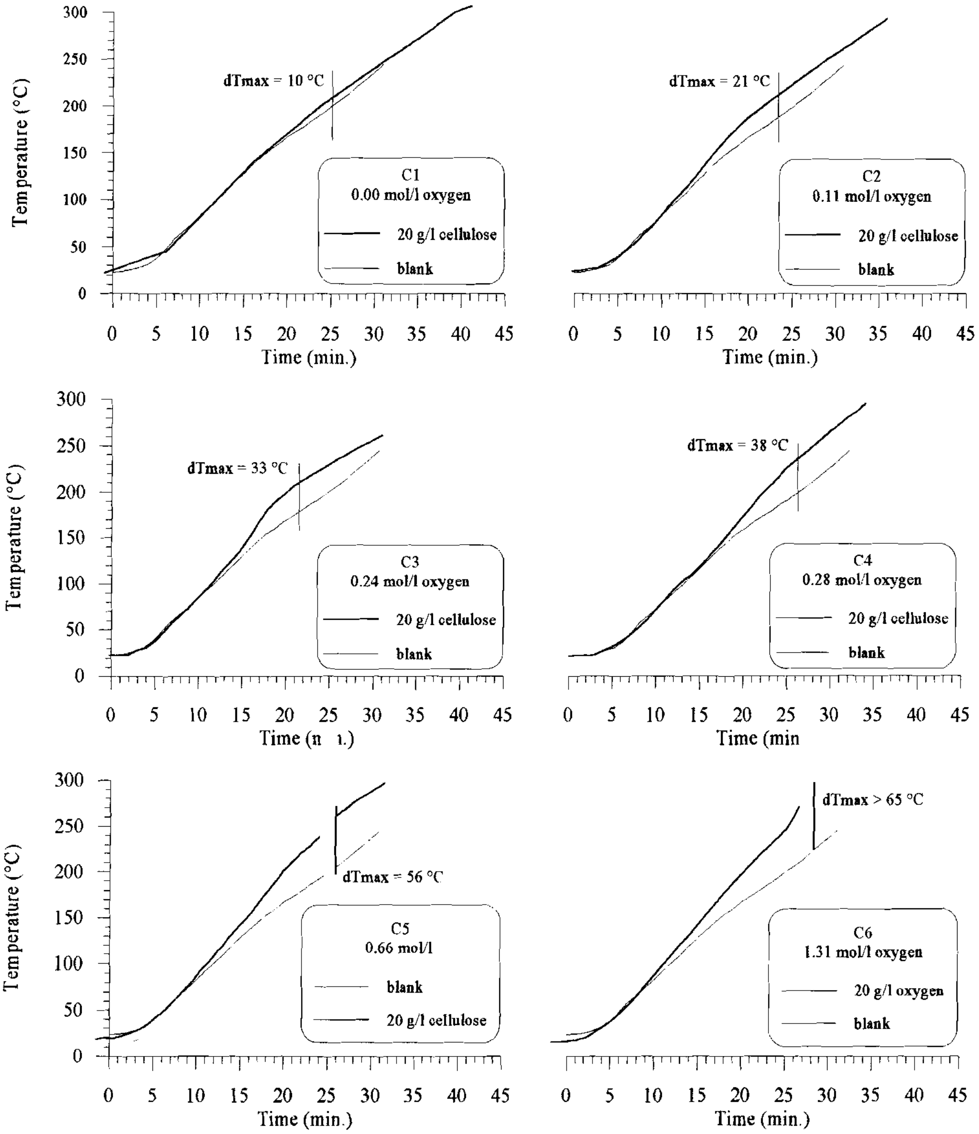

Fig. 2. Energy budget of the wet oxidation of pure cellulose with varying oxygen amounts.

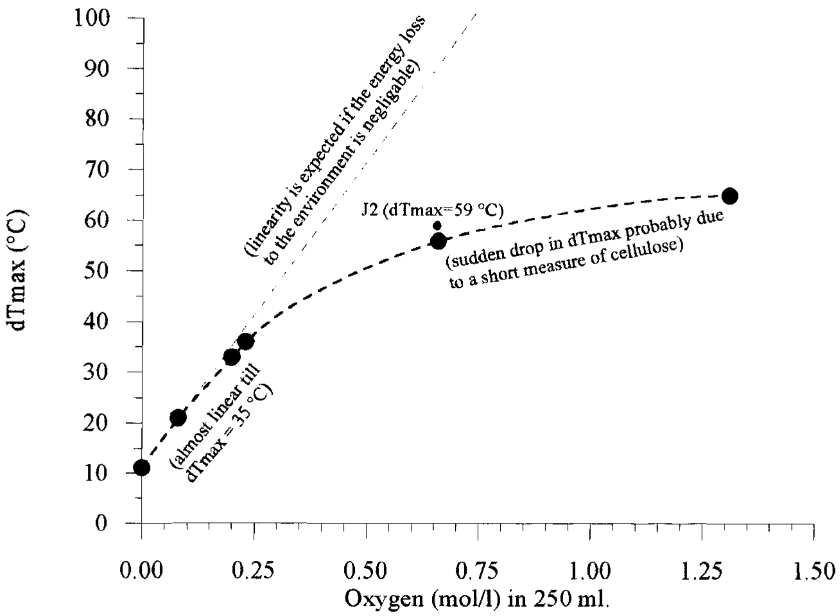

Fig. 3. Relationship between dTmax and the amount of oxygen of the wet oxidation reaction of cellulose.

Table 3 - Jarosite, sludge and oxygen mixtures used for DTA measurements.

No.	reagents (in 250 ml)	gaseous phase	P_0 (bar)	0_2 (in 250 ml)
J1	Sewage sludge	80 vol% oxygen	10	0.33 mol/l
J2	Sewage sludge	80 vol% oxygen	20	0.65 mol/l
J3	80 g/l Na-jarosite	nitrogen	4	0.00 mol/l
J4	Sewage sludge 80 g/l jarosite 100 ml/l 25% NH_4OH	nitrogen	4	0.00 mol/l
J4	Sewage sludge 80 g/l jarosite 100 ml/l 25% NH_4OH	80 vol% oxygen	10	0.33 mol/l
J6	Sewage sludge 80 g/l jarosite 20 g/l MgO	80 vol% oxygen	10	0.33 mol/l

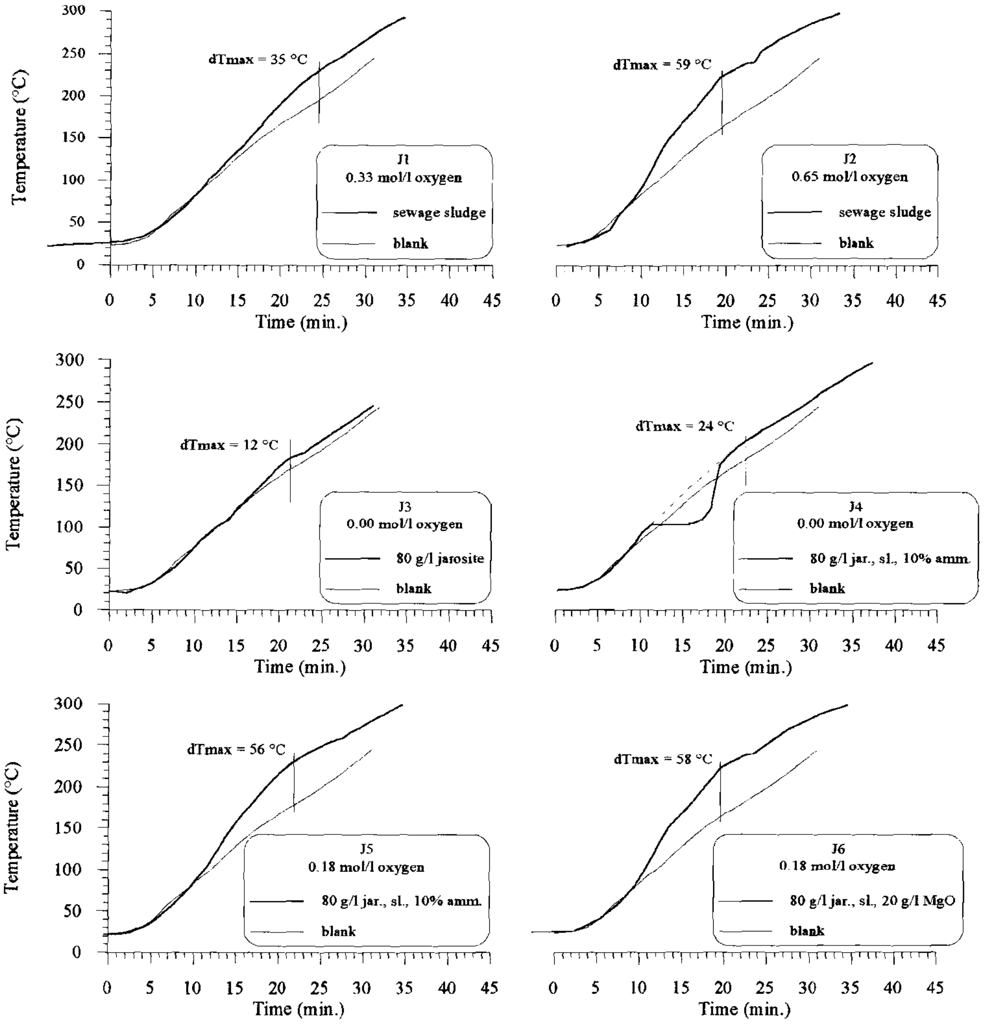

Fig. 4. The energy budget of the jarosite/sludge reaction at varying reagents compositions

Discussion

The graph in Figure 3 indicates the accuracy of this DTA measuring method, which is acceptable for exothermic reactions with moderate energy budgets. Especially at higher energy productions the heat loss to the environment becomes importanant. When measuring a dT_{max} of around 60 °C, the actual dT_{max} is higher than this number. For these stronger exothermic reactions it is recommended that the autoclave is calibrated with a reaction with a known reaction energy. In case of the energy budget of the jarosite/sludge process, the energy production of the VerTech system was chosen, since this process is initially designed for a VerTech type reactor. The energy production of this jarosite/sludge reaction has to be comparable with the wet oxidation of sewage sludge. Without the addition of oxygen, the energy budget might be too low for the reaction to maintain itself. For relative small additions of oxygen, the energy production corresponds to the energy production of the VerTech reaction (test J2). Varying neutralizing agents does not affect the heat of reaction and thus the neutralizing agent does not play a role in the actual reaction; it only fixes the pH at a certain level.

Conclusions

The results of the experiments with cellulose show that this regular 600 ml. Parr autoclave may yield acceptable S-DTA data, as long as the $dT_{max} \leq 40$ °C at an operating temperature range smaller than 300 °C. The graph of dT_{max} against the amount of added oxygen is almost linear if the energy production is not too high, indicating that the energy losses to the environment are negligible for temperature increases till about 35 °C for this type of autoclave. This can be accommodated by decreasing the amount of reactants for which the energy budget is being determined. Calibration with a reaction with a known energy budget is also recommended. For higher temperature increases, the slightly parabolic relationship becomes inaccurate.

Without oxygen, the increase in temperature of the jarosite- sludge process is about 24 °C. With the addition of a relatively small amount of oxygen, the temperature increase is more than doubled: 56 °C. This is almost the same temperature increase as produced by the wet oxidation of sewage sludge in the VerTech reactor. The extra energy will not influence the decomposition of jarosite, as long as the amount of sewage sludge is in over measure. This means that a regular VerTech reactor is suitable for jarosite- sludge treatment applications from an energy point of view.

Acknowledgments

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References

1. Encyclopedia Britanica, English version, Micropedia, 15th edition, Vol. 2, page 752, 'calori meter'

2. Tessel, P., De Bekker, P., Bowers, D. 'The VerTech aqueous phase oxidation system meets Veluwe, Holland's long term sludge management requirements', presented as a poster session at the 1991 WPFC/AWWA Joint Residual Management Conference Research Triangle Park, North Carolina, USA, August 1991.

3. Brandrup, J., Immergut, E.H., Polymer Handbook, 3rd ed., John Wiley and Sons, New York, 1989.

4. Hage, J.L.T, Schuiling, R.D., Van Enk, R. 'An Integrated Jarosite and Sludge Treatment Process", in: J.E. Dutrizac, G.B. Harris (Eds.), Proc. 2nd Int. Symp. on Iron Control in Hydro metallurgy, CIM, Montreal, 1996, pp. 581-596.

5. CRC Handbook of Chemistry and Physics, 65th edition, Ed. In Chief Weast. R.C., 1984-1985, pp. D193-D194.

6. 'Stirred reactors and pressure vessels' a publication by Parr instrument company, Illinois, 1994.

7. Hage, J.L.T., Reuter, M., Schuiling, R.D., Ramtahalsing, I. 'Reduction of Copper with Cellulose in an Autoclave; an Alternative to Electrolysis?', accepted for publication in *Minerals Engineering*. (presented on Minerals Engineering '98, Edinburgh, Scotland).

8. Dutrizac, J.E. 'Converting jarosite residues into compact hematite products', *JOM*, January 1990, pp. 36-39.

Part Two

Scientific Spin Off

Chapter 6

Reduction of Inorganic Compounds in Autoclaves by using Suspended Cellulose

Abstract

Autoclaves are closed vessels in which liquids can be heated above their 'normal' boiling points. As a consequence the pressure will rise. This equipment has permitted a variety of processes like the syntheses of organics and the leaching of metal ores. Pressure technologies can be used for accelerating reactions, for specific syntheses or they offer an environmental or economical alternative for existing processes.

Wet pressure oxidation of sewage sludge, an organic waste product, has become a proven technology. If less oxygen is added than stoichiometrically required for a complete oxidation, cellulose will break down by a different reaction mechanism, releasing electrons. Under these circumstances reduction of inorganic compounds is possible.

Autoclaving

An autoclave is a closed reaction vessel in which the temperature can become higher than the boiling point of the liquid it is containing. It was invented by Denis Papin (1647-1712) around the year 1680. As a physicist he used to be the assistant of Chr. Huygens (1629-1695) in Paris and R. Boyle (1627-1691) in London. His invention was called the Papinian jar [1]. Two hundred years later, in 1859, the Russian chemist N. Beketoff made an attempt to study a chemical reaction under pressure, while studying at the Sorbonne University in Paris [2]. In a sealed glass tube silver was precipitated from a silver nitrate solution which was heated under hydrogen pressure. Hydrogen was introduced through a side compartment of the reactor by the action of acid on zinc. Since the mid-1800's numerous processes have been investigated varying from oxidation, reduction and non-redox reactions. Some of these were commercialized and operate in full scale plants. The first commercial pressure process in the minerals industry was the dissolution of aluminum from bauxite in a pressure vessel at 150 °C, which is still one of the best-known pressure processes [3].

Autoclave applications are rapidly growing in popularity. They can be used for accelerating reactions, as an alternative for known processes for both environmental and economical reasons, or as the basis for completely new processes. The chemical industry uses pressure processes for several syntheses. The synthesis of polyethylene, for example, uses pressures up to 138,000 kPa [4]. In hydrometallurgical processes, autoclaves are frequently used for leaching of metal ores. Recently, a commercial pressure oxidation plant for gold extraction, in which the whole ore is treated, was brought into use in Nevada, USA [3].

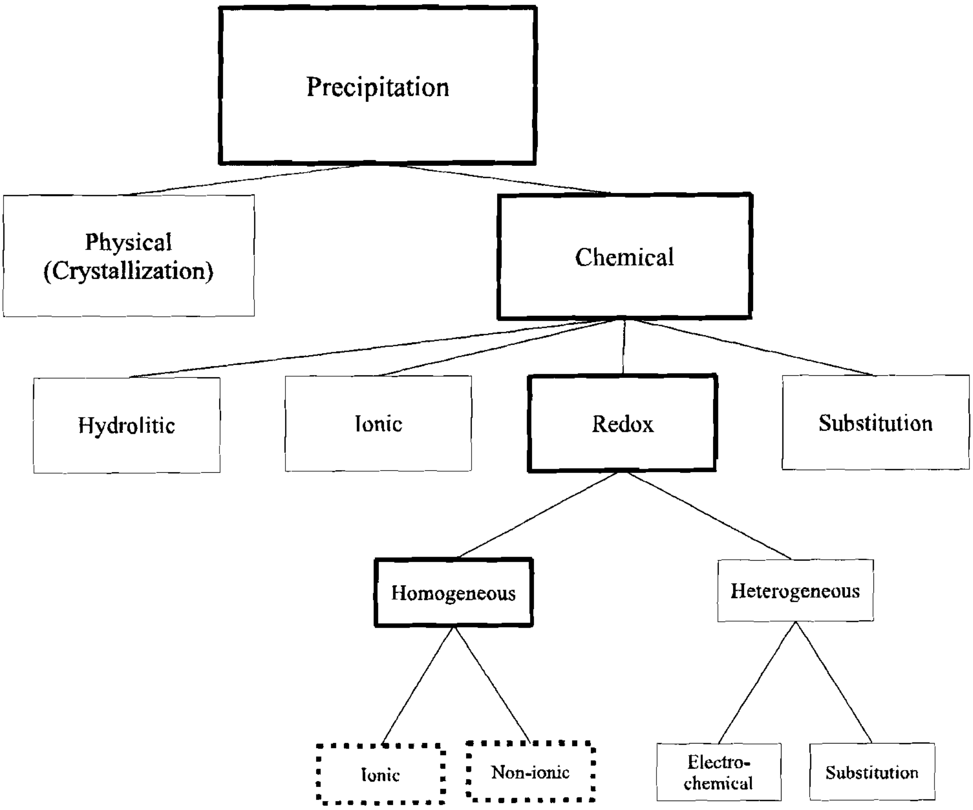

Fig. 1. Overview of Precipitation Reactions

Precipitation by chemical reduction

The redox potential for aerated water systems varies from 0.8 volt at a minimum pH around 2 for mine waters till 0.45 volt at a maximum pH around 10 for oceans [5]. Reduction reactions in this paper are defined as reactions in which the redox potential decreases below these redox potentials. An example in nature of a chemical reduction process is the production of pyrite by bacteria; an example in industry is cementation of silver by iron(II) oxidation [6]. This paper deals with reduction reactions under autoclave conditions. Some essential differences can be noticed when comparising reduction reactions at moderately elevated temperatures and pressure and reduction reactions occurring in nature. First, element concentrations in nature are usually several orders of magnitude lower than the concentrations used in autoclaves. The timescale is another important factor. The maximum residence time in an autoclave is limited to several hours; the reaction time in nature can be a thousand years or more. Mechanisms resulting in accumulation of reduced minerals are not possible under autoclave conditions due to these factors. Figure 1 shows an overview of common precipitation reactions [6]. The precipitation reactions which are the subject in this study are indicated by the boxes outlined in bold.

Reducing agent

Although the reducing agent can vary from hydrogen to elementary strontium, a technically, environmentally, and economically feasible approach restricts the choices. This reagent must be widely available and preferably be a waste product, easy to handle and quickly reacting. It should leave no residues, or, if there are any, they should not pollute the final products, but be easily separable or add value to the final products. Such a reducing agent might vary from liquid manure to scrap iron. This study is focused on cellulose type waste products found in liquid manure and sewage sludge. Cellulose is, together with starch, predominant in plants. Both are built from glucose units, but their structure is quite different. Carbohydrates such as sugars, starches and celluloses all share the same basic formula: $[C_6H_{10}O_5]_n$. They vary in the number of 6-carbon units per molecule: three or less are called sugars, longer chains are called starches and those in which the subscript 'n' attains values in the order of a few thousand celluloses [5]. The long chains of cellulose are hard to digest for bacteria, thus biodegradation is too slow to be a viable technological option for cellulose type waste products. At present, the final treatment step in sewage works in The Netherlands is usually dewatering, followed by storage or burning [7]. Since these techniques are expensive, the search for alternatives is continuing. One possibility is wet pressure oxidation, which is applied in the VerTech plant (Apeldoorn, The Netherlands). Here the sewage sludge of 1.1 million inhabitant equivalents, containing up to 5 wt% solids, is treated in this plug-flow-deep-shaft-reactor at 280 °C by injecting oxygen [8]. Reaction (1) shows the hydrolysis of cellulose into carbon dioxide, hydrogen ions and water, while releasing electrons. For this reaction to proceed, the temperature must be at least 180 °C [9]. The released electrons can not only serve to reduce oxygen, but also ions like Cu^{2+}, SO_4^{2-} or Fe^{3+}. Reaction (3) shows the over-all reaction of wet pressure oxidation.

$$\begin{array}{llll}
{[C_6H_{10}O_5]_n} + 7_n\,H_2O & \rightarrow & 6\,[CO_2]_n + 24\,[H^+]_n + 24\,[e^-]_n & (1)\\
6\,[O_2]_n + 24\,[H^+]_n + 24\,[e^-]_n & \rightarrow & 12\,[H_2O]_n & (2)\\ \hline
{[C_6H_{10}O_5]_n} + 6\,[O_2]_n & \rightarrow & 6\,[CO_2]_n + 5\,[H_2O]_n & (3)
\end{array}$$

Criteria for compounds to be reduced

Although cellulose is potentially a powerful reductant, inorganic compounds tend to be removed by other precipitation reactions than reduction. As for instance hydrolysis will be accelerated due to the high temperature, it means that not all inorganic compounds are suitable for this type of reduction. However, compounds remaining in solution up to 180 °C are potentially reducible. Another potential group are salts which become unstable in water only above 180 °C, but they are rare. A third possibility are compounds that are protected from precipitation reactions up to 180 °C because they are complexed. Ammonia, for instance, forms soluble complexes with silver, gold, cobalt, copper, mercury, nickel, zinc and even iron [6]. So, ammonia can be used as a neutralizing agent and prevents the compounds from precipitation, before their intended reduction takes place.

Neutralizing agent

Areas in the Pourbaix diagram are defined by the Eh as well as the pH. Since the degradation of cellulose generates carbon dioxide, which dissolves in water at high pressure, and partly forms HCO_3^-, in some cases it is necessary to add a neutralizing agent. Most bases are suitable for this task. Magnesium oxide and ammonium hydroxide were investigated.

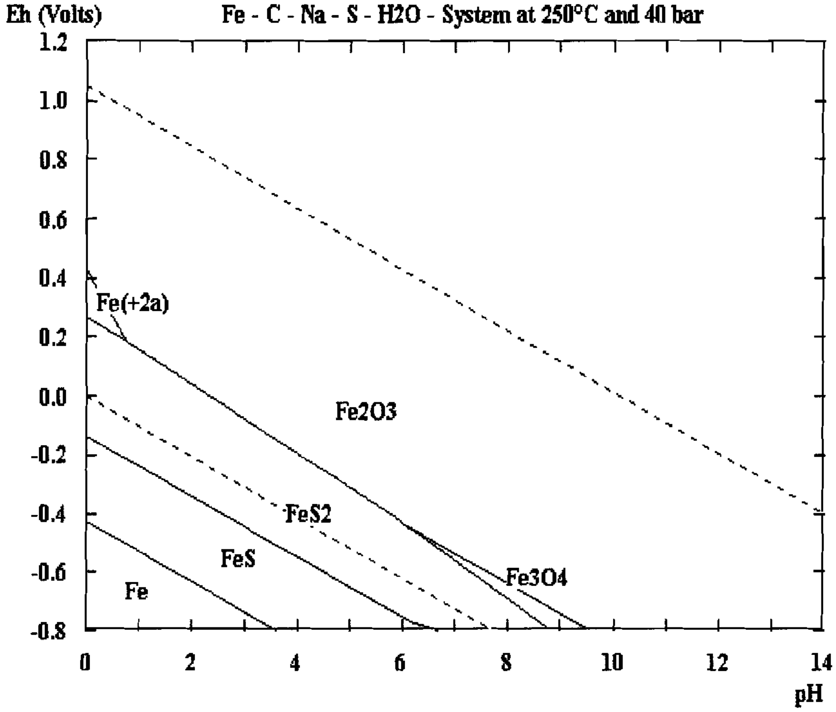

Fig. 2. Pourbaix diagram of the Fe-C-Na-S-H-O system at 250 °C.
Molalitiets: Fe=0.3 mol/kg; S=0.2 mol/kg; Na=0.1 mol/kg; C=1e-12 mol/kg

Reduction of jarosite as an example

Jarosites are ironsulfates of the general formula $M\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, in which *M* stands for components like NH_4^+, $½Pb^{2+}$ or Na^+ [10]. In nature these compounds are found in oxidation zones in sediments where pyrite is transformed to jarosite [11]. In the zinc industry millions of tons are produced every year as a waste product, generally contaminated with metals such as lead and zinc. Since recycling of this waste is not economical feasible, storage is widely used. Jarosites are stable up to 200 °C; above this temperature they start to dissociate [12]. The study of the reduction of jarosite was performed in order to develop a reliable, integrated and efficient treatment process for both sewage sludge and waste jarosite.

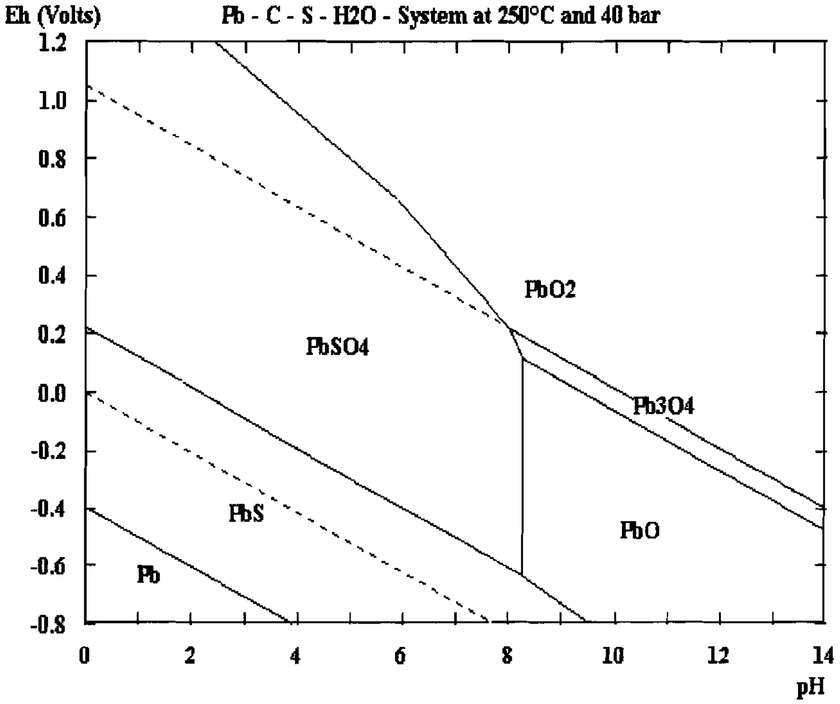

Fig. 3. Pourbaix diagram of the Pb-S-C-O-H system at 250 °C.
Molalities: Pb=0.3 mol/kg; S=0.3 mol/kg; C=1e-12 mol/kg

Industrial jarosite, containing 6 wt% lead, was mixed with sewage sludge in the ratio 1:6. The pH was controlled by ammonia; 10 vol% of 25 wt% ammonia solution was added. A 600 ml. Parr autoclave, type 4563, was filled for 50 vol% with this reactionfluid and flushed with nitrogen gas. After a reaction time of one hour at 250 °C, the vessel was quenched with water. The solids where analysed by XRD. Magnetite was detected as a major product; galena as a minor [13]. The production of galena was also observed starting from a lead jarosite, mixed with elementary sulfur in an ammonia solution [14]. For both minerals the Eh has to be as low as -0.5 V (pH=7), as shown in Figures 2 and 3 [15].

Concluding remarks

Under autoclave conditions the reagent concentrations and the reaction rates are so high that reduction reactions are restricted to almost instantanious processes. This mechanism limits the production of reduced minerals, because the products are limited to the first solid encountered on the Eh scale, which is usually an oxide or a hydroxide. But, when a compound remains in solution till the cellulose starts to react, reduction is possible. Although this principle limit the possibilities of autoclave reduction reactions on the one hand, it can also yield promising alternatives to current processes and even generate new processes.

Acknowledgements

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References

1. Hoetink, H.R. et al, 1959, *Algemene Winkler Prins Encyclopedie*, Elsevier, in Dutch.

2. Habashi, F., 1971, Pressure Hydrometallurgy; Key to Better and Nonpolluting Processes; *Engineering and Mining Journal*, 172, pp. 96-100.

3. Thomas, K.G., 1994, Research, Engineering Design and Operation of a Pressure Hydrometallurgical Facility for Gold Extraction, PhD thesis, Delft University of Technology, 1994.

4. Comings, E.W., 1956, High Pressure Technology, McGraw-Hill, New York.

5. Habashi F., A Textbook of Hydrometallurgy, *Métallurgie Extractive Québec, Enr.*, Canada,1993, ISBN 2-980-3247-0-1

6. Bekker de, P., Berg van den, J., Heerema, K., 1988, Het VerTech Slibverwerkingsproces, *H_2O*, 21, pp. 94-98, In Dutch.

7 Brandrup, J., Immergut, E.H., Polymer Handbook, third edition, John Wiley and Sons, New York,.1989.

8. Krauskopf, K.B., Bird, D.K., Introduction to Geochemistry, third edition, McGraw-Hill, ISBN 0-07-035820-6, 1995.

9. Koot, A.C., Behandeling van Afvalwater, second edition, Uitgeverij Waltman, Delft, ISBN 90-212-3076-3, 1982, In Dutch.

10. Dutrizac, J.E., Kaiman S., 1976, Synthesis and Properties of Jarosite-Type Compounds, *Can. Mineral*, 14, pp. 151-158.

11. Bloomfield, C., Coulter, K.J., Genesis and Management of Acid Sulfate Soils, Adv. Agron, 25, pp. 265-326,1973.

12. Dutrizac, J,E., Converting Jarosite into Compact Hematite Products, *JOM*, January: pp. 36-39, 1990.

13. Hage, J.L.T., Schuiling, R.D., Enk van, R., 1996, An Integrated Jarosite and Sludge Treatment Process, proceedings Second International Symposium on Iron Control in Hydrometallurgy, edited by Dutrizac J.E. & Harris G.B, Ottawa, CIM Montreal, Oct. 20-23: pp. 581-596.

14. Lei, K.P.V., 1990, Hydrothermal Sulfidation of Plumbojarosite for Recovery of Lead and Silver, paper presented of the EPD Congress '90, edited by D.R. Gaskell, The Minerals, Metals & Materials Society.

15. Roine, A., Outokumpu HSC Chemistry for Windows, version 2.0, 1994.

Chapter 7

Production of Magnetite from Sodiumjarosite under Reducing Hydrothermal Conditions

The Reduction of Fe(III) to Fe(II) with Cellulose

Abstract

Jarosite is a waste product of zinc industries using the hydrometallurgical processing route to remove iron from the pregnant solution, generally by the addition of ammonium sulfate. Its formula is ($MFe_3(SO_4)_2(OH)_6$), in which M represents cations like NH_4^+, Na^+, K^+, H_3O^+, ½ Pb^{2+}. The jarosite is usually stored in lined ponds near the factory, since recycling is still not an economically feasible option. A promising recycle technique is reduction of industrial jarosite with sewage sludge under hydrothermal conditions in an autoclave in the presence of a suitable neutralizing agent. The resulting liquid, containing most of the sulfur species, is separated from the solid, containing the metals. Under appropriate conditions iron is mainly precipitated as magnetite.

This paper describes the production of magnetite out of sodium jarosite, starting from pure chemicals. MgO was used as a neutralizing agent, pure, acid washed cellulose as a reducing agent. Na-jarosite was produced in the laboratory. The aim of this study was to find the optimal ratio of jarosite/cellulose/MgO and to describe the reaction mechanism. Several reactions were carried out in an autoclave at 250 °C and one hour retention time. After quenching and solid/liquid separation, the solids were analyzed by XRD and ICP-AES. The liquids were characterized by ICP-AES and spectrometric techniques. In situ filtration was performed during the tests, providing additional information on the reaction mechanism. The optimal ratio for the production of magnetite out of jarosite was 100 g/l Na-jarosite, 30 g/l cellulose and 20 g/l MgO. The jarosite was first converted to goethite, which was recrystallized to magnetite.

Introduction

Most of the world's zinc metal is produced through hydrometallurgical processing, after roasting of the zinc ore at about 950 °C. Zinc sulfide ores typically contain contaminants like cadmium, copper, lead, silver and iron. Iron can be present in concentrations up to 10 wt%; it ends up in zinc ferrites during the roasting process. After roasting the zinc oxides are leached in a 'neutral leach' step, followed by a second, much stronger 'hot acid' leach step for the zinc ferrites. For both leach steps sulfuric acid is used. During the leach processes the zinc and other elements like iron, cadmium and copper are dissolved. An option to purify the solution from iron is the addition of ammonium sulfate at a temperature around 95 °C. The iron will precipitate as jarosite, $M\mathrm{Fe_3(SO_4)_2(OH)_6}$, incorporating other impurities. (M stands for NH_4^+, $\frac{1}{2}Pb^{2+}$, Na^+, etc.) After solid-liquid separation, cadmium and copper ions are removed by cementation with zinc powder. After these treatments the pregnant solution is ready for electrolysis [1]. A schematic flowsheet of such a zinc plant is shown in Figure 1 [2].

The jarosite precipitation technique is widely used for several reasons. It is a process that is relatively simple and easy to control. Jarosite is easily filterable in contrast to alternatives like goethite and hematite. During its formation it is able to incorporate other contaminants. On the other hand, these contaminants make jarosite a waste product that needs extra care for environmental reasons. Usually the jarosite is stored in lined ponds near the factory, but the liners can only be guaranteed for a limited number of years and leachate runoff must be collected in perpetuity. This temporal characteristic of ponds drives the search for alternative solutions. Dutrizac demonstrated the transformation of jarosite to hematite under hydrothermal conditions [3], [4]. The transformation of jarosite into magnetite under moderately elevated temperatures and pressures has been demonstrated as well. Starting from a suspension of pure, synthetic hydroniumjarosite, the production of magnetite is described by Boháček et al [5]. Iron(II)sulfate was added to the suspension at 90 °C. The target was the production of magnetite, suitable for pigment applications. A similar process is mentioned by Kunda et al [6]. The suggested purpose of this process was the recycling of ammonia. Reductive dissolution of jarosite with SO_2 gas in order to achieve a secondary lead/silver ore was described by Konings [7]. In a pressure vessel with a temperature of 110 °C and a retention time of 4 hours using 8 bar SO_2 about 95 wt% of the iron was dissolved as Fe^{2+}. Hydrothermal sulfidation of plumbojarosite (T=150 °C, t=1 hour) with the addition of elemental sulfur was described by Lei and Gallagher [8]. In this process iron was transformed to goethite and lead to galena. The target was also the recovery of lead and silver. The production of magnetic ferrites in concentrated magnesium sulphate solutions by oxidation with nitrate was described by Jonckbloedt [9]. He started with Fe^{2+} which was partly oxidized to Fe^{3+} and precipitated as magnetite. Hage et al [10] produced magnetite from industrial jarosite by reduction with sewage sludge in an autoclave. Their aim was to create an integrated jarosite and sludge treatment process in which no residues remain. The aim of the study described here is to investigate the optimal conditions for this reduction of jarosite to magnetite and to determine the reaction mechanism. This reaction is an illustration of the reducing capacity of cellulose in an autoclave system.

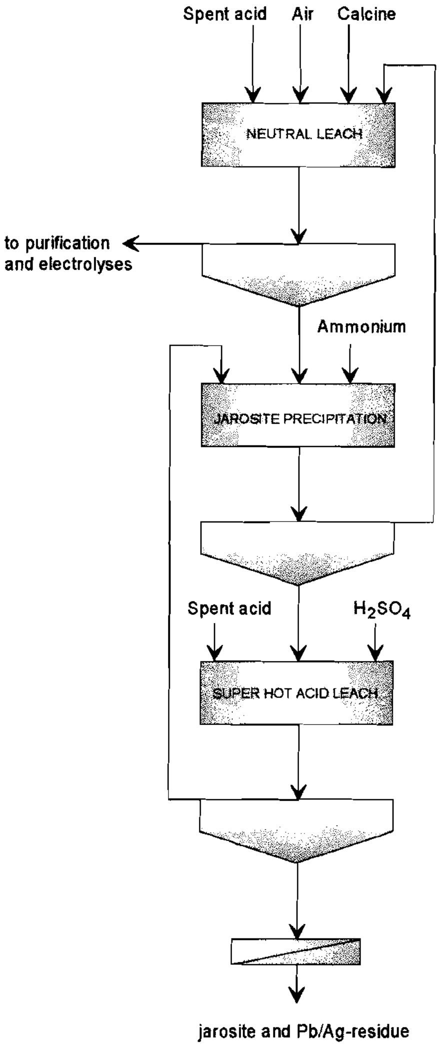

Fig. 1. Flowsheet of the Dor jarosite process (Budelco, the Netherlands)

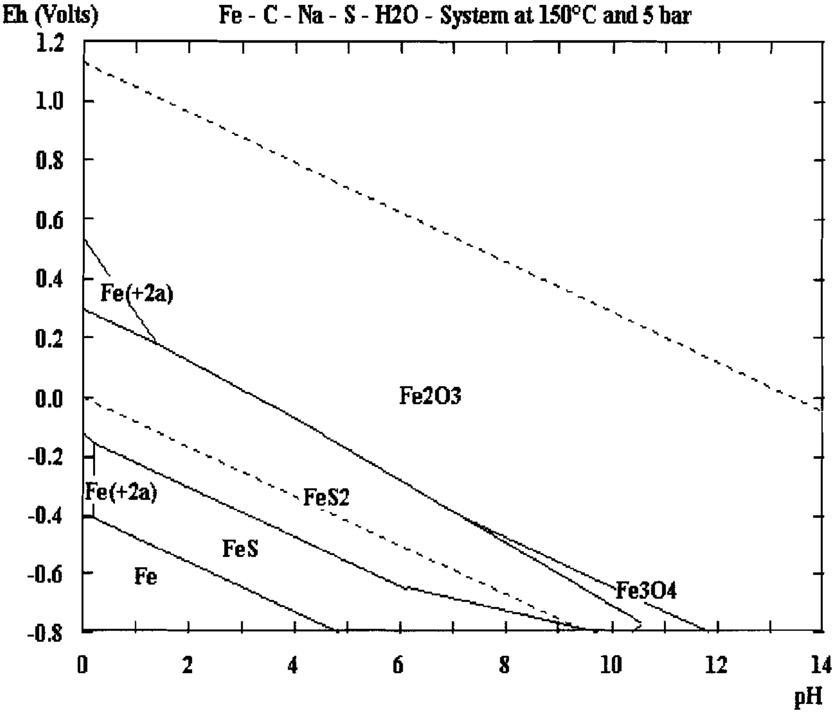

Fig. 2. Pourbaix diagram of the Fe-C-Na-S-H-O system at 150 °C and 4.7 bar.
Molalities: Fe=0.3 mol/kg; S=0.2 mol/kg; Na=0.1 mol/kg; C=1e-12 mol/kg

In this study cellulose is used as as reducing agent for jarosite; cellulose is the major organic component in sewage sludge. Sewage sludge was chosen as a reducing agent in earlier studies. Sewage sludge is a waste product, available in large tonnages and able to create reducing conditions. In Western European countries, North American and Canada a gate fee is usually paid for the sludge. A possibility to treat this sludge is in a wet oxidation plant. In such a plant oxygen is introduced in an autoclave system to produce CO_2 [11]. Nevertheless, part of the carbon ends up in the liquid as a combination of acetic acid, methanol, acetaldehyde, formic acid and other products. Lübke [12] reported the transformation of cellulose into alcohol in the presence of sulfuric acid. He reported that this process was already known since 1819. Transformation of biomass (containing mainly cellulose) in pressure vessels at temperatures to 350 °C and a retention time of about 10 minutes results in petroleum-like products. After upgrading by catalytic hydrodeoxygenation in a central facility the final products are gas oil and kerosine [13].

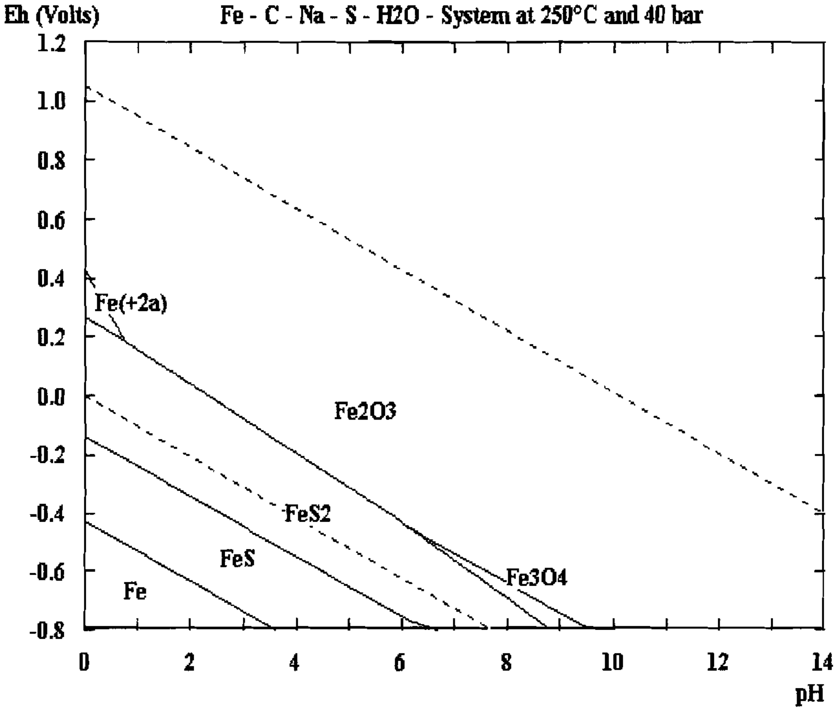

Fig. 3. Pourbaix diagram of the Fe-C-Na-S-H-O system at 250 °C and 39.2 bar. Molalities: Fe=0.3 mol/kg; S=0.2 mol/kg; Na=0.1 mol/kg; C=1e-12 mol/kg

A compound must be in solution at the time cellulose starts to decompose [14]. If this compound is in the solid state, the reducing capacity of this cellulose system is probably too weak to affect the solids. Jarosite becomes unstable at higher temperatures, which makes jarosite potentially a reduceable compound [3]. The Pourbaix diagrams [15] of the Fe, C, Na, S, H_2O system at 150 °C (beginning of the decomposition of cellulose) and 250 °C (setpoint) (Figures 2 and 3) show that the only possibility to produce magnetite *stably* is respectively at pH $\geq$ 6 and Eh $\leq$ -0.4 V and pH $\geq$ 7 and Eh $\leq$ -0.4 V. The parameter for the reduction capacity is the amount of cellulose; to control the pH a neutralizing agent has to be added. The simplified overall reaction at moderately elevated temperatures and pressures is shown in Equation 1.

Equation 1 - Overall Reaction between Jarosite and Cellulose

Jarosite + Cellulose → Magnetite + Carbon + Carbondioxide + TOC + Sodium ions + Sulfate

Materials

Instead of ammonium-jarosite, sodium-jarosite was chosen for the reactions. Better results are expected from Na-jarosite since this is less stable than NH_4-jarosite. After dissolving the iron(III)sulfate, the liquid was filtered to remove solid contaminants. A stoichiometric amount of sodium sulfate was dissolved and added to the iron(III)sulfate. This reaction fluid was heated in a stirred reactor to 95 °C. After 48 hours under reflux the reactor was cooled with water. This procedure is the synthesis route for Na-jarosite, described by Dutrizac [16]. The suspension was filtered and washed three times by repulping the cake. After drying and gently crushing the jarosite was stored. The product was analyzed by XRD (Figure 4) and ICP (Table 2); the D_{50} was 4.44 μm (Figure 5). The deviation of sodium indicates that the product was not pure Na-jarosite, but a mixture of about ⅔ Na-jarosite and ⅓ H_3O-jarosite.

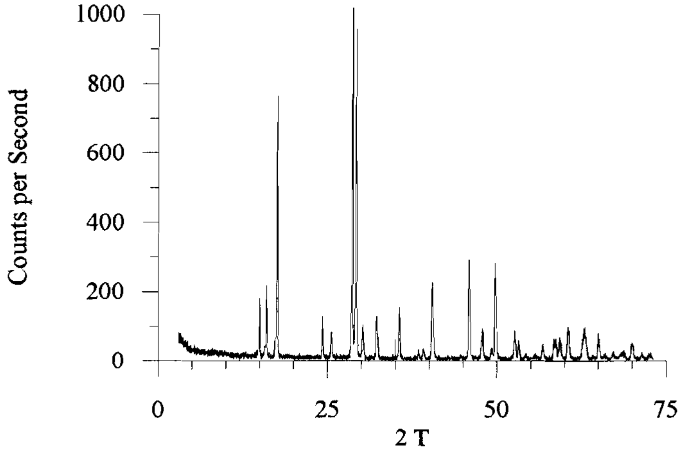

Fig. 4. XRD powder pattern of produced Na-jarosite

Table 2 - Analyses of Synthetic Jarosite by ICP-AES

	theoretical (wt%)	measured (wt%)	deviation (wt%)
Fe	34.6	34.6	0.2
SO_4	39.7	36.3	8.5
Na	4.75	3.17	33.3

Criteria for the selection of a neutralizing agent are few. For the experiments MgO (p.a.quality, produced by Baker Chemicals) was chosen as a neutralizing agent, but NH_4OH and KOH are other possible agents. The main reason MgO was chosen was that it dissolves during the reaction and in this way it may give more information about the reaction mechanism; the more acid produced, the more Mg^{2+} is dissolved. Besides it is one of the cheapest neutralizing agents available. An acid washed quality (97 wt% pure) of cellulose (produced by Baker Chemicals) was used during the experiments.

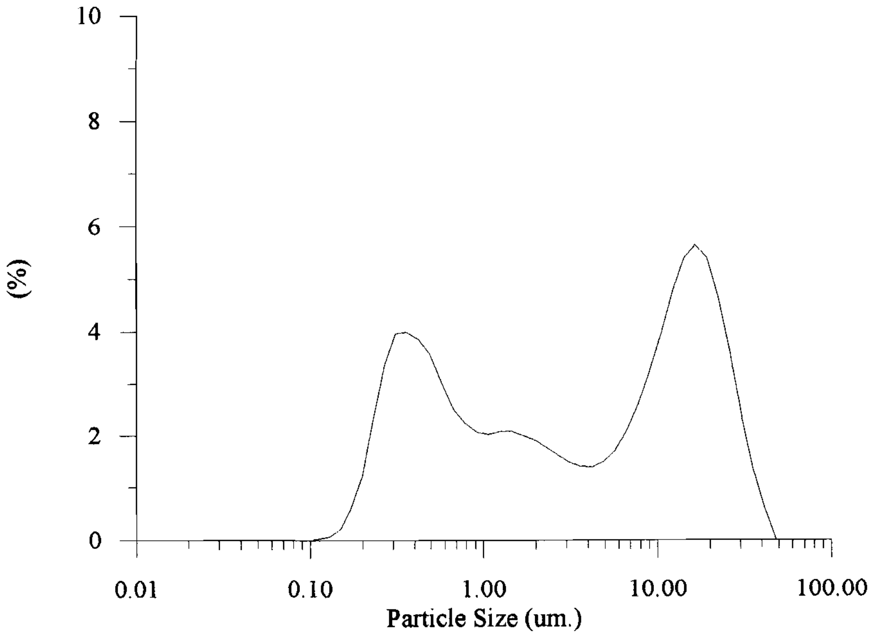

Fig. 5. Particle size distribution of produced Na-jarosite. D_{50} = 4.44 μm.

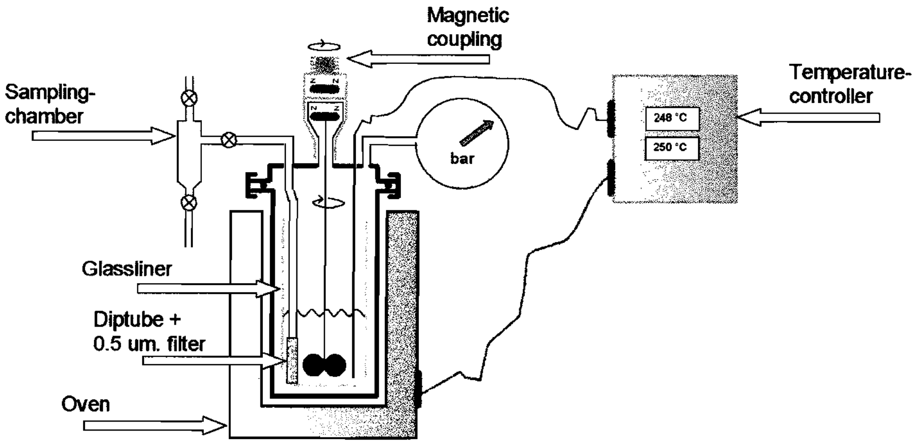

Fig. 6. Schematical view of the autoclave

Methods

All experiments where done in a Parr 600 ml. bench-top continuously stirred autoclave equipped with 500 ml glassliners to protect the autoclave shell (Figure 6). Jarosite, MgO and cellulose were added in powder form. The glass liner was half filled, to about 250 ml. The autoclave was flushed with nitrogen to remove the oxygen. It took about 40 minutes to heat the autoclave from 20 °C to the setpoint, 250 °C; the autogenic pressure at this point is 40 bar. After a retention time of 60 minutes the autoclave was quenched with water and the Eh and the pH were measured immediately. These measurements can only be used as an indication of the Eh and the pH inside the autoclave, since it is not possible to measure these parameters at 250 °C. Besides, the use of platinum electrodes to measure the redox potential are in any case debatable [17]. The acidity will change with increasing temperature; the ionization constant for water (-log K_w) changes from 14 at 24 °C to about 10 at 250 °C [18]. The TSS (Total Suspended Solids) was measured on the day of the experiment. The reaction products were filtered and washed three times with distilled water. The solids were dried for 24 hours at 60 °C and analyzed by XRD and (after '$HF/HClO_4/HNO_3$ destruction') ICP-AES. The solids were prepared for XRD analyses by grinding in an agate mortar under acetone to prevent oxidation. Cups with a constant diameter and depth were used for each sample. During the analyses the settings of the XRD apparatus were the same for all samples, thus the peak heights of the results are comparable. The particle size was measured with a Malvern Mastersizer S long bed, version 2.18. An NCS analyser (Fisons Instruments, type NA 1500 NCS) was used to determine the carbon content in the solids. Part of the liquids were diluted with water and analyzed with spectrometric techniques to determine the concentration of TOC (total dissolved organic carbon). These analyses conform to DIN 38409; 1983-06. TOC was chosen as an overall parameter for the organic compounds, to avoid the analysis of the many produced organic compounds, which are difficult to measure [19]. Another part was diluted with 1 M HCl and analyzed by ICP-AES.

First the optimal ratio of Na-jarosite/cellulose/MgO was studied. The amount of jarosite was kept constant while the amounts of cellulose and MgO were varied. A slurry density of 100 g/l Na-jarosite was chosen for process reasons. Lower concentrations are more difficult to control and the energy production will be too low for possible full scale applications. Higher concentrations are not recommended since the slurry becomes too viscous.

The reaction mechanism was the second target of this work. To investigate the reaction mechanism, the end products as well as their intermediates must be studied. The hypothesis is that first the cellulose starts to decompose, creating reducing conditions. Next the jarosite dissolves, part of the iron(III) reduces and magnetite is precipitated. To substantiate this hypothesis, samples were taken during the reactions. In situ filtered samples of the liquid gave information on the compounds that were in solution. The samples were diluted with 1 M HCl to dissolve the quenched material and were analyzed by ICP-AES. The filter placed on top of the diptube was made of sintered stainless steel with a pore size of 0.5 µm. Samples without this filter were used to obtain XRD-data on the solids. Sampling an autoclave filled with a suspension is nearly impossible without a sluice, so a sluice with a volume of 9 ml was used. Before the actual sample was taken, the diptube was flushed with reaction fluid, since the liquid that was already present inside the diptube does not take part in the reaction. A few seconds is needed for each sample. When sampling only liquid the concentrations inside the autoclave may change. For this reason no more than three samples were taken during a run.

Results

Optimal ratio of jarosite, cellulose and MgO

Table 3 shows the composition of the initial reaction fluids; it is a selection of about 20 experiments. The analyses of the solids and the liquids are listed in Tables 4 and 5. Part of the solids of each sample was prepared for XRD-analyses. The results are shown in Figure 7. In Table 6 the XRD-characteristics of hematite, magnetite and magnesium-sulfate-hydroxide are listed. If neither MgO nor cellulose are added, the product is pure hematite (experiment 5); the addition of 30 g/l cellulose and 20 g/l MgO resulted in magnetite (experiment 6). Based on 'composition 6' a mass-balance is listed in Table 7. The deviations are small, except for carbon. Part of the carbon is transformed into carbon dioxide which is released when the autoclave is opened. The carbon is distributed between liquid, solid and gas. It is noteworthy that about 50 wt% of the carbon ends up in the liquid. The particle size distribution of the magnetite is shown in Figure 8; the D_{50} is 14.90 µm. In comparison with the Na-jarosite, the particle size was increased.

Table 3 - Compositions of the reaction fluids

No.	Na-Jar. (g/l)	cel. (g/l)	MgO (g/l)	pH$_{begin}$	pH$_{end}$	Eh$_{end}$
1	100	30	15	10.0	4.39	0.41
2	100	30	30	10.4	9.50	-0.28
3	100	20	20	10.6	7.74	-0.13
4	100	40	20	11.0	6.91	-0.13
5	100	0	0	3.50	2.20	0.47
6	100	30	20	10.3	8.70	-0.34

Cel. = cellulose

Table 4 - Analyses of the Solids by ICP-AES

No.	TSS[*] (g/l)	Fe (wt%)	Mg (wt%)	SO$_4$ (wt%)	Na (wt%)	C (wt%)
1	59.7	64.3	0.80	1.44	0.04	6.71
2	94.6	32.5	11.5	17.9	0.03	6.21
3	63.0	57.2	3.69	9.06	0.03	2.18
4	64.5	52.9	6.59	15.6	0.04	6.39
5	43.6	69.1	n.d.	5.19	0.14	n.d.
6	52.9	66.7	1.14	1.23	0.02	4.15

[*] TSS = Total Suspended Solids

n.d. = not detected

Table 5 - Analyses of the liquids by ICP-AES

No.	TOC[#] (g/l)	Fe$^{2+/3+}$ (g/l)	Mg^{2+} (g/l)	SO$_4^{2-}$ (g/l)	Na$^+$ (g/l)
1	0.70	n.d.	7.22	37.8	3.45
2	0.66	1.25	8.90	39.6	3.73
3	0.57	n.d.	9.70	37.0	3.16
4	1.12	n.d.	9.88	37.9	2.90
5	n.d.	n.d.	n.d.	38.2	3.32
6	0.70	n.d.	9.79	38.9	3.38

[#] TOC = Total (dissolved) Organic Carbon, determined by spectrophotometric techniques

n.d. = not detected

Table 6 - XRD characteristics of hematite, magnetite and magnesium sulphate hydroxide

Fe_2O_3, syn		Fe_3O_4, syn		$Mg_4[SO_4]_3[OH]_2 \cdot H_2O$	
2T	Intensity (%)	2T	Intensity (%)	2T	Intensity (%)
24.16	**30**	**30.12**	**30**	18.20	15
33.18	**100**	**35.46**	**100**	**26.65**	**46**
35.65	**70**	**43.09**	**20**	**27.70**	**38**
40.89	20	57.00	30	30.13	26
49.53	40	62.58	40	**35.49**	**100**
54.14	45			43.15	19
62.51	30			57.14	46
64.06	30			62.68	44

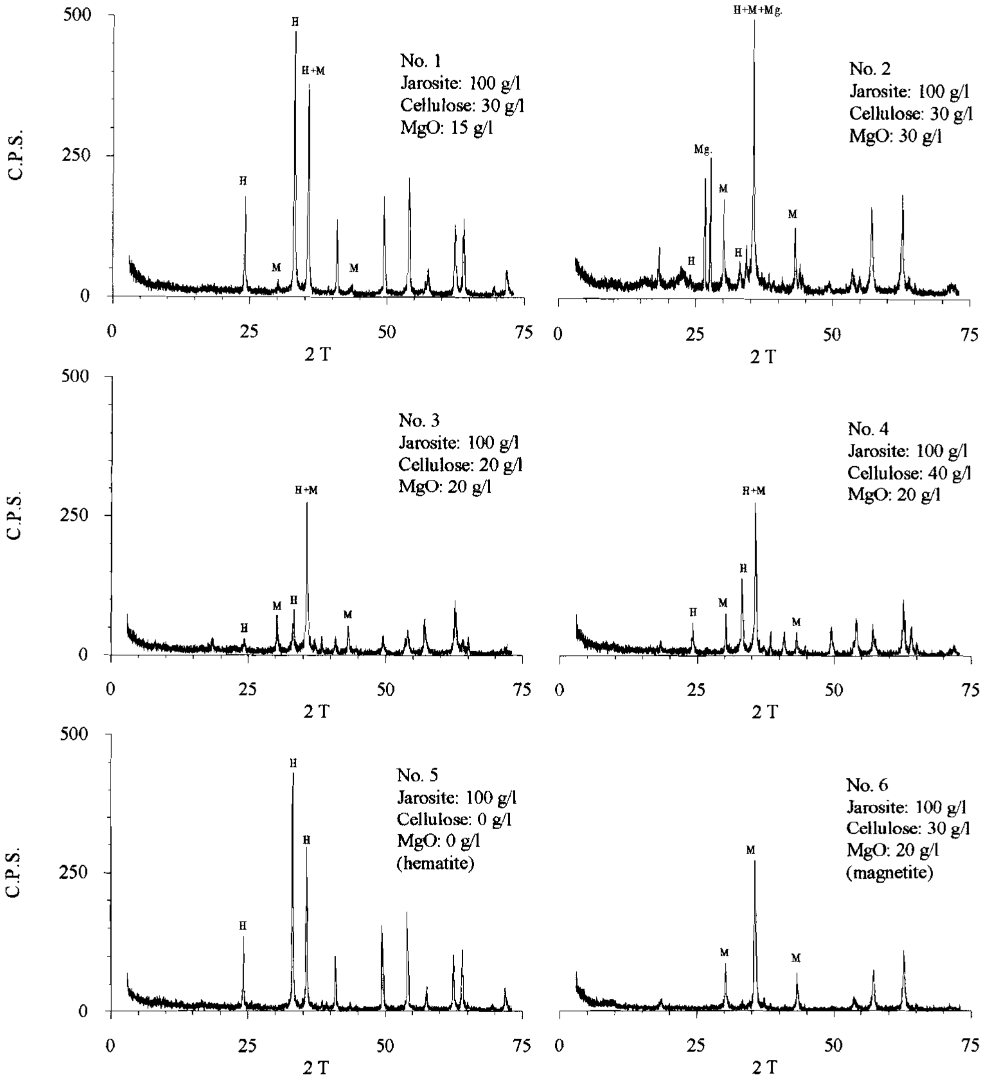

Fig. 7. XRD diagrams of the products. This XRD series show the optimal ratio between Na-jarosite, cellulose and MgO for the production of magnetite. (H=hematite, M=magnetite, Mg..=magnesium-sulfate-hydroxide)

Table 7 - Mass Balance Computation for 'composition 6'

	Input (g/l)			Output (g/l) (measured)		
	Na-J.	MgO	Cellulose	solid	liquid	deviation (%)
Fe	34.64	0.00	0.00	35.31	0.00	1.9
SO_4	36.3	0.00	0.00	0.66	38.9	8.8
Na	3.17	0.00	0.00	0.01	3.38	6.9
Mg	0.00	12.06	0.00	0.60	9.79	-14
C	0.00	0.00	13.3	2.22	6.87	-32

	Input (%) (assumed)		Output (wt%) (calculated)		
	solid	liquid	solid	liquid	gas
Fe	100	0	100.0	0.0	0.0
SO_4	100	0	1.7	98.3	0.0
Na	100	0	0.4	99.6	0.0
Mg	100	0	5.8	94.2	0.0
C	100	0	16.6	51.5	31.9

Reaction mechanism

Three experiments (6a, 6b, 6c) were needed to generate the data listed in Table 8; during each experiment three samples were taken. Iron, sodium and sulfate originated from the jarosite, magnesium from the MgO and TOC from the cellulose. The sodium and sulfate concentrations indicate when the jarosite begins to dissolve. They have not been observed to take part in major precipitation reactions and remain in solution. Iron will be precipitated as goethite due to the relatively high acidity [20]. The concentration of the magnesium ions slowly increases as a result of released hydrogen ions. TOC indicates the temperature at which cellulose starts to decompose. The data from Table 8 is visualised in Figure 9. From this Figure it appears that the breakdown of synthetic Na-jarosite is virtually completed before the cellulose starts to decompose.

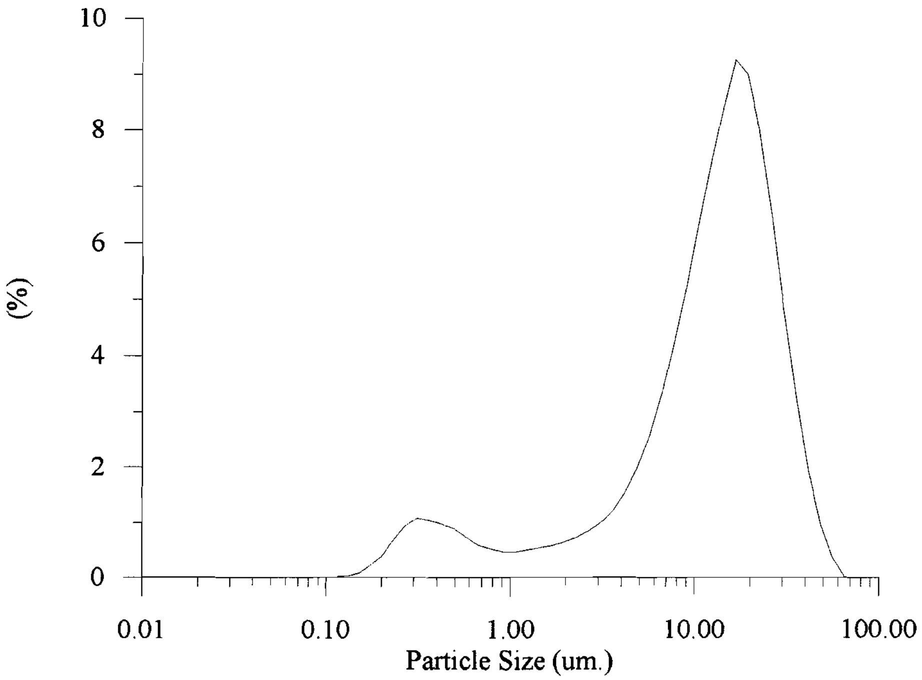

Fig. 8. Particle size distribution of 'experiment 6' magnetite. D_{50} = 14.90 μm.

Table 8 - Samples in Time of Experiment No. 6 (see Table 2,3,4)

Sample No.	time min:sec	temp. °C	$Fe^{2+/3+}$ (g/l)	Mg^{2+} (g/l)	SO_4^{2-} (g/l)	Na^+ (g/l)	TOC (g/l)	pH
start	0:00	22	--	--	--	--	--	10.12
1-6a	11:00	120	n.d.	2.19	13.0	0.61	--	--
2-6a	12:30	130	n.d.	3.25	17.5	1.12	0.02	9.08
3-6a	14:00	140	n.d.	4.25	21.7	1.60	0.03	9.02
4-6b	15:30	150	0.055	5.78	28.3	2.35	0.01	8.95
5-6b	17:00	160	n.d.	6.44	30.8	2.61	0.12	--
6-6b	18:30	170	n.d.	7.56	35.2	3.11	0.12	8.96
7-6c	20:00	180	n.d.	7.68	36.4	3.27	0.30	8.91
8-6c	21:30	190	n.d.	8.00	37.6	3.40	0.88	--
9-6c	23:00	200	n.d.	8.13	37.6	3.47	0.67	8.71
10-6c	24:30	210	n.d.	8.22	37.9	3.50	1.20	--
(Exp. 6)	60:00	250	n.d.	9.79	38.9	3.38	0.70	8.70

n.d. = not detected

A new experiment based on 'composition 6' was carried out. This time samples were taken without the 0.5 µm filter. The samples were washed with distilled water and analyzed by XRD. The samples were taken at 200 °C, 250 °C and 250 °C after 30 minutes retention time (Figure 10). In contrast to what was expected the solid at 200 °C is a poorly crystalline goethite; at 250 °C this material starts to convert to magnetite, and after 30 minutes the sharp peaks indicate a well crystallized material, composed of magnetite and magnesium-sulfate-hydroxide ($(Mg_4[SO_4]_3[OH]_2\cdot H_2O)$). This second product was absent in the first experiment no. 6, indicating the sensitivity of the reaction; the conditions under which pure magnetite is produced are very strict. The production of magnesium-sulfate-hydroxide can be avoided of course by selecting another neutralizing agent like ammonium hydroxide.

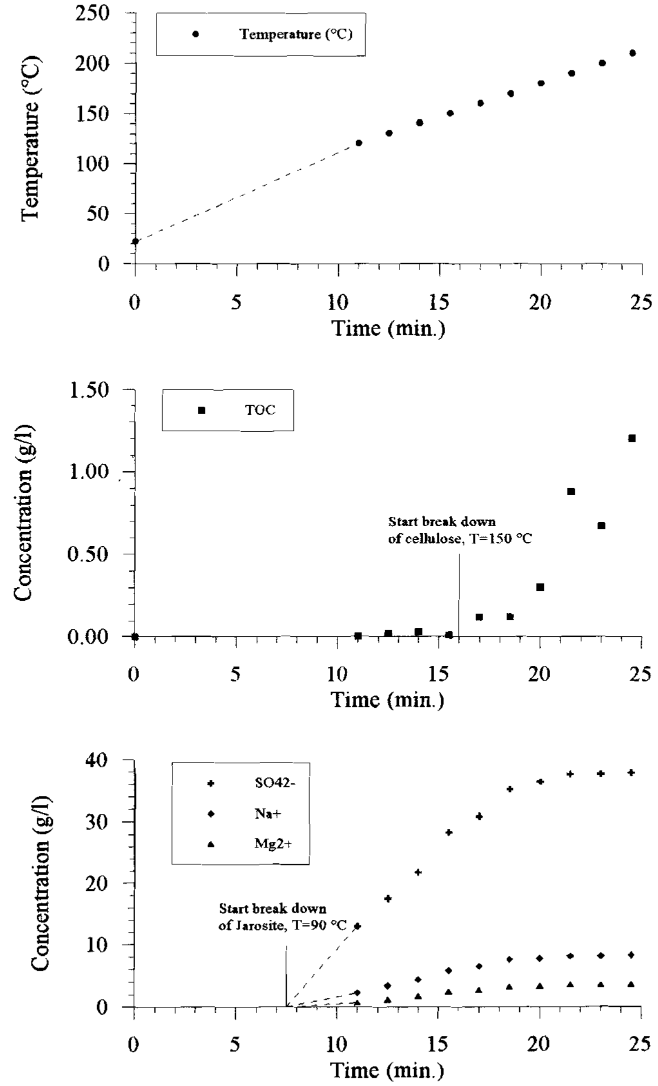

Fig. 9. Filtered samples in time of experiment No. 6

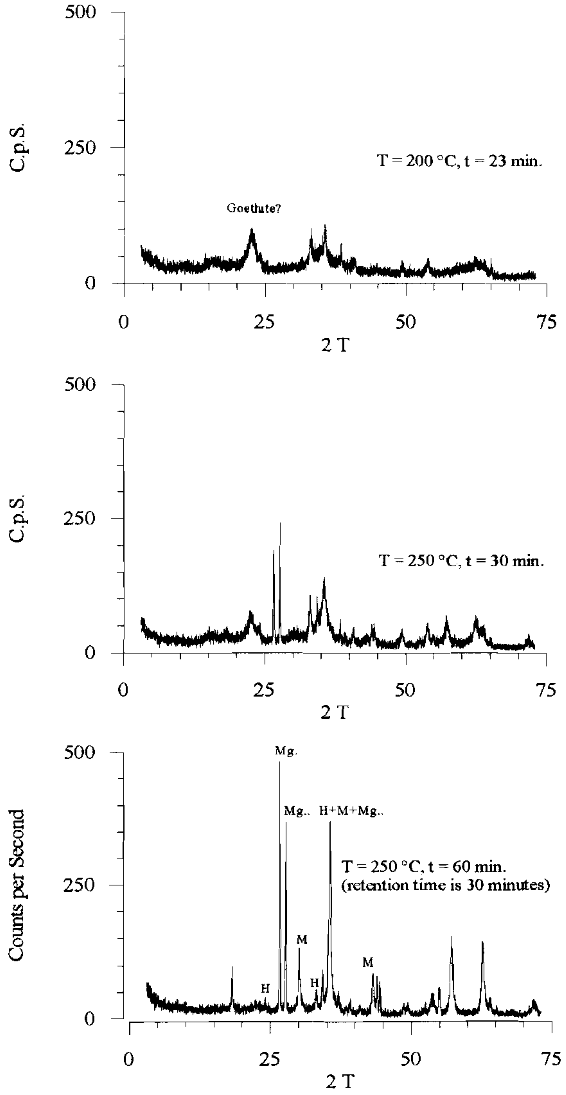

Fig. 10. XRD diagrams from samples in time concerning experiment No. 6

Discussion

Optimal ratio of jarosite, cellulose and MgO

The reduction of iron(III) not only depends on the relative amount of reducing agent, but also on the amount of neutralizing agent. Looking at the XRD-diagrams (Figure 7) it seems that the optimal ratio is critical. Only mixture No. 6 produced a solid containing one mineral. Adding more neutralizing agent (No. 2) or reducing agent (No. 4) resulted in mixtures of hematite and magnetite. Adding less neutralizing agent (No. 3) or less reducing agent (No. 1) resulted in a mixture of hematite and magnetite as well. The Pourbaix diagram (Figure 3) shows a relatively small area in which magnetite can be produced. The composition of the reaction slurry seems to be critical since only one mixture yielded pure magnetite. Nevertheless, other mixtures yield magnetite as well. This system is potentially able to create sufficiently reducing conditions to reduce Fe(III) to Fe(II).

It is noteworthy that pyrite is not produced, in spite of 40 g/l sulphate in solution at 250 °C. Looking at the Pourbaix diagram for the Fe-C-Na-S-H_2O system at 250 °C (Figure 3), it can be expected that for a pH smaller than 6, pyrite or marcasite is produced. Their absence is possibly a kinetic effect; iron is precipitated as oxides before sulphate is reduced. The sulfur present in the solid is in the form of sulphate. In the case of magnetite, magnesium-sulfate-hydroxide is responsible for the sulfur content of the solid. With hematite (experiment 5), sulfate was present as well, but no MgO was added, thus no magnesium-sulfate-hydroxide could be produced. Von Röpenack [21] tried to precipitate hematite from a sulfate solution in an autoclave, but failed to produce a sulfur-free product, preventing its recycling as a raw material in the steel industry. It may be possible to produce magnetite as a sulfur free iron residue, suitable for recycling. Further research is required.

Reaction mechanism

It is difficult to make rigorous statements about the reaction mechanism since the reactions are not isothermal. Therefore the mechanism presented here is a suggested mechanism. The ICP-AES results of Table 8 (Figure 9) show that around 190 °C the breakdown of Na-jarosite is completed. TOC results indicate that cellulose starts to decompose around 150 °C. This breakdown of cellulose releases electrons, necessary for the reduction of iron(III). Most likely several subreactions are occurring subsequently or simultaneously. In an effort to understand the mechanism the main suggested reactions are shown in equations (1)-(9). Reaction (1) shows the dissolution of jarosite, occurring at 90 °C and higher temperatures. Iron was not detected in solution (Table 8) indicating that before magnetite or hematite is produced, any dissolved iron is immediately precipitated as iron(III)hydroxide, due to the high pH (2) [13]. Reactions (3), (4) and (5) show the transformation of cellulose. The overall reaction for the ratio of Na-jarosite/MgO/cellulose of 'experiment 6' is shown in (6). This suggested reaction is based on the carbon measurements from Table 4, the TOC measurements from Table 5 and the mass balance calculated from Table 7. The released electron per glucose unit is based on the ratio of cellulose and jarosite in the initial reaction fluid of experiment 6. Wet oxidation is the combustion of cellulose with oxygen at about 280 °C in an autoclave, releasing carbon dioxide as a final product. During wet oxidation 24 electrons per glucose unit are released instead of one [14]. This difference indicates that the interaction between the oxidizer (oxygen versus Na-jarosite) and reducing agent (cellulose) is of major importance for the reduction capacity. Cellulose can release up to 24 electrons per glucose unit, but the recrystallization reaction of goethite is not able to fully use this reducing potential. The major part of the cellulose is simply 'cracked' into smaller organic molecules. It is most likely that it is not the cellulose that is responsible for the reduction, but one of its breakdown compounds. Iron hydroxide recrystallizes during further processing. Under sufficiently reducing conditions part of the iron(III) from the iron(III)hydroxide (goethite) is reduced to iron(II), producing magnetite (7). When the reducing conditions are not strong enough, hematite is produced (8). The overall reaction for 'experiment 6' is shown in (9).

$$NaFe_3(SO_4)_2(OH)_6 \rightarrow Na^+ + 3\,Fe^{3+} + 2\,SO_4^{2-} + 6\,OH^- \tag{1}$$

$$3\,Fe^{3+} + 9\,H_2O \rightarrow 3\,Fe(OH)_3 + 9\,H^+ \tag{2}$$

$$C_6H_{10}O_5]_n + 7n\,[H_2O] \rightarrow 6n\,[CO_2] + 24n\,[H^+] + 24n\,[e^-] \tag{3}$$

$$[C_6H_{10}O_5]_n \rightarrow 6n\,[C] + 5n\,[H_2O] \tag{4}$$

$$[C_6H_{10}O_5]_n \rightarrow n\,TOC \tag{5}$$

$$[C_6H_{10}O_5]_n \rightarrow 2n\,CO_2 + 4n\,\{C + TOC\}] + n\,H^+ + n\,e^- \tag{6}$$

$$3\,Fe(OH)_3 + H^+ + e- \rightarrow Fe_3O_4 + 5\,H_2O \tag{7}$$

$$3\,Fe(OH)_3 \rightarrow 1\tfrac{1}{2}\,Fe_2O_3 + 4\tfrac{1}{2}\,H_2O \tag{8}$$

$$\begin{aligned} NaFe_3(SO_4)_2(OH)_6 + {}^{1}/_{n}\,[C_6H_{10}O_5]_n \rightarrow\ & Fe_3O_4 + 2\,CO_2 + 4\,\{C + TOC\} + 2\,H_2O + \\ & H^+ + 2\,H^+ + Na^+ + 2\,SO_4^{2-} \end{aligned} \tag{9}$$

In previous studies [9] industrially produced NH_4-jarosite was treated in a similar way. It was mixed with sewage sludge as a reducing agent and ammonia as a neutralizing agent. At 200 °C it takes more than 30 minutes for the complete release of sulfate out of the jarosite. At higher temperatures this reaction has a higher rate. The jarosite used in the work presented here is Na-jarosite, which is less stable than industrially produced ammonium-jarosite.

It was tried to produce magnetite, starting from other iron containing minerals as well. An attempt to process hematite in a similar way met with limited success [22]. Only at extreme conditions (pH > 13, t = 4 hours) was it possible to crystallize a small amount of magnetite. Hematite is apparently too stable for this purpose, while jarosite and goethite are not.

Conclusions

This study illustrates the reducing capacity of an autoclave system with cellulose. It is shown that magnetite can be produced out of Na-jarosite. This reaction not only depends on a reducing agent, but requires the presence of a neutralizing agent as well. For the experiments cellulose was chosen as a reducing agent, and MgO as a neutralizing agent. The optimal ratio to produce magnetite in an autoclave at 250 °C (P=40 bar) and 60 minutes retention time is 100 g/l Na-jarosite, 30 g/l cellulose and 20 g/l MgO. This study shows that this ratio is critical. Adding more or less of either neutralizing- or reducing agent will influence the product; hematite will be produced as well. This study also shows that first the Na-jarosite is transformed to goethite, next cellulose breaks down and finally goethite recrystallizes to magnetite. The hypothesis that only dissolved substances can be reduced in this way is not always true; apparently solids undergoing a reaction can be reduced as well with cellulose in an autoclave.

Cellulose provides the electrons needed for the reduction, and generates byproducts as well. Carbon dioxide is expected, but about 70 wt% of the carbon originating from the cellulose ends up in the solid and in the liquid. Maybe not the cellulose, but an intermediate product creates the reducing conditions. If another compound causes the actual reduction, it may be possible that by adding only this reactant no carbon species other than carbon dioxide are left in the products. Further research should focus on this item.

MgO was used as a neutralizing agent. Although Mg^{2+} was dissolved, part of it ends up in the solid as magnesium-sulfate-hydroxide. This can be prevented by using another neutralizing agent such as ammonium hydroxide. The sulphate content of the solid will be lower as well. If an iron residue with low sulphate content can be produced, this may be recyclable in the steel industry.

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References

1. Van Weert, G., 'Hydrometallurgie deel B', Lecture Notes, Delft, Technical University, MP3310, Januari, 1994, pp. 3-5

2. Elgersma, F., 'Integrated Hydrometallurgical Jarosite Treatment, Ph.D. Thesis, Delft University, 1992, The Netherlands, pp. 1-13.

3. Dutrizac, J.E., 'The hydrothermal conversion of jarosite-type compounds to hematite', Productivity and Technology in the Metallurgical Industries, Eds M.Koch and J.C. Taylor, The Minerals, Metals & Minerals Society, 1989, pp. 587-612.

4. Dutrizac, J.E., 'Converting jarosite residues into compact hematite particles', *JOM*, January 1990, pp. 37-39.

5. Boháček, J., Šubrt, J., Hanslík, T., Tláskal, J., 'Preparing particulate magnetites with pigment properties from suspensions of basic iron(III)sulfates with the structure of jarosite', *Journal of Materials Science*, Vol. 28, pp. 2827-2832, 1993.

6. Kunda, W., Veltman, H., 'Decomposition of jarosite', *Metallurgical Transactions B*, volume 10B, September 1979-439, American society for metals and the metallurgical society of AIME, ISSN 0360-2141/79/0911-0439$00.75/0.

7. Konings, A.J.A., 'Reductive dissolution of jarosite' paper presented at the GDMB-meeting, Antwerp, May 1988 (in German).

8. Lei, K.P.V., Gallagher, N.P., 'Hydrothermal sulfidation of plumbojarosite for recovery of lead and silver', paper presented at the EPD Congress '90, edited by D.R. Gaskell, The Minerals, Metals & Materials Society, pp. 13-20.

9. Jonckbloedt, R.C.L., 'The dissolution of olivine in acid; a cost effective process for the elimination of waste acids', PhD thesis, Utrecht University, The Netherlands, 1997, pp. 89-101.

10. Hage, J.L.T, Schuiling, R.D., Van Enk, R., 'An Integrated Jarosite and Sludge Treatment Process", in: J.E. Dutrizac, G.B. Harris (Eds.), Proc. 2nd Int. Symp. on Iron Control in Hydrometallurgy, CIM, Montreal, 1996, pp. 581-596.

11. Cadotte, A.P., Laughlin, R.G.W., 'The Wetox® Process for Industrial Waste Management', in: M. Moo-Young, G.J. Farquhar (Eds.), Waste Treatment and Utilization, Theory and Practice of Waste Management, Pargamon Press, Oxford and New York, 1980, pp. 157-172.

12. Lübke, A., 'Das Deutsche Rohstoffwunder', Buchdruckerei August Häbich, Stuttgart-Botnang, Verlag für Wirtschaft und Verkehr, Forkel und Co., Stuttgart, 1938, pp. 190-192.

13. Goudriaan, F., Peferoen, D.G.R., 'Liquid fuels from biomass via a hydrothermal process', *Chemical Engineering Science*, Vol. 45, No. 8, 1990, pp. 2729-2734.

14. Hage, J.L.T., Van Weert, G., Schuiling, R.D., 'Reduction of inorganic compounds in autoclaves by using suspended cellulose', in: S.P. Vriend, H. Zijlstra (Eds.), *Journal of Geochemical Exploration*, special issue, 62 nos. 1-3, 1998, pp. 287-291.

15. Roine, A., 'Outokumpu HSC chemistry for windows', version 2.0, 1994.

16. Dutrizac, J.E., Kaiman, S., 'Synthesis and properties of jarosite-type compounds', *Canadian Mineralogist*, Vol. 14, 1976, pp. 151-158.

17. Whitfield, M., 'Thermodynamic limitations on the use of the platinum electrode in Eh measurements', *Limnol. Oceanogr.*, 1974, Vol. 19, pp. 857-865.

18. Eugster, H.P., 'Minerals in hot water', *American Mineralogist*, 71, pp. 655-673. 1986.

19. Barth, T., Skeidsvoll, O., 'Conversion of Algal Biomass to Low Molecular Products by Hydrous Pyrolysis and Comparison to Simulated Maturation of Petroleum Source Rock', in: D.A. Palmer, D.J. Wesolowski (Eds.), Hydrothermal Reactions, Gatlingburg (Tennessee, USA)/ 5th ISHR, July 20-24, 1997, pp. 39-41.

20. Monhemius, A.J., 'Precipitation diagrams for metal hydroxides, sulphides, arsenates and phosphates', 1977, *Journal of Mining and Metallurgy*, pp. C202-C206.

21. Von Röpenack, 'Future changes in the physico-chemistry of zinc-electrowinning', in: T.S. Mackey, R.D. Prengaman (Eds.), Lead & Zinc '90, TMS, Dallas, 1990, pp.641-652.

22. S. Van der Laan, A. Van Vliet, 'A concise analytical strategy applied to waste treatment technology', in: S.P. Vriend, H. Zijlstra (Eds.), *Journal of Geochemical Exploration*, special issue, 62 nos. 1-3, 1998, pp. 287-291.

Chapter 8

Reduction of Copper with Cellulose in an Autoclave;

an Alternative to Electrolysis?

Abstract

Copper is widely used in electricity wire and electronic devices, which makes it one of the most important base metals. Hydrometallurgical processing routes are typical for ores with low copper content. The low-grade copper ores are stacked in large heaps and sprinkled with dilute sulfuric acid; this is called heap leaching. The collected leach liquor is concentrated and purified in a solvent extraction step, and subsequently processed by electrowinning. Copper plates out and the generated acid is recycled to the heap leach. This paper deals with an alternative for the electrolytic processing step by autoclaving a mixture of cellulose and copper sulfate solution.

In the laboratory a 600 ml. Parr autoclave was used. First the exact ratio of cellulose and copper ions was determined. Cellulose was suspended in a copper sulfate solution and heated in an autoclave till 250 °C. After a retention time of 60 minutes at this temperature the pressure vessel was quenched with water. The liquid was analyzed by ICP and the solids by ICP and XRD. The copper ions were precipitated as elemental copper with a particle size around 80 μm. A solid byproduct was an easily separable, black organic phase, probably carbon. The generated dilute sulfuric acid contained dissolved organic carbon. The low pH of this acid restricts the choice of construction materials for the autoclave. Kinetic results indicate a retention time of 30 minutes, after reaching 250 °C. The process is selective for copper with respect to nickel and iron, but arsenic partly precipitates with the copper. This technology might have its potential as an alternative for electrowinning or can be used for small waste streams containing copper in relatively high concentrations.

Introduction

Copper metal is widely used in electrical wire and electronic devices, heat exchange devices, and alloys, such as bronze and brasses. This quality makes copper one off the most useful metals on earth. Depending on the concentration and mineral composition of the ore, a hydro- or a pyrometallurgical processing route is chosen. Hydrometallurgical processing routes are typical for low grade ores (down to 0.2 wt% Cu). After mining, these ores are commonly stacked in large heaps near the mine and sprinkled with dilute sulfuric acid. The liquid is collected, but its copper content of around 1-5 g/l is too low for direct further processing.

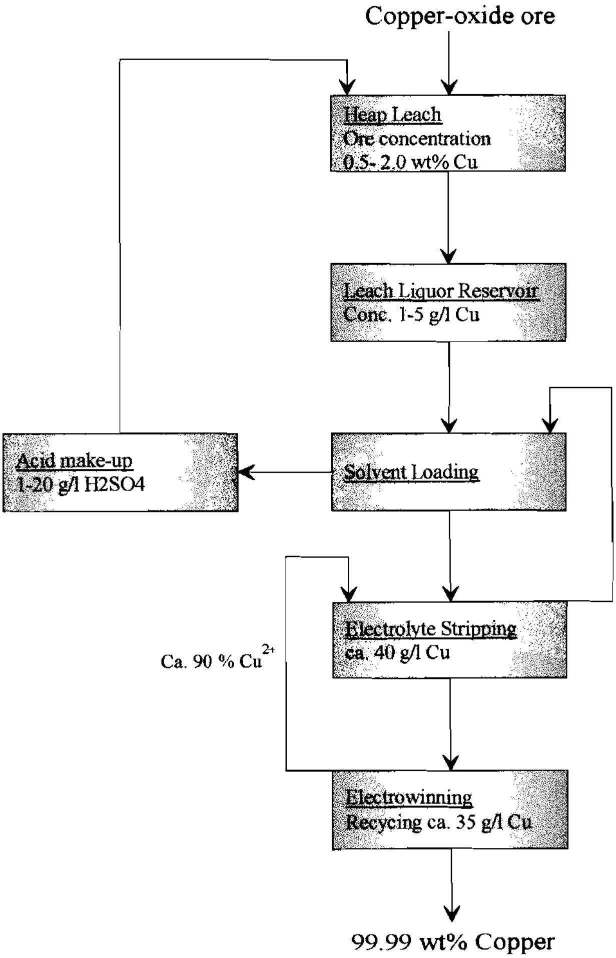

Fig. 1. Schematic flowsheet of a typical copper electrowinning plant

Solvent extraction is used to increase the concentration and to purify the solution; the extractant commonly used is LIX-64 (2-hydroxy-5-dodecylbenzophenone-oxime), usually diluted in a cheap and inert organic phase such as kerosene [1]. After stripping the concentration of the pregnant solution is approximately 40-50 g/l. Normally the process is continued by electrowinning, during which step copper is precipitated on the cathodes. To control acidity about 35 g/l copper is recycled over the solvent extraction unit [2]. A simplified flowsheet of an electrolytic copperwinning plant is shown in Figure 1.

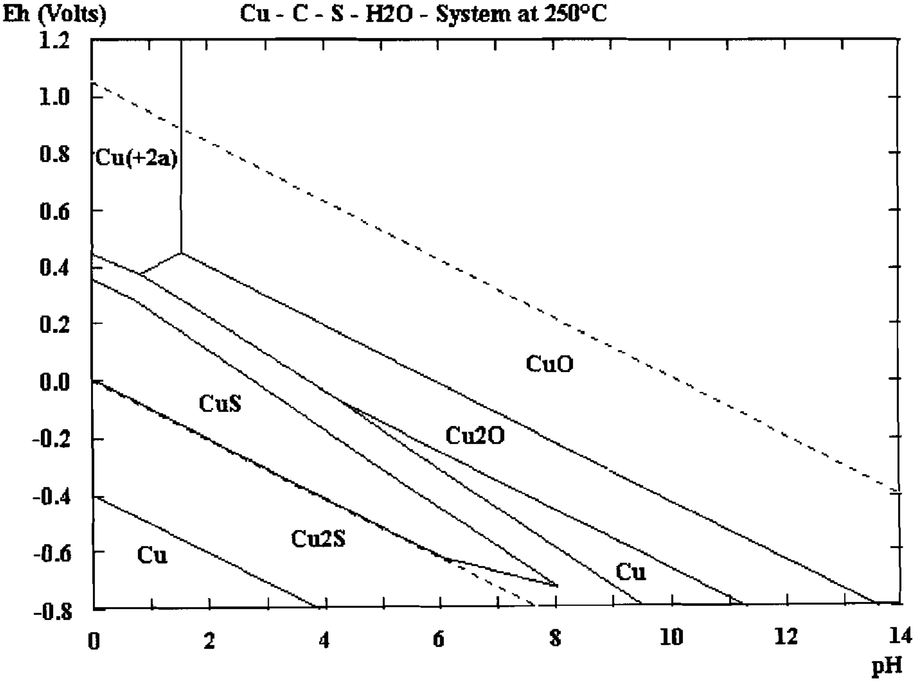

Fig. 2 Pourbaix diagram of the Cu-S-C-H-O system.
Molalities: Cu = 0.629 mol/kg; S = 0.629 mol/kg; C = 1e-12 mol/kg.

Other methods for the precipitation of elemental copper are cementation and non-ionic reduction. Cementation is the precipitation of a metal by another metal; the metal with the more positive electrode potential will dissolve and displace a metal with a less positive potential, for instance copper versus iron. Cementation processes are commonly used to purify pregnant metal refinery solutions. Hydrogen gas or carbon monoxide is used for non-ionic reduction. A copper plant in Tucson, Arizona, based on reduction with hydrogen gas ceased operation in 1970 due to acid generated during the process, but nickel is produced at various locations by this technique.

An alternative non-ionic type reduction process for copper, based on the autoclave oxidation of cellulose is described here. Figure 2 shows a Pourbaix diagram of the copper-carbon-sulfur-water system at 250 °C [3]. In theory, based only on thermodynamics, Cu_2O should be produced under reducing conditions. The kinetics for this reaction have to be slower in comparison to the kinetics for the precipitation of copper. It is not likely that first Cu_2O is produced, subsequently transformed to Cu^0 since Cu_2O is a solid [4]. Cellulose is a model for cellulose type waste materials, such as saw dust, wastepaper or even sewage sludge. They are available in large quantities at low cost. In some countries even a gate fee is paid for treatment of some of these materials [5]. Cellulose is used as a reductant, but it can generate extra heat as well by adding oxygen [6]. This type of reductant makes this process potentially cheaper than conventional electrolytic processes. Cellulose type material, such as wood chips, has also potential as absorbant of metals like gold [7] and others [8]. A simplified suggested overall reaction is defined by (3) in Equation 1. The electrons needed for the reduction of copper (2) are supplied by cellulose (1). To transform 40 gram copper, equivalent to 0.629 moles, 0.315 moles of carbondioxide are released. Carbondioxide is derived from the cellulose, so 0.052 moles of $[C_6H_{10}0_5]$-units are needed. For every 40 gram copper 8.5 gram cellulose is needed according to the suggested reactions. A similar technique was described by Petlicka et al (9). They reported that under autoclave conditions at 200 °C maximum and a retention time of 2 hours elemental copper can be precipitated. Free sulfuric acid and $KMn0_4$ were added to the solution to accelerate the oxidation of the cellulose. Organic particles ended up in the solid product which were hard to separate from the copper. They concluded that a temperature of 200 °C and a retention time of 2 hours was needed for a complete conversion. The required amount of reducing agent (saw dust) was about 125 % of the copper weight. It was suggested that the reaction temperature and the retention time may be lowered by using better stirring equipment. In the process described here a higher reaction temperature was used and no sulfuric acid or $KMn0_4$ was added. Previous studies show that a higher temperature results in a better oxidation of the organic material (10). For this reason a temperature of 250 °C was chosen for most of the experiments.

Equation 1 - Suggested Overall Reaction Between Copper Ions and Cellulose

$$[C_6H_{10}O_5]_n + 7n\,H_2O \rightarrow 6n\,CO_2 + 24n\,H^+ + 24n\,e^- \tag{1}$$

$$12n\,Cu^{2+} + 24n\,e^- \rightarrow 12n\,Cu^0 \tag{2}$$

$$12n\,Cu^{2+} + [C_6H_{10}O_5]_n \rightarrow 12n\,Cu^0 + 6n\,CO_2 + 24n\,H^+ \tag{3}$$

Materials

During the reactions, $CuSO_4 \cdot 5\,H_2O$ was used of pro analysis quality. For the selectivity tests iron sulfate, nickel sulfate and arsenic acid were used of p.a. qualities as well. Acid washed cellulose from 'Baker Chemicals' was chosen as reductant. Destilled water was used as process water. All experiments were done in a Parr 600 ml. bench top mini reactor, which was constructed from 'alloy 20' (35 % iron, 34 % nickel, 20 % chromium and other metals in lower concentrations). Glassliners were used inside this continuously stirred reactor to protect the wall. The 4-bladed, double stirrer with a diameter of 4 cm was set on a stirring speed of 600 rpm. The temperature was controlled by Parr 4842 PID controller, which has autotune facilities to obtain smooth heating curves (11).

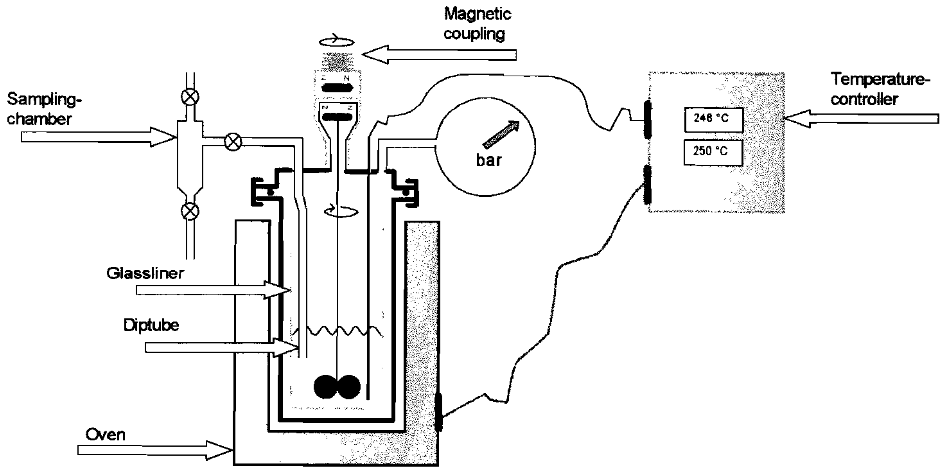

Fig. 3. Overview of the autoclave

Methods

The reaction slurry was prepared inside the glassliners. The volume of a glassliner was 500 ml, which was filled to 50 vol%. Before the reaction takes place, the autoclave was flushed with nitrogen to remove the oxygen, left in the gaseous phase. About 30 minutes is needed to heat the autoclave from room temperature to the setpoint of 250 °C. After a retention time of usually 60 minutes the autoclave was quenched with water. The solid reaction products were filtered over a 45 µm filter with 3 bar air pressure, washed three times with distilled water and subsequently dried for 24 hours at 60 °C. The solids were analyzed by XRD and the liquids by ICP. The particle size detector was a *Mastersizer-S Long Bench* from Malvern. This apparatus is based on laser technology and can measure particles between 0.1 and 3000 µm. To study kinetics a dip-tube was placed inside the autoclave to take samples during the reaction. The diptube was connected to a sampling chamber, which was flushed once, just before a sample was taken. The volume of the sampling chamber was 9 ml. A schematical view of the autoclave is shown in Figure 3.

Results

Optimal ratio of copper ions and cellulose

First the ratio of copper sulfate to cellulose was studied. In theory 8.5 gram cellulose is needed to reduce 40 gram copper ions. The cellulose concentration was varied between 5 and 15 g/l and the copper concentration between 10 g/l and 40 g/l, which is a normal concentration for regular electrolysis. The copper yield was calculated from the ICP data; the results are shown in Table 1. It was not possible to measure the pH correctly with an electrode, due to the low pH. The pH was measured by titration with 1 molar NaOH and subsequently calculated; the results are shown in Table 2. In all cases the measured acidity is slightly lower than the theoretical value. A possible explanation for this phenomenon is the dissolution of carbon dioxide in the reactionfluid. It is remarkable that a weight ratio of copper versus cellulose of 20/5 does not yield the same result as 40/10, which is the same ratio. This has probably to do with the higher quantity of acid produced. The optimal amount of cellulose was 10 g/l; the copper concentration may vary from 10 g/l till 40 g/l for a full conversion. The XRD pattern of the copper product based on a reaction fluid containing 20 g/l copper and 10 g/l cellulose is shown in Figure 4. The d_{50} of this sample was 82 µm (Figure 5). Most of the carbon out of the cellulose appears to be transformed to carbon dioxide gas and the remainder is distributed between the solid, probably as elemental carbon, and the liquid phase as total dissolved organic carbon (TOC). The TOC concentration was determined by spectrophotometric techniques. For the 'optimal ratio' (40 g/l Cu^{2+} and 10 g/l cellulose) the TOC concentration was 1.31 g/l.

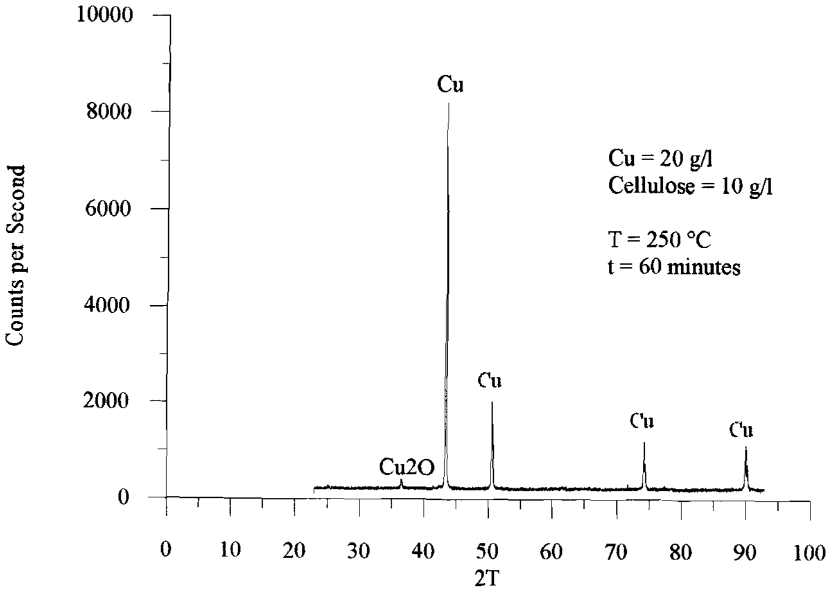

Fig. 4. Typical XRD-Graph of one of the Experiments

Table 1 - Amount of precipitated copper; t = 60 minutes, T = 250 °C.

Cel. (g/l)	Cu^{2+} = 40 g/l	Cu^{2+} = 20 g/l	Cu^{2+} = 15 g/l	Cu^{2+} = 10 g/l
5	58.2 wt%	63.9 wt%	75.4 wt%	99.6 wt%
10	99.9	99.7	99.6	99.7
15	99.5	99.1	99.2	100.0

Table 2 - pH titrations with 1M NaOH

Cel. (g/l)	Cu^{2+} = 40 g/l ($pH_{calc.}$ = -0.10)	Cu^{2+} = 20 g/l ($pH_{calc.}$ = 0.20)	Cu^{2+} = 15 g/l ($pH_{calc.}$ = 0.33)	Cu^{2+} = 10 g/l ($pH_{calc.}$ = 0.50)
5	0.07*	0.76*	0.55*	0.46
10	-0.10	0.13	0.13	0.40
15	-0.02	0.16	0.19	0.47

* no full conversion of Cu^{2+}

Kinetic studies

This study is based on a reaction fluid containing 20 g/l copper and 10 g/l cellulose. After 35 minutes setpoint was reached at 250 °C. Samples were taken during the next hour. This experiment was also carried out at 225 °C. After solid/liquid separation the liquids were analysed for copper and the yield of metallic copper calculated. The results are listed in Table 3 and the graphs shown in Figure 6. At 250 °C the minimum retention time is 30 minutes; at 225 °C it is 70 minutes. When a linear Arrhenius plot is extrapolated to 260 °C, the retention time is expected to be 14 minutes at 260 °C. Such short retention times would be advantages for full scale pressure vessels which can be much smaller at this temperature, for the same capacity.

Table 3 - kinetic studies

Temp. 250 °C				Temp. = 225 °C			
t. (min.)	t' (min.)	Cu^{2+} (g/l)	Yield (%)	t. (min.)	t' (min.)	Cu^{2+} (g/l)	Yield (%)
0	--	20.0	0.0	0	--	20.0	0.0
30	0	14.3	28.4	26	0	13.3	33.5
34	4	9.4	53.1	31	5	9.5	52.7
36	6	7.7	61.7	36	10	8.1	59.7
40	10	6.2	69.0	46	20	7.0	65.3
48	18	4.0	80.3	76	50	3.7	81.7
60	30	0.2	99.0	96	70	0.2	99.0
120	60	0.1	99.6				

t' = time after reaching setpoint

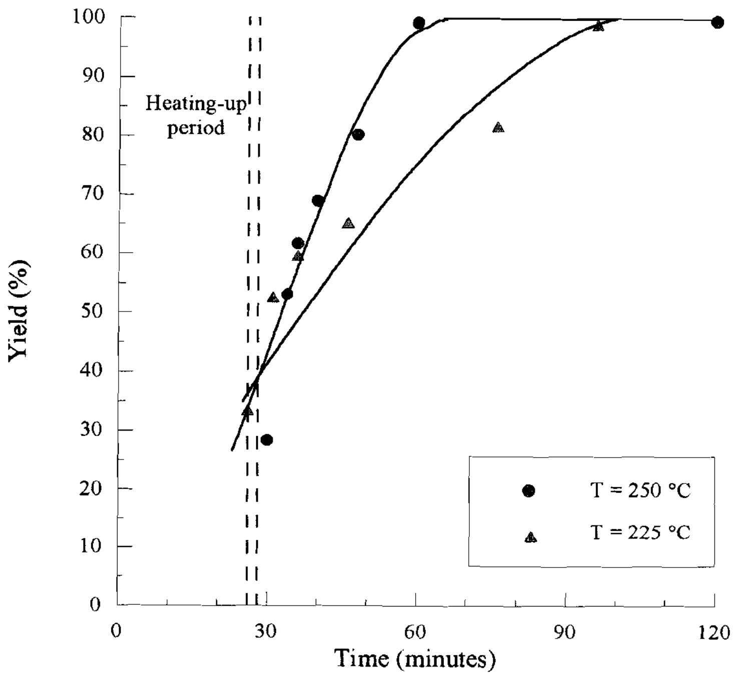

Fig.6. Yield of metallic copper versus time for 20 g/l Cu^{2+} (as sulfate); solutions with 20 g/l cellulose.

Selectivity

Leach liquors or waste waters usually contain other metals besides copper. Metals such as iron, nickel and arsenic are common in copper ore and are present in leach liquors. Solvent extraction concentrates the copper solution and separates the copper from other metal ions. If cellulose reduction is selective with respect to copper, the autoclave may offer an alternative. To test the selectivity a solution was prepared containing 20 g/l coppersulfate,10 g/l iron(III) sulfate, 5 g/l nickel sulfate and 33 mg/l arsenate acid (H_3AsO_4); 10 g/l cellulose was added. After a retention time of 60 minutes at 250 °C the autoclave was quenched. The copper product was carefully separated from the solid organic phase by three times decanting with double distilled water and subsequently filtered over a 0.45μm filter. A sample of 5 g/l copper was dissolved in aqua regia; iron, nickel and arsenic were analyzed by ICP and the copper content was calculated. To calibrate the ICP-ES apparatus, standards were prepared in a copper matrix similar to the sample. The results of this selectivity test are listed in Table 4. Only relatively small amounts of the other compounds are precipitated, except for arsenic. The amount of sulfur is too high to compensate all the iron, nickel and arsenic. Figure 7 shows that the sulfur in the sample can also be present as elementary sulfur, since the combination of pH and Eh is within this region.

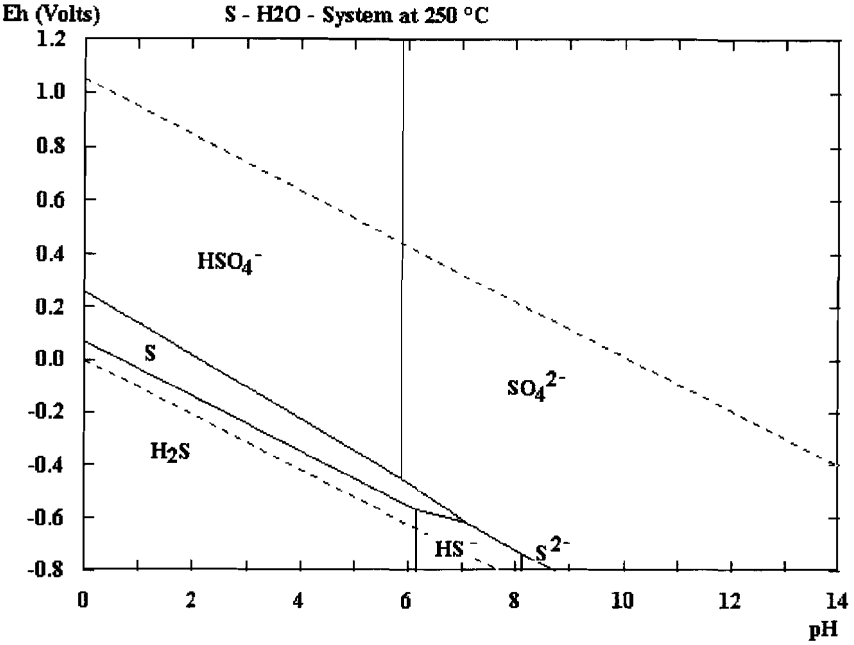

Fig. 7. Pourbaix diagram of the S-H-O system. Molality: S = 0.629 mol/l.

Table 4 - Selectivity of the autoclave reduction of copper

reaction fluid			final product			relative precipitated amount		
Cu	=	20 g/l	Cu	≤	99.62 wt% (calc.)			
Fe	=	10 g/l	Fe	=	0.011	Fe	=	0.022 wt%
Ni	=	5 g/l	Ni	=	0.044	Ni	=	0.18 wt%
As	=	33 ppm	As	=	0.095	As	=	57.8 wt%
S	=	48 g/l	S	=	0.23	S	=	0.006 wt%
Cel.	=	10 g/l						

Energy production

In a full scale operation it is a benefit if the reaction is able to maintain itself inside the autoclave without external heating. When choosing a conventional, horizontal, multi-compartment (Sherrit Gordon type) autoclave, pumps will generate extra heat (12), but this is not enough to run an autoclave if there is no internal heat development from the reaction. To measure the energy production the temperature during the reaction was continuously measured, while the reactor was heated with a constant power output of 780 Watt. Double distilled water was used for the blancs; this is a situation in which no energy is generated. Three reaction fluids were prepared: **1.** 10 g/l cellulose, **2.** 20 g/l copper as copper sulfate and **3.** 10 g/l cellulose plus 20 g/l copper ions. For every experiment a new blanc was determined. To remove oxygen, the reactor was flushed with nitrogen gas. The results are shown in Figure 8. The energy effect of the combustion of cellulose as well as for the heating of copper sulfate solution is zero. Cellulose together with copper sulfate, however show a different

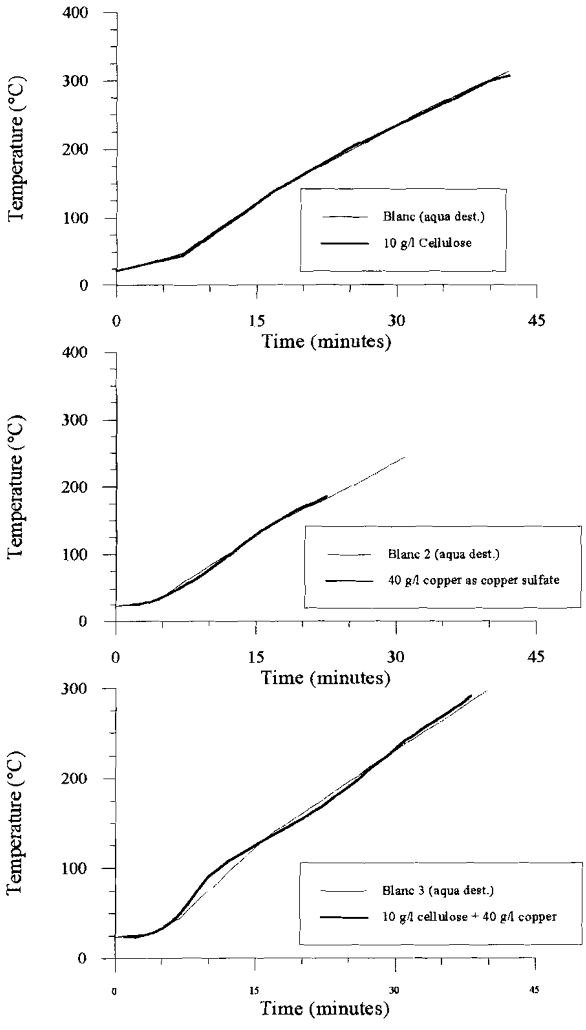

Fig. 8. energy budget measurements

result. Up to 100 °C energy is released from the reaction fluid, producing a maximum temperature difference of about 20 °C after 11 minutes. Till 200 °C there is a small energy demand, which changes sign above 200 °C. From the kinetic data it is appered that the copper reduction starts at 200 °C. It is not clear what reactions are causing the energy effects below 200 °C. The blanks provide an idea of the accuracy of this method, since every experiment was done following the same procedure. After 30 minutes the temperature of Blank1 was 234 °C, Blank2 236 °C and Blank3 230 °C respectively, giving an average temperature of 233 °C (with a standard deviation of ± 3 °C).

Discussion and engineering aspects

Autoclaving versus electrolysis

Expensive steps in hydrometallurgical processing of low grade copper ore are mining, heap leaching, solvent extraction and the electrowinning step. This proposed technique influences the solvent extraction and replaces the electrowinning step. At low copper concentrations, a solvent extraction step remains necessary to increase the copper concentration. A lower copper concentration will dramatically increase the hydraulic load and as a result it will be too expensive to run an autoclave commercially in a full scale copper winning plant. Nevertheless, some major changes to this unit can be achieved. Basically a solvent extraction unit consists of an extraction step and a stripping step. The size of the extraction stage remains the same, since the amount of leach liquor remains the same, but the selectivity rendered by this autoclaving process increases the choice of extraction reagents. The organic reagent must load all the copper, but selectivity against iron is less important. The hydraulic load of the autoclave will be much lower than the hydraulic load of a tankhouse. This is due to the large recycle stream of the electrolytic process, where almost 90 vol% of the pregnant solution is recycled over the solvent extraction unit. In an autoclave, on the other hand, all copper is removed in one step. This results in a smaller stripping stage. The recycle stream to the solvent extraction plant contains dissolved organic carbon and inorganic impurities in higher concentration than usual. A larger bleed stream or even a purification step may be required. Casting of the copper particles into standard units will be as easy as with regular copper cathodes; the small particle size might even be a benefit.

Proposed flow sheet

The proposed flowsheet is shown in Figure 9. In comparison with a flow sheet based on electrolysis some additional equipment is needed. To separate the solid carbon particles from the copper a solid/solid separation like hydrocycloning is required. An extra benefit of hydrocycloning is that separating and washing of both carbon and copper is possible in one stage. After filtering and drying the carbon product can be used as a fuel in power plants. Instead of the proposed purification of the acid electrolyte after autoclaving, it can also be envisaged to use it as a leaching agent in heap leaching. The dimensions of an autoclave based on the production of 100.000 ton copper per year are listed in Table 5. The autogenic pressure of 3.9 kPa is a consequence of the temperature. The kinetic studies show that the retention time is at least 30 minutes under these conditions. Maintenance of the autoclave is estimated at about 2 months per year. The maximum allowable water (slurry) loading is 72 vol% (11). The computation of the size of the autocalve is shown in Calculation 1. A volume of 240 m^3 is a huge system, but increasing the temperature by 10 °C results in a much smaller type, assuming a linear Arrhenius plot till 260 °C. The process is not producing enough energy to maintain itself and the energy generated by the pumps is probably insufficient; it will be necessary to add more energy to the system. This study did not focus on this problem, but a way of achieving extra energy is by heating the autoclave or by adding extra cellulose and air. The wet oxidation of the cellulose will yield the needed energy. The low pH and low redox potential of the reaction fluid constrains the choice of construction materials for the autoclave. If no suitable metals are available, a brick liner may be required. Brick liners are commonly used in pressure vessels for pressure leaching of gold ore (12).

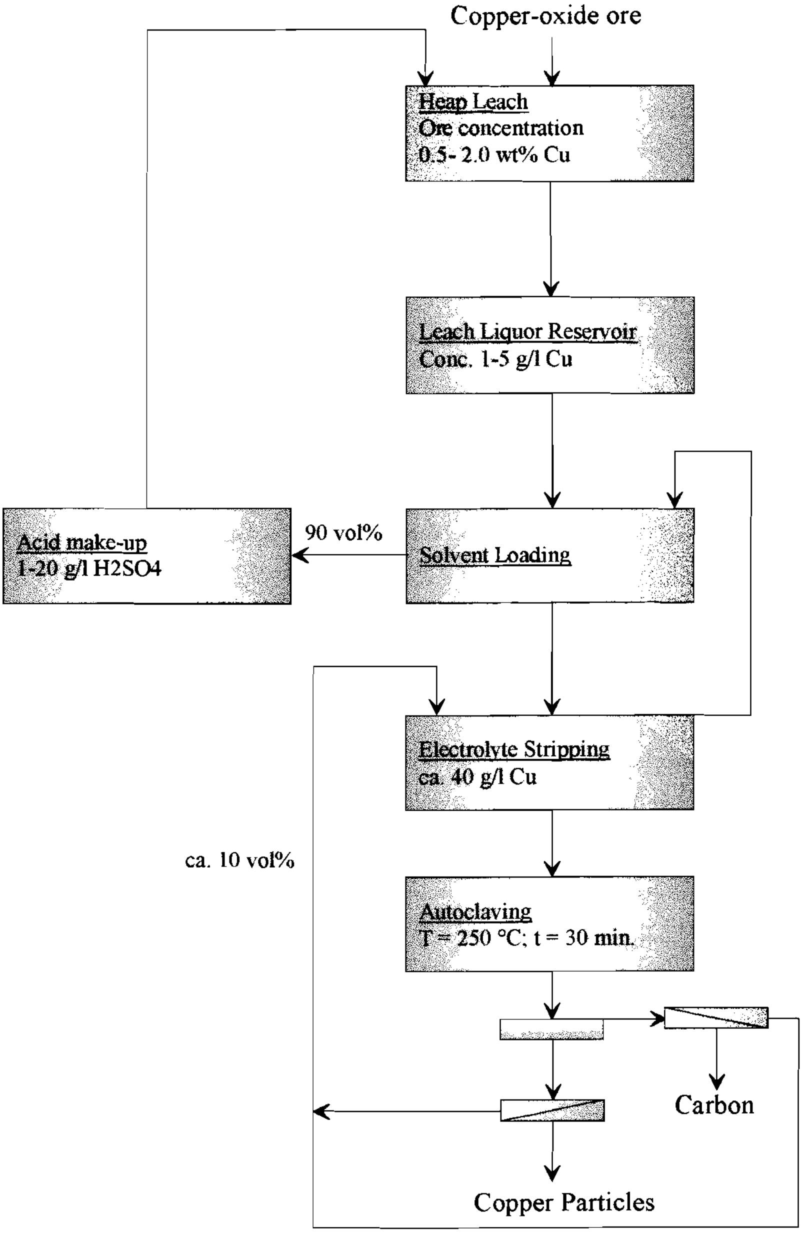

Fig. 9. Schematical Flowsheet of a Copper Process based on Autoclave Techniques

Table 5 - Dimensions of an autoclave based on a production of 100.000 ton/year copper

Reaction temperature	250 °C	260 °C
Pressure	3,923 kPa	4,630 kPa
Reaction time	30 minutes	14 minutes
Yearly production	100.000 ton	100.000 ton
Availability	300 days/year	300 days/y.
Maximum allowable water loading at 250 °C (13)	72 vol%	70 vol%
Concentration pregnant solution	40 g/l	40 g/l
Final acidity	62 g/l H_2SO_4	62 g/l H_2SO_4
pH_{end}	≈ -0.1	≈ -0.1
Calculated autoclave volume ca.	240,000 liter	116,000 liter

This process not only has its potential for full scale operations, but for smaller operations as well. An exemple is the purification and recovery of copper from waste solutions produced by, for instance, galvanic industries. Due to the selectivity quality, pure copper will be produced, in spite of the presence of other metal ions. From a technical point of view, lower copper concentrations are not a problem for this reduction method.

Calculation 1 - The autoclave size at 250 °C, based on 100.000 ton/year copper

$$\text{Size} = \frac{\text{Production (mass/time)} * \text{Retention time (time)}}{\text{Concentration (mass/volume)}} * \frac{1}{\text{Loading (\%)}}$$

$$\text{Size} = \frac{(100.000\text{e}6 \,/\, 300 * 24 * 60) \quad * \quad 30}{40} * \frac{1}{0.72}$$

Conclusions

At this moment electrowinning (SX/EW) and cementation are the only processes used for the reduction of copper. The proposed autoclave method can be an alternative for producing copper. The cellulose-type reduction material can be a waste material, such as saw dust or wastepaper. The solvent extraction step however is still needed in a full scale operation since the copper concentration of regular heap leach liquor is too low to run the autoclave commercially. The size of the autoclave and the energy need are dramatically increased. Nevertheless, due to the selectivity for copper of this reduction process, the solvent extraction unit can be smaller and less effective to generate the same purity of copper. Cheaper reagents might be used. This process can also be run in small scale operations such as waste liquor treatment systems of galvanic industries, or at remote locations where energy and refinery metallurgists are at a premium. A patent for this process was filed under number 97202904.5-2309 (14).

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References

1. Habashi, F., *A Textbook of Hydrometallurgy*, 1993, Imprimerie d'Édition Marguis Limitée.

2. Biswas, A.K, Davenport, W.G., *Extractive Metallurgy of Copper (vol. 20)*, 1994, Pergamon International Library.

3. Roine, A., *Outokumpu HSC Chemistry for Windows 2.0*, 1994.

4. Hage, J.L.T., Van Weert, G., Schuiling, R.D., Reduction of Inorganic Compounds in Autoclaves by using Suspended Cellulose, *Journal of Geochemical Exploration*, June 1998, **62**, 287-291.
5. Oral communication with VerTech Treatment Systems B.V., Apeldoorn, The Netherlands, 1997.

6. De Bekker, P., Van Den Berg, J., Heerema, K., *Het VerTech Slibverwerkingsprocess*, 1988, H_2O, **21**, 94-98, in Dutch.

7. Petersen, F.W., Van Der Plas, P.J., Van Zyl, C.J., The mechanism of gold lock-up in refractory wood chips, *Minerals Engineering*, 1997, 10(11), 1259-1267.

8. Gaballah, I., Kilbertus, G., Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluent using modified barks, *Journal of Geochemical Exploration*, 1998, **62**, 241-286.

9. Petlička, J., Klir, L., Redukce Mědi z Roztoků Měď'natých a Zinečnatých Soli Dřevěnými Pilinami. (Copper Reduction from Copper-Zinc Solutions by the use of Sawdust). *Hutnické Listy*, 1969, **čis. 5**, 354-358, in Czech.

10. Hage J.L.T., Schuiling R.D., Van Enk R., An integrated Jarosite and Sludge Treatment Process, in: Dutrizac J.E., Harris, G.B. (Eds.), *Proc. 2nd Int. Symp. on Iron Control in Hydrometallurgy*, CIM, Montreal, pp. 581-596, 1996.

11. *Stirred Reactors and Pressure Vessels*, 1994, catalog by Parr Instrument Company, 211 Fifty-Third Street, Moline, Illinois 61265 USA, (fax 309/762-9453)

12. Thomas, K.G., *Research, Engineering Design and Operation of a Pressure Hydrometallurgy Facility for Gold Extraction*. 1994, ISBN 0-9698067-0-1, Ph.D. thesis TU Delft, The Netherlands, sold via CIM, Montreal.

13. *Parr Operation Instructions*, No. 230M, *Safety in the Operation of Laboratory Reactors and Pressure Vessels*, pp. 3, Parr Instrument Company, 211 Fifty-Third Street, Moline, Illinois 61265 USA, (fax 309/762-9453)

14. *Process for the Recovery of Metals*, European Patent no. 97202904.5-2309, 22/09/1997, CES B.V., The Netherlands.

Appendices

Appendix 1

Analysis of the gaseous phase

The volatile organics yielded by the jarosite/sludge reaction are analyzed in order to determine the reaction mechanism. *Gas chromatography* (GC) and *mass spectrometry* were used Therefore, 300 ml. reactionfluid, containing 100 g/l Asturiana jarosite and sewage sludge was prepared. This mixture was put into a glassliner with a volume of 500 ml and heated at 250 °C in a 600ml. Parr autoclave, after flushing the headspace with argon. The starting pressure was 4 bar of Argon. Argon was chosen because of its potency to remain inert during the reaction. It can not originate from the mixture. After one hour treatment, a gas sample was analyzed. The result of the GC analysis is shown in Figure 1. An aliquot of the produced gas was analyzed by a mass spectrometer (V.G., type SIRA 24). In accordance with the GC analysis, carbon dioxide was detected as the major compound in the gaseous phase. Traces of nitrogen gas (N_2), nitrogen oxide gas (NO) and hydrogen gas (H_2) were detected. This hydrogen gas is supposed to be a product of the decomposition of cellulose and other organics, rather than a product of the decomposition of water.

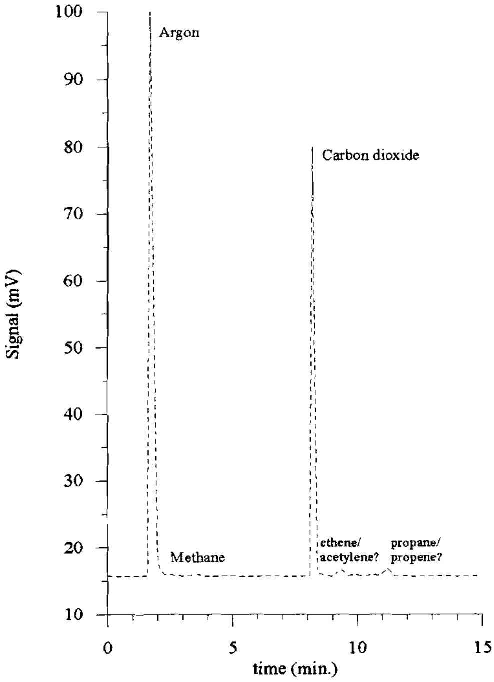

Fig. 1. GC analysis of the gaseous phase of a 'standard' jarosite/sludge reaction

Appendix 2

Analysis of the liquid phase

In this thesis the dissolved organic products are measured as 'total dissolved organic carbon' (TOC). Nevertheless, the analysis of organic compounds in the liquid phase contributes to a better understanding of the decomposition of cellulose. Therefore a sample of treated pure cellulose was prepared. A reaction fluid of 250 ml containing 20 g/l cellulose was treated in a Parr 600 ml. autoclave at 250 °C for one hour. Before heating, the headspace was flushed with nitrogen gas to remove oxygen from the gaseous phase. After cooling and separation the solids, a effluent sample was analyzed with an *ion chromatograph* (Shimadzu, type C-R4A Chromatopac). The result is shown in figure 1. The major phase is identified as formic acid (HCOOH).

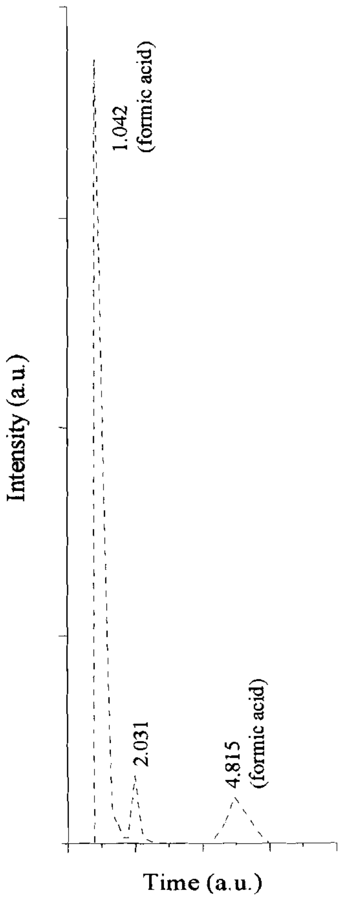

Fig. 1. IC analysis of decomposed cellulose

List of Publications

1. Hage, J.L.T., Schuiling, R.D., van Enk, R., 'An Integrated Jarosite and Sludge Treatment Process', in: Dutrizac, J.E., Harris, J. (Eds.) Second International Meeting on Iron Control and Disposal, Ottawa, CIM, October 20-23, 1996, pp. 581-593.

2. Hage, J.L.T., Van Weert, G., Schuiling, R.D., 'Reduction of Inorganic Compounds in Autoclaves by using Suspended Cellulose', in: Vriend, S.P., Zijlstra, H. (Eds.), *Journal of Geochemical Exploration*, Vol 62, nos. 1-3, special issue, 1998, pp. 287-291 (presented on Geochemical Engineering: current application, August 22-23, 1997, Utrecht, the Netherlands).

3. Hage, J.L.T., Van Enk, R., Schuiling, R.D., 'Jarosite- and Sludge Treatment', poster presented on the fourth NAC congres, 7-8 Mei, 1998, Veldhoven, the Netherlands (first price in its catagorie 'Earth Sciences and Society: Bridging the Gap').

4. Hage, J.L.T., Reuter, M.A., Schuiling, R.D., Ramtahalsing, I.S., 'Reduction of Copper with Cellulose in an Autoclave; an Alternative for Electrolysis?', *Minerals Engineering*, Vol. 12, No. 4, April 1999, (presented on Minerals Engineering, September 14-16, 1998, Edinburgh, Scotland).

5. 'A new method for the recycling and immobilization of metals in jarosite', Final Technical Report, Brite Euram Program, Contract no. BRE2-CT94-0975, Geochem Research B.V., VarTech Treatment Systems, INPL-LEM (France), University of Barcelona, Asturiana de Zinc S.A. (Spain), November 1998.

6. Hage, J.L.T., Schuiling, R.D., Vriend, S.P., 'Transformation of Na-jarosite into Magnetite', accepted for publication after minor revisions in *Canadian Metallurgical Quarterly*.

7. Hage, J.L.T., Van Weert, G., Vriend, S.P., 'Quantitative analyses of industrial jarosites', to be presented at Lead-Zinc 2000, October 22-25, 2000, Pittsburgh, Pennsylvania, USA.

8. Hage, J.L.T., Schuiling, R.D., 'Comparative column elution of jarosite waste and its autoclaved product, evidence for the immobiliztion of deleterious elements in jarosite', submitted to *Minerals Engineering*.

9. Hage, J.L.T., van Enk, R., Koster van Groos, A.F., 'Differential thermometric analysis of autoclave reactions, with the co-treatment of industrial jarosite and sewage sludge as an example', submitted to *Hydrometallurgy*.

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Hans

Curriculum Vitae

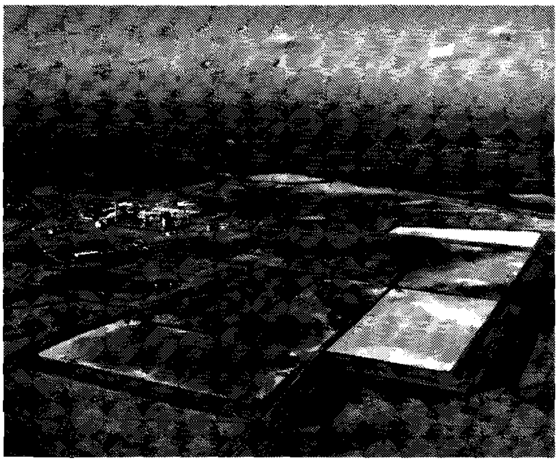
Hans Hage was born on August 29th 1967 in Nieuw-Nickérie, Surinam. When he was three years of age, his parents returned to Holland. In 1980 he started his secondary school at the MAVO in Neede and in 1986 he obtained his HAVO diploma at the *Rijksscholengemeenschap* in Haaksbergen. In the same year, he started to study Chemical Engineering at the Polytechnic of Enschede. As part of his training for the specialism 'Environmental Engineering and Industrial Safety' he worked at AVEBE (Foxhol) and Riza (Lelystad). At AVEBE he studied the flow characteristics of several hydrocyclones, which were to be used in their new potato starch factory. At Riza he formulated and interpreted a nitrogen balance for the lake *Veluwemeer-Drontermeer*. These data were used in a long term study after eutrophication (unlimited growth of algae) in Dutch surface waters. His B.Sc. thesis was performed at the research group for Catalysis and Material Science at the faculty of Chemical Engineering of the Technical University Twente. He worked on a new impregnation method for TiO_2/V_2O_5 catalyst in α-alumina support. This catalyst is used for the reduction of NO_x to N_2 in smoke gases. In June 1991 he got his degree.

In September 1991 he continued his study at the faculty for Earth Sciences of Utrecht University. In 1992 he joined the *Netherlands Indian Ocean Program* (NIOP). The aim of this program was to study climate changes since the last ice age. His M.Sc. thesis concerned the transformation of jarosite with sewage sludge in a pressure vessel. This research was continued and partly financed under the *Brite Euram Program* of the European Community, which made this Ph.D. thesis possible. As a Ph.D. student he joined the Geochemical Engineering research group of the faculty for Earth Sciences from July 1994 to July 1998.

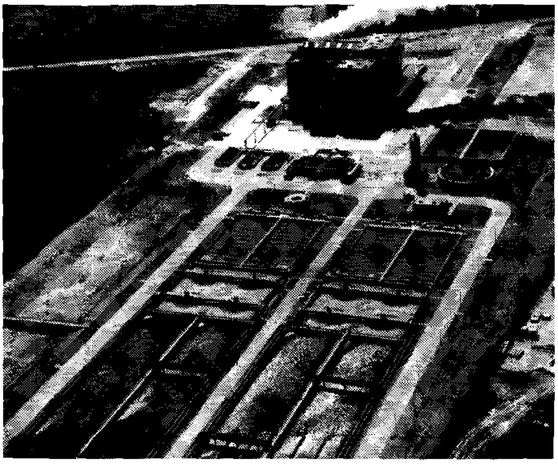
Jarosite- and Sludge Treatment

The Advantage of co-Treatment of Two Waste Products, a Waste-to-Waste Technology

J.L.T. Hage M.Sc, R. van Enk M.Sc, prof. dr R.D. Schuiling *Geochem Research BV, The Netherlands, tel: 030-2541728, fax: 030-2544222*



Zinc-plant in Budel, Holland; lined ponds filled with jarosite



Sewage-works and refuse-incinerator at the same site, Dordrecht, Holland

Jarosite, $M\mathrm{Fe}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6$, is a waste-product from electrolytic zinc-refineries ($M=\mathrm{NH}_4^+, {}^1/_2\ \mathrm{Pb}^{2+}$, etc.).

Total accumulated storage is about 20 million tons worldwide.

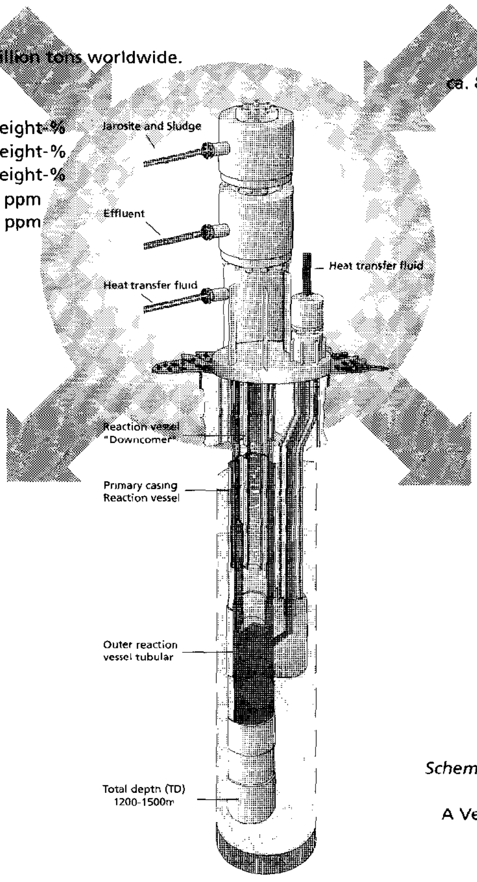
Analyses:

SO_4	40 weight-%	Opal	5 weight-%
FeO	30 weight-%	Gypsum	5 weight-%
Pb	6 weight-%	Others	9 weight-%
Zn	4 weight-%	Ag	100 ppm
NH_4	1 weight-%	Cd	300 ppm

Sewage-sludge is the residue from sewage-works.

Daily production in the Netherlands is ca. 800 tons; burning or storage is required.

Analyses:
60 weight-% organics, mainly cellulose
40 weight-% inorganics,
mainly sand and clay-minerals



Schematically outlining of the VerTech-reactor

A VerTech-reactor is a continuous autoclave, operating at 300 °C and 85 bar.

The not combusted organics in the solid are a benefit for the pyrometallugical solid residue treatment.

Metal-concentrate
ca. 100 kg. per ton jarosite,
to be sold to a lead-zinc-smelter.

Expected analyses:
Pb 55 weight-%
Zn 35 weight-%
Ag 0.1 weight-%
Cd 0.3 weight-%
Others 6 weight-%

High density slag poured into moulds
ca. 500 kg. per ton jarosite,
to be sold to the
building-industry.
This product contains all
the iron, silicon and calcium.

The not combusted organics dissolved into the liquid play an essential role in the biological effluent treatment

Nitrogen-gas
ca. 5 kg. per ton jarosite,
to be released into the air.

Sulfur
ca. 150 kg. per ton jarosite,
to be sold to the sulfur
processing industry.

Purified water
to be drained off
into surface waters.

Process-costs ≤ 'gate-fee' jarosite + 'gate-fee' sludge + proceeds of metal-concentrate + proceeds of artificial rocks + proceeds of sulfur

The partners in this project are Asturiana de Zinc SA, Geochem Research BV, INPL-LEM,
University of Barcelona and VerTech Treatment Systems BV