THE IRON ELEPHANT

A Brief History of Hydrometallurgists’ Struggles with Element No. 26.

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ABSTRACT

The paper reviews the history of modern iron control processes in hydrometallurgy. Particular attention is paid to the processes developed in the 1960s by the electrolytic zinc industry for the removal of iron from zinc sulphate leach liquors - namely the Jarosite, Goethite and Hematite processes. Problems faced by the industry in the safe disposal of the iron residues produced by these processes are discussed. The lessons learnt over the past half century by the zinc industry are projected on to the current efforts to develop hydrometallurgical processes for the treatment of copper sulphide concentrates. It is argued that any attempt to create a “hydrometallurgical copper smelter” is doomed to ultimate failure, unless and until methods are developed that can recover iron from solution in a form that can be directly utilised by the steel or pigment industries.

KEYWORDS

History of iron control; jarosite process; goethite process; hematite process; copper sulphide concentrate leaching.
INTRODUCTION

You suddenly realise that age is catching up with you and that technology is moving on apace when you are asked to talk about the history of a process or a technology that you’ve grown up with. Such was my reaction when, out of the blue, I received an email last year from the chairman of the CIM’s Historical Metallurgy Committee, asking me if I would give a talk on the early developments of iron control in hydrometallurgy. Once I’d got over the initial shock of realising that I had now become living history, I was of course flattered that the invitation was to give a talk at the prestigious IMPC, a conference series that has been going for as long as I have been in the business. That this particular IMPC was to include the 4th Symposium on Iron Control in Hydrometallurgy, made the invitation even more appealing and appropriate, because I was the co-chairman of the First Symposium on Iron Control, together with my old friend, John Dutrizac (known by many as Dr Jarosite), which was held 30 years ago in Toronto.

I first became involved with iron at the very start of my career in hydrometallurgy – the research topic for my Masters degree thesis at UBC, back in the mid 1960s, was “Reductive leaching of Goethite with SO₂”. My thesis supervisor was the late Professor Ian Warren, who himself was a protégé of Professor Frank Forward, one of the founding fathers of modern hydrometallurgy. Little did I realise at that time, now 50 years ago, that the problem of iron and how to deal with it in hydrometallurgical processes would be a theme that followed me throughout much of my 40-year career in academia.

IRON MINERALOGY AND CHEMISTRY

So what is it about iron in hydrometallurgy that has merited four decennial, international conferences – 1986 in Toronto, 1996 in Ottawa, 2006 in Montreal and now 2016 in Quebec, not to mention the thousands of scientific and technical research papers and patents that have been published worldwide outside these conferences?

As we all know, iron is a pretty common element and it is one that we certainly couldn’t live without. It’s an essential part of our biology, where it plays a critical role in the transference of oxygen from the air into our bloodstreams, and it is indispensable for our modern way of life in the form of metallic iron and steels, from which most of the things around us are manufactured.

Let’s start with a few facts about the geological occurrences of iron, element number 26 in the Periodic Table. To source these, I turned to the very first paper in the Proceedings of the First Iron Control Symposium, which was by Chen and Cabri (1986) from CANMET, entitled “Mineralogical overview of iron control in hydrometallurgical processing”. In this excellent review, we read that iron is the second most abundant element in planet earth, after aluminium, and it is the fourth most abundant element in the earth’s solid crust. Iron is an essential component of the crystal structure of over 600 minerals, most of which are classed as oxide minerals (i.e. oxides, silicates, phosphates, arsenates, sulphates, hydroxides and so on) and relatively few are sulphide minerals. Some of this large number of minerals are considered to be ore minerals, but most are gangue minerals, as far as the mineral processor is concerned. Chen and Cabri listed the most important of the iron-bearing minerals in a series of tables in their paper, giving either their chemical formulae, or, where minerals form solid solutions, their compositional ranges. They classified the occurrence of iron in non-ferrous ores into three different modes: i. Ore minerals; ii. Gangue minerals; and iii. Solid solution minerals.

i. Ore minerals: where iron is an essential constituent of a mineral used as a source of another metal, e.g. chalcopyrite, CuFeS₂, a copper ore. Other examples are pentlandite, (Fe,Ni)₉S₈, a nickel ore, and ilmenite, FeTiO₃, a titanium ore.

ii. Gangue minerals: where iron is an essential constituent of a mineral that is undesirable in the ore, e.g. pyrite, FeS₂, often the most abundant species in sulphide ores. Iron oxides, carbonates and silicates are common gangue minerals in many oxidised non-ferrous ore bodies.

iii. Solid solution minerals: this is the substitution of iron for an essential element in the crystal structure of either an ore or a gangue mineral. The most common example of a solid solution ore mineral is sphalerite, (Zn,Fe)S₄, the principal source of zinc, where up to 17% of the zinc can be substituted by iron. Much of the early work on iron removal from hydrometallurgical solutions was centred on the treatment of zinc leach liquors and we shall
consider this work in some detail shortly. Other examples of solid solution ore minerals include tetrahedrite, \((\text{Cu,Fe,Zn})_{12}(\text{Sb,As})_4\text{S}_{13}\), and cobaltite, \((\text{CoFe})\text{AsS}\).

Given that non-ferrous metals have been produced from ores for hundreds of years, or in the cases of copper and lead, for thousands of years, one might be forgiven for asking why, suddenly, has iron become the focus of so much attention by non-ferrous metallurgists? The simple answer is that it is due to the rise in importance of hydrometallurgy compared with pyrometallurgy for the production of non-ferrous metals. In the traditional high temperature smelting processes used for the production of copper, lead, zinc and other non-ferrous metals up to the beginning of the 20\(^{th}\) century, iron in the smelter feeds ended up in the slags, together with many other deleterious impurity elements. Iron in silicate slags is present mainly as fayalite, ferrous silicate, \(\text{Fe}_2\text{SiO}_4\). This is a chemically and environmentally inert material, which can be safely discarded without detrimental effects to the local surroundings. This benign method of discarding unwanted iron is one of the main advantages that pyrometallurgy has over hydrometallurgy.

To understand the problems faced by hydrometallurgists who want to discard iron, we need to remind ourselves of the chemical behaviour of dissolved iron. The most concise way of doing this is to use an \(\text{Eh-pH}\), or Pourbaix-type diagram, as shown in Figure 1.

![Eh–pH diagram for the Fe–H\(_2\)O system at 298°K](image)

Figure 1. \(\text{Eh-pH}\) diagram for the Fe–H\(_2\)O system at 298°K

This diagram, which illustrates the behaviour of the simple Fe-H\(_2\)O system, shows that iron in the ferrous oxidation state (Fe\(^{2+}\)) is soluble across a broad pH range from highly acidic to mildly alkaline, whereas ferric iron (Fe\(^{3+}\)) is soluble only in acid solutions (\(\text{pH}<3\)) and oxidising conditions (\(\text{Eh}>0.77\text{V}\)). Outside these conditions, iron is insoluble and, in the absence of other anions, at ambient temperatures exists as ferric hydroxide, \(\text{Fe(OH)}_3\), or in alkaline reducing conditions, as ferrous hydroxide, \(\text{Fe(OH)}_2\).

The relatively small area of solubility of ferric iron, up in the top left hand corner of the Pourbaix diagram, shows us that, theoretically, it is quite easy to get iron out of solution by oxidising it to the ferric state and making sure the \(\text{pH}\) is greater than about 3. This will swiftly cause iron to precipitate from solution as ferric hydroxide. Most other common base metals (Cu, Zn, Pb, etc) remain soluble under these conditions and so hydroxide precipitation provides in principle a ready method of separating dissolved iron from other more valuable metals in leach liquors.

The precipitation of so-called ferric hydroxide is a very complex process, which even today is not fully understood and it was even less so, back in the 1960s. Ferric iron is a powerful complexant,
which will form complex ions with many anions, such as chloride, sulphate, fluoride, or phosphate, and the presence of different anions affects the form and composition of the hydrolysis product of ferric iron. Kinetic factors are also important, thus temperature, rate of change of pH and even the type of neutralising agent used, e.g. lime or sodium hydroxide, can all affect the outcome of hydrolysis. The usual result of rapid hydrolysis at ambient temperatures is the formation of a ferric hydroxide gel, with an open network structure, producing a soft, low density, material with a very high internal surface area. From a practical, process point of view, the physico-chemical properties of freshly precipitated ferric hydroxide have two main consequences: firstly, the large surface area of the hydroxide gel makes it an excellent absorbent material for dissolved metal and semi-metal ions and so it can be used to scavenge deleterious impurity ions from process solutions; and secondly, the open structure of the gel occludes a lot of mother liquor, which makes filtration and washing of the gel extremely difficult. In practice, this latter property means that in general it is not practically or economically feasible to use hydroxide precipitation to remove more than about 1 to 2 g/l of ferric iron from process solutions.

Such was the situation with regard to iron precipitation up to the early 1960s and it manifested itself most clearly in the electrolytic zinc industry, and so, in looking at the history of iron control, we should start with the zinc industry, which is where most of the iron control processes that we are familiar with today were pioneered. It also happens that, in 1980, I published a review of the electrolytic zinc process, which provides a convenient snap-shot of the state of development of the iron removal processes at that time, a decade or so after their first introduction into the zinc industry (Monhemius, 1980).

THE ELECTROLYTIC ZINC PROCESS

Until the beginning of the 20th century, zinc was produced exclusively by pyrometallurgical processes, mainly horizontal or vertical retorts, in which zinc oxide ores were mixed with carbon and heated in the absence of air. The carbon reduced the zinc oxide to zinc metal, which at the reaction temperatures used was formed as a vapour that was condensed to liquid metallic zinc in the cooler parts of the reactor.

The advent of the First World War in 1914 brought about an increased demand for zinc for military purposes and this provided the impetus for the industrial application of a completely new method of zinc production, which had been experimented with and developed only at bench scale during the late 19th century. This new technology was of course what we now know as the electrolytic zinc process, namely, the use of electrolysis to plate pure zinc on to an electrode from zinc sulphate solution. The first industrial electrolytic zinc plants were both started up in 1915, one by Cominco, in Trail, British Columbia, and the other by the Anaconda Copper Company in Anaconda, Montana. The process proved to be successful and its use grew during the first half of the 20th century, until by the 1950s, just under half the world’s zinc was being produced electrolytically. The growth in the use of the electrolytic process then stalled for a decade or so until, in the 1970s, it began to grow again and its growth has continued steadily until today, when it now accounts for more than 90% of the world’s zinc production. The reasons behind this two-stage historical growth pattern can be related directly to the behaviour of iron in the electrolytic zinc process. To understand this relationship, we need to look at the process in some detail.

In principle, the electrolytic zinc process is very simple and can be described by three chemical equations:-

Step 1. Roasting \[ \text{ZnS} + 1.5\text{SO}_2 = \text{ZnO} + \text{SO}_2 \]

Step 2. Leaching \[ \text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O} \]

Step 3. Electrowinning \[ \text{ZnSO}_4 + \text{H}_2\text{O} = \text{Zn}^\circ + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 \]

It can be seen from these three equations why the electrolytic zinc process is often referred to as the “Roast-Leach-Electrowin”, or “RLE”, process. Thus the first step involves roasting zinc sulphide ( sphalerite) mineral flotation concentrate in air to convert it to zinc oxide, forming gaseous sulphur dioxide, which is converted to sulphuric acid as an essential co-product of zinc production. Roasting is carried out at about 900°C in multiple-hearth roasters, or fluidised-bed reactors, the latter being more usual in modern plants. The hot roasted ore, known as “calcine”, is transferred to the
leaching tanks for the second step, where it is dissolved in sulphuric acid, contained in the acidic spent electrolyte returned from the electrowinning cells. After leaching, the neutral zinc sulphate solution is treated to remove impurities and is then sent to the electrowinning tankhouse for the third and final step, where zinc is plated on to aluminium cathodes and oxygen is released at the surface of lead anodes in the electrowinning cells. A simplified flowsheet of this process is shown in Figure 2.

During the roasting process, any iron in the zinc concentrate, which typically can run as high as 12 wt%, will combine chemically with zinc to form a mixed oxide, known as zinc ferrite, $\text{ZnFe}_2\text{O}_4$. Zinc ferrite is insoluble under the conditions of acidity and temperature used to dissolve the major zinc oxide part of the roaster calcine. Thus in the traditional two-stage leaching process, ferritic zinc reported in the leach residue and this loss of zinc resulted in overall zinc recoveries in the range of 85-93%, depending on the iron content of the zinc concentrate. These relatively low recoveries were the most serious drawback of the electrolytic process and restricted its application to low-iron zinc concentrates. This was the situation until the early 1960s, at which time 40-50% of the world’s zinc was produced by the electrolytic process, with the remainder coming from various pyrometallurgical processes.

It was well known even then that zinc ferrites will dissolve readily in sulphuric acid, provided that strong acid solutions are used and the temperature is kept close to boiling. However, under these conditions, most of the iron in the calcine will dissolve, in addition to the zinc and the insuperable problem at the time was how to get the dissolved iron out of the leach solution before sending it to electrolysis for recovery of the zinc. The only known way of removing iron was to neutralise the acidity of the leach solution to raise its $\text{pH}$ to about 3 to cause the precipitation of iron as ferric hydroxide. As already described, this is a bulky, gelatinous, material that occludes a great deal of solution and the difficulties of filtering and washing residues that contain large amounts of ferric hydroxide were insuperable. Thus the only practical approach at that time was to use only low-iron zinc concentrates for the electrolytic process, while high-iron concentrates were treated pyrometallurgically, where the iron could be readily handled by causing it to enter the slag phase, which could be safely discarded.

A step-change in the history of zinc ore processing occurred in the mid-1960s, when several processes were developed in which iron could be precipitated from solution as crystalline, easily filterable materials, which could be readily washed to remove leach solution. Such materials include iron oxides, both hydrated and anhydrous, and importantly, basic iron sulphates known as jarosites. These new processes were incorporated into the traditional two-stage zinc leaching process, so that not only oxide zinc, but also ferritic zinc could be recovered from the calcine feeds, so that typical recoveries in zinc leaching plants rose to 95-97%. The introduction of these iron-removal processes rang the death knell for zinc pyrometallurgy, as the electrolytic zinc process began its second growth.

**Figure 2. RLE Process - Simple Flow Diagram**

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The Jarosite Process

The most important of the iron removal processes developed in the 1960s is the Jarosite process, in which iron is precipitated from the acidic zinc sulphate leach liquors as one of a group of basic ferric sulphates, known as jarosites. The composition of jarosite is $\text{MFe}_3\text{(SO}_4\text{)}_2\text{(OH)}_6$, where M represents a monovalent cation from the group comprising Na$^+$, NH$_4^+$, K$^+$, Ag$^+$, Rb$^+$, 0.5Pb$^+$ and H$_2$O$^-$. Precipitation is brought about by adjusting the pH to about 1.5, at a temperature of about 95°C, and adding a source of the monovalent cation, which is usually NH$_4^+$ or Na$^+$ in industrial practice, leading to the formation of ammonium or sodium jarosite, respectively. The jarosite forming reaction can be represented in simplified form as follows:

$$3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{M}^+ + 6\text{H}_2\text{O} = \text{MFe}_3\text{(SO}_4\text{)}_2\text{(OH)}_6 + 6\text{H}^+$$  \hspace{1cm}(1)

In order to ensure complete reaction, the hydrogen ions formed during the reaction have to be neutralised to maintain the pH at about 1.5. The precipitated jarosite is in a crystalline form that can be readily filtered and washed free of the mother liquor.

As occasionally happens with technological advances, very similar versions of this process were developed independently, and virtually simultaneously, in different parts of the world. In this case, patents on variants of the jarosite process were lodged by zinc companies in Spain, Australia and Norway within months of each other in the mid-1960s, as detailed in the table below. These three companies later formed a consortium to license jarosite technology to the rest of the world’s zinc industry. The jarosite process has been described extensively in the literature. It is very flexible, capable of being readily integrated into existing as well as new zinc leach plants and it is adaptable enough to cope with different plant practices (Gordon & Pickering, 1975).

<table>
<thead>
<tr>
<th>Country</th>
<th>Company</th>
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<th>Date</th>
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<td>Spain</td>
<td>Asturiana de Zinc SA</td>
<td>Spanish Pat. 304601</td>
<td>Oct. 12, 1964</td>
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<tr>
<td>Australia</td>
<td>Electrolytic Zinc Company of Australia Ltd.</td>
<td>Australian Pat. 401724</td>
<td>Mar. 31, 1965</td>
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<tr>
<td>Norway</td>
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<td>Norwegian Pat. 108047</td>
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The Integrated Jarosite process developed by Norzink incorporated most of the various process options and a simplified flowsheet of the Norwegian process is shown in Figure 3 (Steintveit, 1970). Comparing this flowsheet with that of the basic electrolytic process shown in Figure 2, it can be seen that three extra unit operations have been added, namely, pre-neutralisation, jarosite precipitation and jarosite leaching. The solid residues from the neutral leaching tanks, which contain the undissolved zinc ferrites from the calcine feed, are transferred to the so-called “hot acid leach” tanks. Here, leaching is carried out at 95°C in a very acidic solution comprising a mixture of return electrolyte from the tankhouse, plus extra sulphuric acid. These conditions break down the zinc ferrite structure and most of the zinc and iron dissolves, together with much of the copper and cadmium contained in the neutral leach residues. The hot acid leach solution leaving the stage is still very acidic, typically containing about 40 g/l free acid. This is partially neutralised in the pre-neutralisation stage by the addition of fresh zinc calcine to reduce the acidity to about 10 g/l (pH ~1). Only oxide zinc in this calcine dissolves and so the ferrite residue from pre-neutralisation is returned to hot acid leaching. The hot pre-neutralised solution then passes to the next stage where iron is precipitated as ammonium jarosite, NH$_4$Fe$_3$(SO$_4$)$_2$(OH)$_6$, by the addition of ammonia to the solution. The temperature is maintained at 95°C in these tanks and the pH is controlled at 1.5 by the addition of fresh zinc calcine to consume the acid produced by the hydrolytic jarosite reaction (Equation 1).

Jarosite precipitation decreases the iron concentration over a period of several hours from an initial value of typically around 20 g/l in the pre-neutralised solution down to about 1 g/l. This amount of iron is deliberately left in the solution passing to the neutral leach tanks in order to form ferric hydroxide, which has the beneficial effect of absorbing certain deleterious impurities from the leach solution. The jarosite precipitated at this stage also contains undissolved ferritic zinc from the calcine added as a neutralising agent during the precipitation reaction. In order to recover this undissolved...
zinc, the final step in the process is jarosite leaching, which is carried out under conditions similar to those used in the hot acid leaching stage. This treatment dissolves the zinc ferrite in the mixture, while the jarosite itself remains virtually unattacked. The solution from jarosite leaching is returned to the pre-neutralisation stage, while the acid-washed jarosite is discarded. The overall recovery of zinc by this process from typical zinc calcines containing 56-57% Zn and 10-11% Fe is 98%, with similar high recoveries of other valuable metals in the calcine, such as Cd, Cu, Pb and Ag.

Figure 3. Integrated Jarosite Process

The main advantages of the Jarosite Process, compared with the other iron removal processes discussed subsequently, arise principally from the nature of jarosite itself. Being a basic sulphate, it is precipitated from relatively acid solutions, thus allowing efficient usage of calcine added as neutralising agent. It also enables excess sulphate to be removed from the closed leaching cycle. This is a distinct advantage in many zinc plants where excess sulphate originating from the calcine creates sulphate balance problems in the leach circuit. Furthermore once formed, jarosite is very resistant to acid attack and therefore undisolved calcine mixed with jarosite can be readily recovered by acid washing. These properties confer a considerable degree of flexibility on the operation of the process and allow for optimisation to meet particular process requirements.

The principal disadvantages are two-fold. Firstly the necessity to add a precipitation reagent, normally ammonia, to cause the formation of jarosite is an on-going operational expense. The theoretical consumption of ammonia is 37 kg/1,000 kg of jarosite, but in practice, the consumption is usually less than 30 kg/1,000 kg, because ammonium jarosite always contains some H$_3$O$^+$ in solid solution. Secondly, the low iron content of jarosite, theoretically 35 %, means that considerable quantities are produced for disposal. For a calcine of the composition quoted above, i.e. 56-57% Zn and 10-11 % Fe, of the order of 0.53 ton of jarosite will be produced per ton of zinc produced.

The Conversion Process

The Conversion process, developed by Outokumpu in Finland in the early 1970s (Huggare et al., 1974), is a modification of the Jarosite process in which zinc ferrite leaching and jarosite precipitation take place simultaneously in the same reactor. The overall reaction may be represented in simplified form as follows:

$$3\text{ZnFe}_2\text{O}_4 + 6\text{H}_2\text{SO}_4 + (\text{NH}_4)\text{SO}_4 = 2\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{ZnSO}_4$$  (2)
The process depends upon the fact that zinc ferrites are more soluble in sulphuric acid than jarosites. Thus, by controlling the acidity at an optimum value, conditions can be created where ferrites will dissolve while jarosites will precipitate. As shown by the above equation, the reaction consumes sulphuric acid and so the process is controlled by the feed rate of acid to the Conversion reactor. This is the key difference between the Conversion process and the Jarosite process. In the latter, the starting solution contains excess acid, which is neutralised by the addition of calcine, and there is the danger that improper control can lead to over-neutralisation, which in turn can lead to precipitates with difficult solid-liquid separation characteristics. In contrast, because the Conversion reaction is controlled by adding acid, the problems of over-neutralisation are eliminated and the process is very stable in operation, producing very consistent precipitates. The major drawback of this process is that long residence times in the Conversion reactor are necessary.

The Goethite Process.

In the Goethite process, iron is precipitated from solution as hydrated ferric oxide, FeOOH. The process used commercially was developed a few years after the Jarosite process by the Société de la Vieille Montagne in Belgium (SVM, 1968) and involves reduction of iron to the ferrous state, followed by oxidation with air at a temperature of about 90°C and at a pH controlled at about 3.0. The reaction involved is:

$$4Fe^{2+} + O_2 + 6H_2O = 4FeOOH + 8H^+$$ (3)

The oxidation of ferrous iron by oxygen is catalysed by copper present in the leach liquor, and it is vital that the rate of oxidation is balanced by the rate of precipitation, so that the concentration of ferric iron in solution does not rise above 1 g/l. There is no reagent requirement to supply monovalent cations, as in the Jarosite process and, theoretically, no sulphate is removed from the process stream in the iron product. However, in practice, sulphate contamination of the goethite is quite heavy, due to adsorption and the formation of some basic sulphates, and the iron product usually contains 2-5 wt% sulphur.

The main differences between the Goethite and Jarosite processes occur after the hot acid leaching of the zinc ferrite residues. In the Goethite process, the liquor from hot acid leaching, containing 100 g/l Zn, 25-30 g/l Fe$^{3+}$ and 50-60 g/l H$_2$SO$_4$, is first subjected to a reduction stage, where ferric iron is reduced to the ferrous state by reaction with unroasted zinc sulphide concentrate at 90°C:

$$2Fe^{3+} + ZnS = 2Fe^{2+} + Zn^{2+} + S^0$$ (4)

After reduction of iron is completed, unreacted zinc sulphide, together with the elemental sulphur formed by the reaction, is separated and returned to the roaster. The solution is then pre-neutralised to 3-5 g/l H$_2$SO$_4$ with calcine. The ferritic residue from pre-neutralisation is separated and returned to hot acid leaching and the solution is passed to the precipitation reactor. Air is injected to oxidise the ferrous iron, which hydrolyses and precipitates as crystalline goethite. Calcine is added during precipitation to consume the acid produced by hydrolysis and thus to control the pH at the desired value. Following iron precipitation, a solid-liquid separation is made, with the solution returning to neutral leaching and the goethite precipitate, plus undissolved calcine, being discarded. It is not possible to use an acid wash to recover undissolved zinc in the discard material because goethite, unlike jarosite, would redissolve. A flowsheet of the Goethite Process is shown in Figure 4. A detailed description of Metallurgie Hoboken-Overpelt’s (now Umicore) zinc electro-winning plant, which used Vieille Montagne (VM) technology, including the Goethite process, was given in a paper by Van Den Neste (1977).

A rather similar process, now known as the paragoethite process, was developed in Australia a couple of years after the VM process by the Electrolytic Zinc Company of Australasia Ltd (now Pasmimco EZ) (Allen et al., 1970), although this process version was not used commercially until 1985, when it was first used by the Italian company, ENIRISORCE, at its zinc refinery in Porto Vesme, Sardinia (Cubeddu et al., 1996). In the paragoethite process, iron in the ferric state is precipitated directly, without prior reduction, as a hydrated ferric oxide of undetermined nature. This is done by controlled addition of the iron-bearing liquor to a continuous precipitation reactor, where the ferric iron
Figure 4. The Goethite Process

Concentration is maintained at less than 1 g/l. Precipitation is carried out at 70-90°C and the pH is maintained at 2.8 by the addition of calcine as neutralising agent. The reaction involved is:

$$2\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} + 6\text{H}^+$$ (5)

Comparison of this reaction with that given above for the Vieille Montagne process (Equation 3) shows that more acid is produced by this process and therefore the neutralisation requirements are greater. Consequently, the loss of zinc, due to undissolved calcine in the iron product, will be greater in this process.

The Goethite process does not have the inherent flexibility of the Jarosite process. Very careful control of the conditions during precipitation, especially pH, is required for successful operation of the process. The relative solubility of goethite in sulphuric acid is a major disadvantage, because the iron precipitate cannot be acid-washed to recover undissolved zinc arising from the calcine added for pH control. This problem can be overcome by using selected calcine with a low ferrite content for neutralisation during goethite precipitation. However, this remedy is not generally available to plants tied to single major sources of raw material, where gross variations in the compositions of the calcines do not occur. In such plants, the use of the Goethite process would almost inevitably lead to lower overall zinc recoveries than could be achieved with the Jarosite process and this is the principal reason for the much wider usage of the latter process.

The Hematite Process

A process for the precipitation of iron as hematite, $\text{Fe}_2\text{O}_3$, from zinc leach liquors was first developed in Japan by the Akita Zinc Company and put into operation in 1972 in its Iijima zinc refinery (Onozaki et al., 1986). Ferritic zinc leach residue from the main leach circuit is re-leached with spent electrolyte and make-up acid in the presence of $\text{SO}_2$. The reaction is carried out at 95-100°C in autoclaves, lined with lead and acid-resistant brick, at a total pressure of 0.2MPa (30 psi). The ferrites dissolve readily in the presence of $\text{SO}_2$ and iron enters solution in the divalent state:

$$\text{ZnFe}_2\text{O}_4 + \text{SO}_2 + 2\text{H}_2\text{SO}_4 = \text{ZnSO}_4 + 2\text{FeSO}_4 + 2\text{H}_2\text{O}$$ (6)

Excess $\text{SO}_2$ is stripped from the solution and copper is removed as sulphide by $\text{H}_2\text{S}$ precipitation. The solution, containing about 90 g/l Zn, 60 g/l Fe and 20 g/l $\text{H}_2\text{SO}_4$ is neutralised with limestone, first at pH 2 to produce a marketable grade of gypsum and then at pH 4-5, with air oxidation to oxidise and precipitate some of the iron and other impurities. The precipitation of gypsum helps to maintain the sulphate balance in the process by removing sulphate formed during the oxidation of $\text{SO}_2$. 
The neutralised solution, which contains about 45 g/l iron is then passed to titanium-clad autoclaves, where the iron is oxidised and precipitated as hematite by oxidation with oxygen at 200°C and a total pressure of 2MPa (300 psi). The reaction involved is:

\[2 \text{FeSO}_4 + 2 \text{H}_2\text{O} + 0.5 \text{O}_2 = \text{Fe}_2\text{O}_3 + 2 \text{H}_2\text{SO}_4\]  

(7)

The residence time in the autoclaves is about 3 hours. The final solution, after hematite precipitation, contains 3-4 g/l Fe and this is returned to the main leach circuit. A flowsheet of the process is shown in Figure 5.

Figure 5. The Hematite Process

At the high temperatures used for iron precipitation in this process, hematite will continue to form even in relatively acidic conditions. Thus the necessity to add calcine to consume protons produced by the hydrolysis reaction is eliminated. This is a major advantage of this process and it means that theoretically no zinc should be lost with the iron residue. However, in practice, the iron residues contain 0.5-1.0% Zn, together with about 3% S, the sulphur arising presumably from the coprecipitation of basic iron sulphates. A second advantage of the process is the high iron content of the hematite residues, theoretically 70% Fe, but in practice closer to 60% Fe, which leads to much smaller quantities of iron residues for disposal. For example, a given quantity of iron precipitated as hematite will have less than half the weight that the same quantity of iron would have if precipitated as jarosite.

Ruhr Zink introduced a similar hematite process at its zinc plant in Datteln, Germany, in 1979 (Von Röpenack, 1986). RZ’s objectives were to eliminate residues from the process that were suitable only for dumping and in particular to produce iron as hematite with a purity suitable for steel production. Unfortunately, RZ never achieved the latter objective as its hematite always contained too much zinc and sulphur for the steel-makers. Instead RZ was only ever able to sell its hematite to the cement and tile industries. Thus the economic justification for the process was always under strain and after only just over a decade of operation, the RZ hematite process ceased operation in 1993. The
major disadvantage of the hematite process is, of course, the high capital and operating cost of the pressure equipment used and, at present, the process is only still in use in the original Akita zinc plant in Japan.

DISPOSAL OF IRON WASTES

For a typical sphalerite concentrate containing 53 wt% Zn and 7 wt% Fe, the compositions and quantities of the iron residues that would be produced by the three iron-removal processes are shown in Table 1. It can be seen that jarosite has the lowest concentration of contained iron and consequently there is more of it produced per ton of zinc compared with the other two processes. Thus for every ton of zinc metal produced, about half a ton of jarosite will arise. A typical zinc refinery producing 150,000 tons of zinc per year has to dispose of about 75,000 tons of jarosite per annum. A similar sized plant using one of the other two processes would produce about 50,000 tons of goethite, or 30,000 tons of hematite, yearly.

<table>
<thead>
<tr>
<th>Process</th>
<th>Jarosite</th>
<th>Goethite</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt/wt. zinc metal</td>
<td>0.5</td>
<td>0.32</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe wt%</td>
<td>25-30</td>
<td>40-45</td>
<td>50-60</td>
</tr>
<tr>
<td>Zn wt%</td>
<td>4-6</td>
<td>5-8</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>S wt%</td>
<td>10-12</td>
<td>2.5-5</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 1. Compositions and Quantities of Iron Residues (Onozaki et al, 1986)

When these processes were first introduced in the late 60s and early 70s, disposal of the iron residues was not considered to be a particularly difficult or onerous task. Different disposal strategies were adopted depending on the local circumstances of each plant. Thus Norzink in Norway used to dump its jarosite into the deep fjord on which its plant was sited, whereas in Australia, EZ used to ship its jarosite in ocean barges to the edge of the continental shelf and dump it into the deep ocean. Asturiana de Zinc in northern Spain, like many other plants that followed it, disposed of its jarosite in lined tailings ponds in the vicinity of the plant, with recovery and recycling of process water from the ponds.

The initial success of these iron control processes, which resulted in much higher zinc recoveries from the electrolytic process and also widened the range of zinc concentrate compositions that could be economically treated by the process, led to an acceleration in the replacement of the older pyrometallurgical zinc processes by the more modern, “cleaner”, electrolytic process. Thus the proportion of world zinc produced electrolytically jumped from about 45% in 1960 to 75% by 1980. However this period of growth coincided with birth and growth of the environmental movement and the introduction of environmental legislation and stricter regulation in much of the industrialised world. It wasn’t long before the environmental activists and subsequently, the regulators, began to target the iron residues produced by the electrolytic zinc plants around the world, in particular those producing jarosites for discard, as being sources of long term pollution of the environment. Licenses for new jarosite ponds became harder to get, or in some countries, impossible. But the zinc industry, having sunk so much capital into building electrolytic zinc plants and having no alternative zinc production technology to turn to, spent much of the next two decades, i.e. the eighties and nineties, devising various “work-arounds”, such as jarofix, jarochaux, etc., (Rosato & Agnew, 1996) to enable continuation of the use of the technically successful iron control processes devised a quarter of a century earlier.

EPILOGUE - THE IRON ELEPHANT

At the most recent decennial Hydrometallurgy conference, held in 2014 in Victoria, BC, the concept of the “hydrometallurgical copper smelter” came under discussion again. Thus, in spite of the vast amount research and development work carried out in the last quarter of the last century to devise hydrometallurgical processes to produce copper from sulphide concentrates, all of it ultimately commercially unsuccessful, the goal of a hydrometallurgical process that can compete head-on with modern copper smelters continues to tantalise up-coming generations of hydrometallurgists.

The “elephant in the room” that haunts and, thus far, has defeated the hydrometallurgical copper smelter concept is how to deal successfully with iron in the copper concentrates – hence my
title for this paper: “the Iron Elephant”. The size of this elephant for would-be copper makers is several times larger than that faced by today’s zinc producers. A typical copper concentrate will contain around 30 wt% Fe and 25 wt% Cu, compared with a typical zinc concentrate with around 10 wt% Fe and more than 50 wt% Zn. Thus a ton of copper produced hydrometallurgically from copper concentrate would necessitate the disposal of around six times as much iron as that arising from the production of a ton of electrolytic zinc. Given the difficulties faced by today’s zinc producers in disposing of their iron residues in ways that satisfy the demands of the regulators, the NGOs and the general public, the task of disposing of the vastly greater amounts iron from any copper concentrate leaching process has thus far proved insuperable.

For thousands of years, since the Copper Age began, copper smelters have been using an elegantly simple way of disposing of the iron that is an inevitable by-product of copper making processes – it ends up in the slag. As mentioned earlier, copper smelting slags are composed principally of ferrous silicate, or fayalite, which is an inert, dense, environmentally stable, glassy substance that immobilises iron and other deleterious impurity metals in its silicate matrix. Unlike jarosites and goethites of hydrometallurgical origin, copper smelting slags can be safely dumped without special precautions and with little or no danger of long-term adverse consequences for the environment. This is an enormous advantage for the smelting route and it accounts for the fact that, in spite of all the very significant advances that have been made in copper hydrometallurgy over the past half century, copper smelting still accounts for about three quarters of the world’s copper production and, in my opinion, this situation will not change until hydrometallurgists can find a way to slay the Iron Elephant. I first aired this point of view publicly at an AIME annual conference in New Orleans in 1979 (Thorsen & Monhemius) and the situation has not changed much in the intervening nearly 40 years.

The best way that this formidable beast can be dispatched is to convert the iron in copper concentrates into iron oxide with a purity acceptable for steelmaking or pigments, the only industries with capacities big enough to absorb the quantities of iron oxide that would be produced by a commercially-sized hydrometallurgical copper smelter. To achieve the required purities, the best currently-available technical solution is to use solvent extraction to purify dissolved iron from all contaminants. The most likely solvent extraction reagents for this purpose are either carboxylic or alkyl phosphoric acids, both of which have a high affinity for ferric iron; then to make pure Fe₂O₃ powder for direct use as a pigment, or following pelletisation, sintering and reduction, to produce DRI pellets as feed for EAF steelmaking. Pure iron oxide can be produced by stripping the iron-loaded organic acids with hydrochloric acid and then using the well-established industrial process of pyrohydrolysis to convert the FeCl₃ strip solution to Fe₂O₃ and HCl (Jewell & Marcotte, 1986). An alternative, but industrially unproven method is hydrolytic stripping (Monhemius & Thorsen, 1980) in which the iron-loaded carboxylic acid is reacted with water at temperatures of 150-200°C to precipitate hematite directly from the organic phase and to regenerate the organic acid for recycle to extraction.

REFERENCES


