Chloride and Nitrate Systems in hydrometallurgy
Applications and opportunities

G. Van Weert
CHLORIDE AND NITRATE SYSTEMS IN HYDROMETALLURGY
APPLICATIONS AND OPPORTUNITIES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR AAN DE TECHNISCHE UNIVERSITEIT DELFT, OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. P.A. SCHENCK, IN HET OPENBAAR TE VERDEDIGEN TEN OVERSTAAN VAN EEN COMMISSIE AANGEWZEEN DOOR HET COLLEGE VAN DEKANEN, OP DINSDAG 12 DECEMBER 1989 TE 14.00 UUR

DOOR
GEZINUS VAN WEERT
SCHEIKUNDIG INGENIEUR
GEBOREN TE ROTTERDAM
Gives a choice between spending risk money on exploration for unknown deposits or on metallurgical development for known, but unworkable deposits, mining management will almost always choose the former. This cannot be done in perpetuity.

The understanding of hydrodynamics by mineral processors and extractive metallurgists is generally not commensurate with their professional requirements. This is particularly evident in the field of bio-metallurgy.

Bio-oxidation of sulphide ores and concentrates will be limited to small tonnages of sulphides since the rate of oxygen transfer decreases approximately with the horsepowere squared in mineral slurries (Ref. Henzler, H.-J. and Kauling, J. “Scale-up of mass transfer in highly viscous liquids”, 5th European Conference on Mixing, Wurzburg, West Germany, June 10-12, 1985).

The introduction of the non-agitated flotation column allowed plant operators to become equipment designers and builders, breaking a near century monopoly on technology by the flotation cell manufacturers.

The application of chemical engineering to metallurgical problems requires the realization that the latter deals largely with three phase systems, whereas chemical engineering offers principally mathematical derivations for two phase systems.

All successful, “self containes” base metal processes utilize hydro- and pyro-metallurgical unit operations.
The scientific and engineering knowledge of three phase systems relating to metallurgical processes is rudimentary, hence metallurgical engineering is still largely trial driven.

The ability of the nitric acid system to attain a redox potential in aqueous solutions that is more oxidizing than can be achieved with gaseous oxygen, has not been taken advantage of in the extractive metallurgical industry.

In chloride metallurgy process design, given a choice between operating a super- or sub-azeotropic system, the latter should receive preference for reasons of simplicity.

"Hydrometallurgy" should be defined as the treatment, usually water based, of metal bearing materials by an oxidant (reductant) and/or a lixiviant, involving the dissolution of some component and the economic and environmentally acceptable recovery of the component, the oxidant (reductant) and/or the lixiviant, gaseous oxygen excepted.

Successful management of industrial research personnel requires sharing, or even declining authorship of research work.

In the 21st century, the world will become a globally managed biosphere.

G. van Weert.
12 december 1989

To Roel, with great appreciation.

To Jonathan,
Elisha,
Daniel and
Samuel, the future generation

I Corinthians 10:31
I am indebted to the Institution of Mining and Metallurgy, the Canadian Institute of Mining and Metallurgy, the Metallurgical Society and the Society of Mining Engineers of the AIME, the University of British Columbia, the American Institute of Chemical Engineers, John Wiley and Sons, Gordon and Breach Science Publishers Inc., Pergamon Press Ltd., Hayes Publishing Co., Babcock Contractors Limited, Técnicas Reunidas, S.A., Maschinenfabrik Andritz, Hitachi, Ltd., among others, for the use of certain of the figures and tabular information included in the text.

I am particularly grateful to the management of Falconbridge Inc. for permission to publish operational details of the nickel chloride pyrohydrolyzer described in Chapter 6, Part One, of this thesis; to the staff of Falconbridge Nikkelverk A/S, for providing plant data and drawings, and to the staff of the Falconbridge Metallurgical Centre for providing photomicrographs and density measurements.

My deepest appreciation is for the support and individual efforts of my co-workers I have had the privilege to work with over the years. Industrial research and development is a team effort, yielding mainly incremental gains after efforts by many at all levels of the organization. This is reflected in the number of authors listed in Part Two. In view of the prominence of pyrohydrolysis in this thesis, I like to particularly thank Mr. John Valen of Kristiansand-S, Norway, for his fortitude in the development of the nickel chloride pyrohydrolyzer and Mr. Ragnar Jahnsen, also of Kristiansand-S, Norway, for his courage in recommending the construction of the Falconbridge Matte Leach Plant.
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Summary.
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Curriculum Vitae.
SURVEY OF THE THESIS.

This thesis is divided in two parts. Part One offers seven chapters, starting with a definition of the subject. The hydrometallurgical treatment of chalcopyrite was chosen to highlight the differences between chloride and nitrate systems on the one hand and the sulphate system on the other. Chapter 2 discusses the development of the sulphate based Sherritt-Cominco Copper Process, leading to a review of lixiviant and oxidant regeneration in Chapter 3. The chloride and nitrate systems for chalcopyrite treatment form the contents of Chapters 4 and 5, respectively. Opportunities for chloride and nitrate hydrometallurgy are proposed in Chapter 7.

Chapter 6 contains a general discussion of the thermal hydrolysis of metal chlorides, and a very specific description of the development, design and operation of a fluidized bed pyrohydrolyzer for partially dried nickel chloride crystals, with which the author has been closely associated, and which material has not been published heretofore. Economics of this process route are discussed.

Part Two contains eight papers, selected from publications by the author. The listing is evenly divided between chloride and nitrate hydrometallurgy; four papers each. The publications dealing with chloride systems reflect development work carried out for (then) Falconbridge Nickel Mines Ltd., some of which was implemented and some of it not. The publications dealing with the nitrate system involve the oxidation of "refractory" auriferous sulphides, aimed at commercializing the nitrate system for this purpose. Paper 2.6 only appeared as a preprint, hence the format and duplicate use of the historical gold price review in paper 2.7. The last paper, 2.8, fittingly, deals with capital and operating costs in the nitrate system.
1: Introduction.

1.1 Definitions.

Hydrometallurgy is a relatively new discipline compared to pyrometallurgy. Chloride metallurgy is an even more recent entry, whereas nitrate hydrometallurgy can be said to be still in its infancy. To elucidate this statement it is necessary to review some definitions.

The U.S. Bureau of Mines has published a dictionary of mining, mineral and related terms [1].* The following definition of hydrometallurgy is given:

Hydrometallurgy.

The treatment of ores, concentrates and other metal bearing materials by wet processes usually involving the dissolution of some component, and its subsequent recovery from the solution.

In this definition the term treatment may refer to mixing, gas dispersion, liquid solid separation, purifications of solution, electrowinning or electrorefining, hydrogen reduction, etc. Hydrometallurgical treatment usually involves the dissolution of some component, which step is also known by the term leaching.

Leaching.

"(a) The removal in solution of the more soluble minerals by percolating waters,"

"(b) Extracting a soluble metallic compound from an ore by selectively dissolving it in a suitable solvent, such as water, sulphuric acid, hydrochloric acid, etc. The solvent is usually recovered by precipitation of the metal or by other methods,"

* References, figures and equations in this thesis are numbered from 1 consecutively in each chapter.
"(c) Dissolution from ore or concentrates after suitable comminution to expose the valuable minerals, by aqueous and chemical attack. If heat and pressure are used to intensify or speed this, the work is called pressure leaching."

"(d) The process of decomposition under natural agencies of an outcrop. Surface waters penetrating downwards may dissolve some or all of the mineral in their path, thus carrying it away from the surface zone. This process is referred to as leaching."

1.2 Heap Leaching.

The leaching processes as defined by the U.S. Bureau of Mines dictionary segregate in two categories. The first category applies generally to in situ leaching, i.e. dump leaching and heap leaching, in which the solvent used for the dissolution of the metal species is circulated through an open natural environment. The other category involves leaching and other hydrometallurgical treatments in a closed system. Due to environmental considerations it is only in the latter system that solvents or lixiviants can be considered that are not compatible with the natural environment.

In this dissertation the term solvent shall not be used to denote a leaching agent dissolved in water. There is a dichotomy in the definition of "solvent". Webster’s dictionary [2] defines solvent as "a substance that dissolves or makes a solution of another substance." However, a prominent technical encyclopedia [3] defines the term: "By convention, the component present in the greatest proportion in a homogeneous mixture of pure substances (solution)". By the latter definition, water would be the solvent in hydrometallurgy. The International Union of Pure and Applied Chemistry (IUPAC) recently issued its own recommendations [4] on the terminology, and defined solvent as follows:

"A liquid (usually the major component of a solution) which is used to dissolve a solute or solutes" Again this would (usually) define water as the hydrometallurgical solvent. Instead of "solvent", the term "lixiviant" is therefore proposed as a generic term for the active proton ingredient causing a solid phase to dissolve in a hydrometallurgical process solution. The lixiviant can be a base or an acid, and can be derived from a gas (NH₃ or Cl₂), liquid (H₂SO₄) or solid (CaO or NaOH). "Lixiviant" has not been defined in the chemical/metalurgical terminology. Webster's dictionary [2] does not define the noun lixiviant either, only lixiviation as "the operation or process of extracting alkaline salts from ashes by pouring water on them; leaching". To claim this ancient Latin term for generic use in hydrometallurgy allows the currently impossible distinction in terms between proton exchanges and electron exchanges (pH reactions vs. redox reactions). The active agents in redox reactions would be called "oxidants" or "reductants". Such a nomenclature would allow the hydrometallurgist to be more concise.

1.3 In Situ Leaching.

Historically, hydrometallurgy has been largely restricted to contained systems. The dissolution of ore components in situ or in dumps or heaps has been largely left to natural processes. This changed after the second world war due to a number of factors. One factor was a depletion of rich copper ore deposits and the corresponding increase in the price of copper. In the Western United States, oxide ore deposits overlie the sulphide copper ores. These overburden had been removed and accumulated over the years in large dumps. The copper contained in these dumps was suddenly viewed as a valuable resource already in place and dump leaching with sulphuric acid became widely practised. Sulphuric acid, or rather sulphate, is compatible with the natural environment. Removal of the copper from these dump leach solutions was normally carried out by contacting the solutions with scrap iron, often de-tinned cans. This paved the way for two further developments important to hydrometallurgy, namely the switch from metal recovery by cementation to metal recovery by solvent extraction. Many of these solvent extraction (SX) agents were developed by General Mills (now Henkel Corporation) and allowed the electro-winning of copper from dump leach solutions. That development was a most important breakthrough for the hydrometallurgical industry since it moved from a contained system to the open environment. It also bypassed the smelter/refinery route for producing refined copper, another important breakthrough, technically and economically. An excellent and down-to-earth description of that development has been given by Joe E. House in the Gaudin Lecture at the 1981 SME - AIME Annual Meeting. It should be required reading for any student contemplating a career in the extractive metallurgy field [5].

Sulphuric acid is said to be compatible with environmental requirements since it is naturally generated from oxidizing copper ores, and since H₂SO₄
and its salts have no appreciable vapour pressure. The latter point is very important since in the natural environment the vapour phase cannot be contained or controlled. The development of the solvent extraction-electrowinning process for copper is now history, but it introduced another important factor, namely the willingness and capability of the industry to consider heap leaching of gold bearing materials. With the knowledge gained of dump percolation with sulphuric acid, the industry now turned to percolation leaching of gold bearing heaps with cyanide solutions. Unlike copper, gold bearing dumps are uncommon and the industry learned the hard way – how to construct heaps of ore that could be efficiently aerated and percolated. Cyanides cannot be said to be compatible with the environment and can under certain circumstances have a substantial vapour pressure. These problems have been and are being overcome by the use of impervious linings and low concentration cyanide solutions which are then subsequently treated for gold recovery by contacting with active carbon. Heap leaching of gold bearing ores is presently responsible for approximately half the U.S. gold production. Despite concerns by environmentalists over the odd spill and seepage of cyanide and bird kills in the holding ponds for solutions, percolation leaching of heaped gold ores can definitely be considered a success story, which indicates that the mining industry will move into areas of more sophisticated and novel hydrometallurgy when the economic incentive is available.

1.4 Agitated Vat Leaching.

Historically, however, hydrometallurgy has largely been associated with the treatment of ores and concentrates and other metal bearing materials in man-made equipment, often closed to the atmosphere, in association with pyrometallurgical operations or as part of an overall upgrading or refining process. In such systems the choice of lixiviant or oxidant does not need to be governed by environmental compatibility. Looking at the general processes in use in hydrometallurgy it can be seen that a wide number of lixiviants are being used. The Bayer process for producing alumina is one example. It uses a caustic lixiviant to solubilize the oxide and recrystallizes aluminum hydroxide by seeding. Gold extraction operations generally use cyanide although some attempts have been made to introduce thiourea. The use of the latter reagent is popular in Russia. The development of the ammonium sulphate leach of nickel/cobalt bearing materials under oxygen pressure resulted in a separate branch of closed system hydrometallurgy.

1.5 Sulphate Hydrometallurgy.

The bulk of the hydrometallurgical processes practiced today, however, are based on sulphate systems. There are some very good reasons for this:

1 Sulphuric acid is the "natural" lixiviant to use for the treatment of sulphides since sulphuric acid can be produced readily from most base metal minerals.

2 As pointed out earlier, sulphuric acid and its salts benefit from not having a discernable acid vapour pressure.

3 Sulphuric acid and sulphate can readily be removed from solution by precipitation as gypsum. Although this is not without problems, in actual operation it allows for a very convenient and low cost removal of sulphate ions from solutions. Gypsum precipitation has more recently been supplemented by a second sulphate removal option resulting from pressure autoclave operation, i.e. the formation of jarosites, represented by the formula A2B(SO4)3.(OH)6 where A and B are univalent and trivalent cations, respectively.

4 The solubility of base metal sulphates is quite sufficient for hydrometallurgical processes, with lead being the exception.

5 The containment of sulphuric acid and sulphates in processing equipment is rather simple; sulphuric acid being only modestly corrosive.

6 Electrorefining of metals in sulphate solutions is possible and practiced for nearly all base metals, with the exception of lead.

7 Electrowinning of metals in sulphate solutions yields oxygen gas on the anode, a gas which can be readily released in a tank house atmosphere without environmental problems. Although this is sometimes accompanied by the formation of acid mist, that problem is normally well controlled through the use of additives or ventilation.

8 The sulphate ion is also quite stable, i.e. it cannot be readily reduced to a lower sulphur valency. This allows for a steady redox potential in the sulphate system and regeneration of the lixiviant, i.e. H2SO4, in electro-winning operations.
There is a large commercial market for sulphuric acid, not tied to metallurgical usages. Sulphuric acid produced from base metal sulphides can often be sold locally.

1.6 Chloride and Nitrate Systems.

The latter point with regard to the inability to change the redox potential substantially in a sulphate system is both a strength and a weakness. For instance it is very difficult to produce hydrogen sulphide gas from sulphuric acid treatment of minerals and it is also very difficult to produce sulphate ions from sulphide minerals, in solution. On the other hand, the narrow redox band makes a sulphate system less destructive for the equipment, i.e. easier to contain. For those operations where a high or low redox potential is desired, or required, hydrometallurgists have looked at other systems, particularly the chloride and nitrate systems. The industrial development of these systems had to await materials of construction to contain the chloride and nitrate media and each system has had its own development in this regard. Stoneware and glass were commonly used until the 1930's. Industrial containment of nitrate systems on a large scale became feasible only after the first world war when the nickel chromium alloys now known as the austenitic stainless steel 300 series were introduced. The development of chloride processes had to await the development of special rubber formulations and plastics due to the very corrosive action of reducing chloride solutions on all metals, except titanium and tantalum. It is interesting that, despite the development of stainless steel occurring prior to that of plastics by about 25 years, the chloride system has found industrial applications in extractive metallurgy prior to the nitrate system.

1.7 "Hydrometallurgy".

In summary, hydrometallurgy is a relatively new discipline compared to pyrometallurgy. Most developments have taken place in the last 100 years. The industry is slowly moving into a direction of accepting non-sulphate systems for the processing of base metals and gold from ores and concentrates and other materials in closed systems and in systems open to the environment. Since hydrochloric and nitric acids are the major lixiviant alternatives, examples of applications and opportunities both in chloride and nitrate metallurgy will be given and discussed.

Finally, the author wishes to offer a more restrictive and representative definition of the term "Hydrometallurgy". The definition by the U.S. Bureau of Mines would easily cover gravimetric analysis, for instance, and fails to cover the essence of the practice of hydrometallurgy.

Hydrometallurgy. The treatment, usually water based, of metal bearing materials by an oxidant (reductant) and/or a lixiviant, involving the dissolution of some component and the economic and environmentally acceptable recovery of both the component, the lixiviant and/or the oxidant (reductant), gaseous oxygen excepted.

1.8 References


2. Sulphate versus Chloride and Nitrate Hydrometallurgical Systems.

2.1 General.

The purpose of this section is not to give an exhaustive outline or a review of the great variety of sulphate based hydrometallurgical systems, followed by a comparison with chloride and nitrate systems. It is rather intended to highlight the differences from a fundamental and practical standpoint, with emphasis on the economic recovery of the dissolved component and the lixiviants, in the case of chloride and nitrate systems. In doing so, one specific sulphate system will be discussed in detail. The same application will be discussed for the chloride system in section 4 and for the nitrate system in section 5.

In nature, metals occur largely in the form of inorganic compounds called minerals, although the precious metals and copper can be found in their native state, i.e. as a metal or alloy. Minerals have definite compositions and crystal structure, and metal bearing minerals can occur as sulphides, oxides, halides, carbonates, silicates or with other anions. The metal itself can form the anion, such as in molybdenates, vanadates etc. Some metals occur as arsenides, such as the valuable PtAs₂ (Sperryite) or mixed sulphide/arsenides, such as FeAsS (arsenopyrite), or CoAsS (cubaltite). Rare earth metals occur principally as a phosphate, (M)PO₄ (monazite). Oxides constitute the dominant mineral species in the earth crust and many metals such as Al, Ti, Fe, Mn, Cr, W, Sn, U and Zr are derived principally from oxide minerals. Where sulphides have “weathered”, or oxidized, near the earth surface, base and other metals are recovered from such oxide residues. Heap leaching of copper oxide and gold have already been discussed in Chapter 1. Weathering can also effect oxide or silicate mineral deposits; one well known example is that of the nickel bearing laterites of the semi-tropics [1]. Oxide minerals are processed to the respective metals by a variety of techniques, mainly pyrometallurgical, involving a reduction with carbon, or magnesium in the case of titanium. Iron and aluminum production from oxides represent by far the largest tonnages and have evolved in specialized fields of technology. Some of the other oxides are reduced to ferroalloys, such as Mn, Cr, W and Ti. This avoids the problem of iron separation, which is acceptable for products destined for the steel industry. We shall return to the problem of iron separation shortly, since it is as fundamental to hydrometallurgical engineering as lixiviant regeneration.
Hydrometallurgical processing in contained systems is used for the recovery of naturally occurring Mn, Cr, W, U, Cu and Ni oxides. Acidic sulphate systems predominate, with only tungsten and nickel the exceptions. Both are processed in ammoniacal systems, after pre-treatment. Hydrochloric acid is used to remove iron from the tungsten mineral wolframite:

\[
\text{FeWO}_4 + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\text{WO}_4
\]  

(1)

Ammoniacal leaching of nickel bearing laterites requires the reduction of nickel oxide to the metallic state. It is selective for nickel and cobalt and has the great advantage of being selective against iron oxides which are predominant in laterite. This solves the problem of iron (and magnesium) separation in the Caron process [2]. The same problem has to date effectively prevented the application of acidic processes to lateritic ores.

Simple dissolution of oxides, such as zinc oxide, in an aqueous regime, involves a proton (H*) exchange, as expressed simplistically in the following reactions:

\[
\text{ZnO} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O}
\]  

(3)

Sometimes the dissolution involves a valency change for the metal, such as in the oxidizing leach for UO₂ (uraninite):

\[
\text{2UO}_2 + 4\text{H}^+ + \text{O}_2 \rightarrow 2\text{UO}_2^{2+} + 4\text{e}^- + 2\text{H}_2\text{O}
\]  

(5)

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-
\]  

(6)

\[
4\text{H}^+ + 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^-
\]  

(7)

The dissolution of MnO₂ (pyrolusite) in hydrochloric acid is an example of a reducing leach:

\[
\text{MnO}_2 + 4\text{H}^+ \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}
\]  

(9)

\[
\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}^{0}
\]  

(10)

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-
\]  

(11)

\[
\text{MnO}_2 + 4\text{H}^+ + 2\text{Cl}^- \rightarrow \text{Mn}^{2+} + \text{Cl}_2 + 2\text{H}_2\text{O}
\]  

(12)

The reason reaction (3) goes to the right is due to acidity or proton concentration, i.e. pH. The reason reactions (8) and (12) proceed to the right is due to an electron exchange. Neither UO₂ nor MnO₂ dissolve in sulphuric acid per se. Uraninite dissolution requires an oxidant and, although reaction (6) is written for gaseous oxygen, sodium chlorate, sodium nitrate and manganese dioxide are commonly used. Pyrolusite (MnO₂) requires a reductant. One additional reason reaction (12) proceeds to the right is the limited solubility of chlorine, or to put it into another way, the low activity of one of the reaction products in the system. Since reactions (8) and (12) involve valency changes they effect the electrode potential of the system, i.e. Eh. This subject will be further discussed under lixiviant regeneration in Chapter Three.

Acidity and valency changes are available in Eh-pH diagrams, also known as Pourbaix diagrams. These became available in the early nineteen sixties [3] and greatly aided the practice and study of hydrometallurgy. The electropotential - pH equilibrium diagrams for sulphur, chlorine and nitrogen are given here as Fig. 2-1, 2-2 and 2-3. The lines (a) and (b) on these diagrams represent the limits of water decomposition with regard to hydrogen and oxygen, respectively. These diagrams will be referred to when comparing sulphate systems with chloride and nitrate ones.
Fig. 2-1. Potential-pH diagram for the stable equilibria of the system sulphur-water, at 25°C. The part of this diagram lying outside the line log C=0 refers to solutions which are not saturated with solid sulphur but which contain 1 g-at/l (32 g/l) of sulphur, dissolved in the forms H₂S + HS⁻ + S⁻ + HSO₄⁻ + SO₄⁺ + S₂O₇²⁻. The part inside this line refers to solutions saturated with solid sulphur [3].

Fig. 2-2. Potential pH equilibrium diagram for the system chlorine-water, at 25°C. Stable equilibria (for solutions containing 1 g-at Cl/l) [3].
Although the most common minerals in the earth surface are oxides and their compounds, the bulk of non-ferrous base metals are found and recovered as sulphides. Hydrometallurgical processes for base metals center on the processing of sulphides or their semi-processed intermediates such as matte, speiss and calcine. This thesis compares the various lixiviant systems by reference to attempts to process the principal copper mineral, i.e. CuFeS₂ (chalcopyrite).

One of the most recent, serious and well documented efforts to develop a hydrometallurgical process for refining copper from sulphide concentrates is represented by the Sherritt-Cominco Copper Process. The main objective of the effort was to develop a process applicable to a wide range of concentrates with respect to copper content, other metals content, and impurities, within the economic parameters set by present smelting and refining practices. Other important objectives were to recover sulphur in its elemental form and not as sulphur dioxide to assure improved working conditions and a negligible impact on the environment [4]. Since the final process choice was a sulphate system, the S-C process offers an excellent example of the advantages and disadvantages of sulphate hydrometallurgy. The article by Swinkels and Berezowsky [4] will be used to highlight the process design considerations.

In the choice of leach system the following factors were considered by Swinkels and Berezowsky:
- Recovery of elemental sulphur from sulphides
- Recovery of precious metals
- Recovery of other metals, i.e. Zn, Mo, Ni
- Complexity of purification and metal recovery
- Materials of construction

Table I summarizes the various leach systems considered by the project team or suggested by others. Both the ammonium sulphate system and the nitric acid system were rejected on the basis of their low elemental sulphur yield, the complexity of the copper winning step and potential problems in precious metals recovery.

The choice between a sulphuric acid and a chloride system was a value judgment, and indeed considerable work was carried out in the chloride system in addition to the sulphate work. The basic reasons which swung the development to sulphuric acid were the potential problems of a complex copper winning step, recovery of other metals and materials of construction in the chloride system. The authors allowed that, given adequate answers to the winning step and to materials of

**Fig. 2-3**

![Potential pH equilibrium diagram for the system nitrogen-water, at 25°C.](image)

(The partial pressures indicated for NH₃, N₂, N₂O and NO refer to solutions containing 1 g-at of dissolved nitrogen per litre in all the forms NH₄, NH₄OH, HNO₂, NO₂⁻, HNO₃, NO₃⁻ [3].)
Having decided on sulphuric acid as the lixiviant and a sulphate circuit throughout the process, Swinkels and Berezowsky started out with a simple oxidation leach/metal winning circuit, given here as Fig. 2-4. The overall oxidation reaction can be represented by:

\[ \text{CuFeS}_2 + \text{H}_2\text{SO}_4 + \frac{5}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + \text{Fe(OH)}_3 + 2\text{S}_2 \quad (13) \]

**Table I. Choice of Lixiviant to Process Copper Sulphides**

<table>
<thead>
<tr>
<th>Lixiviant</th>
<th>Elemental PM Yield</th>
<th>Construction System</th>
<th>Metal Recovery</th>
<th>Winning of other Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2SO_4</td>
<td>High</td>
<td>In Residue</td>
<td>Difficult</td>
<td>Conventional</td>
</tr>
<tr>
<td>Cl^-</td>
<td>High</td>
<td>Feasible</td>
<td>Very difficult</td>
<td>Easy</td>
</tr>
<tr>
<td>(NH_4)_2^+</td>
<td>All SO_4</td>
<td>Difficult</td>
<td>Easy</td>
<td>SX to H_2SO_4</td>
</tr>
<tr>
<td>HNO_3</td>
<td>Low</td>
<td>Low</td>
<td>Easy</td>
<td>SX to H_2SO_4</td>
</tr>
</tbody>
</table>

This reference highlights one of the many choices facing the hydrometallurgist contemplating treatment of base metal sulphides, i.e. what to do with the sulphide sulphur. There is no hydrometallurgical process that yields commercial grade sulphuric acid; hence the product choice is between elemental sulphur or sulphate, which needs to be removed from the circuit as gypsum or jarosite. Elemental sulphur can be made directly in the process slurry, or from H_2S gas via the Claus reaction. Either choice poses problems in handling. The production of H_2S will be discussed in Section 2.3.

Swinkels and Berezowsky, having the objective to produce elemental sulphur rather than sulphate, correctly decided against the ammonium sulphate system. Nitric acid treatment of chalcopyrite yields sulphur, as will be discussed in Chapter Five. Their subsequent choice between chloride and sulphate in favour of the latter as a "value judgment" highlights another fact of life in the hydrometallurgical industry, namely that the application of chloride and nitrate hydrometallurgical systems is generally limited to situations where other lixiviants cannot perform the desired task. In a way the same can be said for ammoniacal systems.
The removal of elemental sulphur from the unreacted sulphide residue was difficult. The iron precipitate was slimy and it entailed a difficult liquid-solid separation. High copper, silver and gold losses were incurred in iron slimes.

"Some activation method to improve the extractions ahead of the direct chalcopyrite process was needed. Obviously, with higher extractions, less unreacted sulphide residue remains and the residue will be higher in elemental sulphur, which puts a different aspect on the sulphur removal. The iron slimes problem dictated selective removal of the bulk of the iron prior to the oxidation leach of the copper minerals."

The problems mentioned highlight further obstacles faced by the hydrometallurgist in treating base metal sulphides. The major one is the removal of iron from the circuit. In this version of the S-C Process, iron removal is achieved by utilizing autoclave oxidation, which requires oxygen gas and capital intensive equipment. Losses of copper to the iron precipitate were found to be high.

Another obstacle is the different reactivity of various minerals in hydrometallurgical systems. In pyrometallurgy reaction rates are so high, that differences between minerals become insignificant. In selective hydrometallurgical systems, such as pressure oxidation where a high oxidation potential cannot be achieved, and isn’t desired since it would promote the formation of sulphate instead of elemental sulphur, unreactive sulphides can accumulate in a recycle system. There is another obstacle to having to process various minerals: they may react differently to the same process conditions. Pyrite will oxidize to sulphuric acid, rather than elemental sulphur. This is true for the nitrate system as well. The acid inventory of the system becomes subject to variations in response to feed fluctuations.

Reviewing the problems encountered, Swinkels and Berezowsky decided to investigate concentrate pretreatments to obtain higher extractions, better removal of elemental sulphur and selective removal of the bulk of the iron prior to solubilizing the copper. The latter decision is presented here as fundamental to the design of a hydrometallurgical process in that it parallels the conventional, pyrometallurgical division between smelter and refinery. The task of the copper smelter is largely the separation and removal of iron and sulphur from the copper (values). In treating concentrates directly, hydrometallurgists have generally attempted to compete with the smelter/refinery combination, and with very limited success. Since it is tempting, and often easy, to solubilize all mineral constituents, many proposals for hydrometallurgical processes fall into this trap, only to be defeated by the subsequent metals separation and solution purification steps. This statement holds for chloride and nitrate systems as well. This is why all major, economically successful, base metal recovery processes involve both hydro-and-pyrometallurgical process steps.

Returning to the pretreatment step selected for the S-C Process, the most elegant pretreatment consisted of an "Activation Leach", of which the principal reaction is a metathesis:

\[
\text{CuFeS}_2 + \text{CuSO}_4 \xrightarrow{150\,^\circ\text{C}} 2 \text{CuS} + \text{FeSO}_4
\] (14)

The CuS precipitates can readily be oxidized in a subsequent oxidation step, yielding CuSO\(_4\) solutions for copper electro-winning and for recycle to the "Activation Leach". Unfortunately, while this pretreatment method is stated to be very effective for CuFeS\(_2\) (bornite), it is less so for chalcopyrite. Pyrite does not react. Again process development is stymied by the different reactivity of different minerals. Bornite is also more reactive than chalcopyrite in nitrate oxidation, see Chapter 5.

A similar metathesis has been proposed by Lurgi [6], for complex sulphide concentrate treatment in the sulphate system. After roasting, the calcine is leached in spent zinc electrolyte. The filtrate contains copper and zinc sulphates. The copper is precipitated as copper sulphide using an equivalent amount of zinc in the form of zinc sulphide concentrate. The zinc sulphate solution goes to electrowinning. The copper sulphide can be treated by conventional pyrometallurgy. Since the metathesis occurs under pressure, it is labelled the "pressure exchange process". The authors then propose, while acknowledging the demonstrated feasibility of this metathesis in the chloride system [7]: "its application to the purely sulphate route to avoid corrosion and problems involved with undeveloped technology in associated processing steps when dealing with chloride systems". The same aversion to new hydrometallurgical systems displayed by Sherritt-Cominco also surfaced here with Lurgi.

The pretreatment adopted for the S-C Process was that described earlier by McGauley [8], i.e. a partial desulphurization carried out in a multiple hearth furnace with reducing conditions in the lower hearths and controlled oxidizing conditions in the upper zones. The
S-C Process simplified block diagram is given as Fig. 2-5. What started as a simple concept eventually turned into a complex flow sheet, including a pyrometallurgical step, SO₂ production, H₂S production and three leaching stages followed by a purification step, each with its own liquid/solid separation requirement.

Why the complexity? An analysis of the flow diagram and particularly of the three boxes on the right side shows that sulphur and iron removal have been separated physically. The oxidation leach yields the sulphur product and the precious metals concentrate and the required solid/liquid separation step would be performed as on anode slimes in a conventional copper refinery.

The activation leach was put in to generate a low acid - low copper bleed stream from the electro-winning circuit to allow elimination of zinc, other base metals and iron. The latter is recycled to the acid leach, the main function of which is to produce an iron reject stream prior to copper dissolution. The S-C Process designers opted for jarosite production:

\[
6\text{FeSO}_4 + 2\text{NH}_4\text{OH} + 1.5\text{O}_2 + 7\text{H}_2\text{O} \rightarrow 2(\text{NH}_4)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 2\text{H}_2\text{SO}_4 \tag{15}
\]

At high ferrous sulphate and/or sulphuric acid concentrations, it is difficult to make anhydrous ferric oxide and the product of oxyhydrolysis is a mixture of basic ferric sulphates with poor filtration characteristics and poor stability. At the expense of consuming either ammonia or a sodium salt, jarosite with a well defined crystal structure can be made. It filters well and weathering tests have shown it to be acceptably stable.

Finally, in order to be able to acid leach and generate the iron bleed stream, thermal activation was incorporated in the S-C process. It allows H₂S gas to be produced, which means the altered chalcopyrite is subjected to a reducing leach and not an oxidizing one, as originally conceptualized. Could the nitrate or chloride system have done better? Before reviewing attempts to develop processes for chalcopyrite in these media, it will be useful to first review the differences between chloride, nitrate and sulphate systems.
2.3 Sulphate vs. Chloride/Nitrate Chemistry.

Non-oxidative processing of sulphides with sulphuric acid is technically not feasible due to the high acid strength required to generate H$_2$S. This is apparent from the Eh-pH diagram for the Zn-S-H$_2$O system given in Figure 2-6 [9]. Reducing conditions (low redox potentials) are also required, otherwise elemental sulphur is formed:

$$\text{ZnS} + 2\text{H}^+ \rightarrow \text{Zn}^{+2} + \text{H}_2\text{S} \quad (16)$$

$$\text{ZnS} + 2\text{e}^- \rightarrow \text{Zn}^{+2} + \text{S}^0 \quad (17)$$

In fact, the S-C Process makes use of the insolubility of zinc sulphide in low sulphuric acid solutions by removing zinc from the bleed stream with H$_2$S (see Fig. 2-5). High acid concentrations are also required in the chloride system to yield H$_2$S from ZnS ( sphalerite), which explains why non-oxidative leaching of naturally occurring sulphides is not practiced in hydrometallurgy. Of the common minerals, only Fe$_2$S$_3$ (pyrrhotite) will readily dissolve in this manner (See Part Two). The whole subject of oxidative and reductive leaching of a variety of metal sulphides has been reviewed by Peters [10] in reference to the Eh-pH diagrams for the systems discussed here. For sulphides, nitric acid can only be used as an oxidant.

Unlike hydrochloric and nitric acids, sulphuric acid is poorly dissociated at low pH, and it is difficult to create the hydrogen ions (protons) in concentrations necessary to generate H$_2$S gas at the required atmospheric and hydrostatic pressures, i.e. high enough to form H$_2$S bubbles.

The ion activity in sulphate and chloride solutions has been reviewed by Peters [11]. Sulphate ion (SO$_4^{2-}$) activity in common hydrometallurgical solutions is very low, as can be seen in Table II, abstracted from Peters' review and based on work by Majima et al [12].

In typical hydrometallurgical solutions, sulphuric acid seems to behave more like a monobasic than a dibasic acid. At low ionic strength, the proton activity is greater than the proton concentration. An increase in ionic strength through the addition of sulphate salts decreases the proton activity (aH$^+$). Concentrated sulphuric acid will not dissolve sphalerite.

Fig. 2-6. a) EH-pH diagram for Zn-S-H$_2$O system at 25°C.

Hydrochloric acid acts the other way. The presence of additional chlorides in solution increases the H$^+$ ion activity substantially. Hence, as metal chlorides are produced, the activity of H$^+$ ions is often enhanced, and so is the vapour pressure of HCl over these solutions. The activity of H$^+$ ions as a function of chloride concentration was determined by Jansz [13]. Fig. 2-7 and 2-8 are from this reference.
### Table II: Activities in some H₂SO₄ Solutions

<table>
<thead>
<tr>
<th></th>
<th>Pure H₂SO₄</th>
<th>H₂SO₄ + MgSO₄</th>
<th>H₂SO₄ + Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>M H₂SO₄</td>
<td>1.0</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>M MgSO₄</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>I (formal)</td>
<td>3.0</td>
<td>4.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Y⁺ (H₂SO₄)</td>
<td>0.129</td>
<td>0.129</td>
<td>0.128</td>
</tr>
<tr>
<td>a H⁺</td>
<td>2.02</td>
<td>3.82</td>
<td>3.35</td>
</tr>
<tr>
<td>a HSO₄⁻</td>
<td>0.41</td>
<td>0.74</td>
<td>0.80</td>
</tr>
<tr>
<td>a SO₄²⁻</td>
<td>0.0021</td>
<td>0.0020</td>
<td>0.0050</td>
</tr>
</tbody>
</table>

*Y⁺ (H₂SO₄) = (aH⁺/a² + a²H⁺) where C_H = 2C_H₂SO₄ and C = C_H₂SO₄ + C_MgSO₄

Hydrochloric has a much lower molecular weight (36.465) than sulphuric acid (98.082). This means that at industrial strength the following solution compositions exist at room temperature:

<table>
<thead>
<tr>
<th></th>
<th>H₂SO₄</th>
<th>HCl</th>
<th>HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>98</td>
<td>20</td>
<td>32</td>
</tr>
<tr>
<td>Normality</td>
<td>36.8</td>
<td>6.0</td>
<td>10.2</td>
</tr>
<tr>
<td>Wt. grams/liter</td>
<td>1844</td>
<td>1100</td>
<td>1159</td>
</tr>
<tr>
<td>Wt. of acid grams/liter</td>
<td>1805</td>
<td>229</td>
<td>371</td>
</tr>
<tr>
<td>Wt of water, grams/liter</td>
<td>39</td>
<td>880</td>
<td>788</td>
</tr>
<tr>
<td></td>
<td>995</td>
<td>428</td>
<td></td>
</tr>
</tbody>
</table>

It is obvious that concentrated H₂SO₄ can hardly be considered as an aqueous solution; and it does not have the freedom to convert to a metal sulphate solution. Concentrated sulphuric acid is a desiccant, not a lixiviant and can be transported in carbon steel equipment.
As discussed, at lower concentrations, sulphuric acid will protonize and attack metals. The same situation exists for nitric acid. Super concentrated acid of over 90 wt% HNO₃ can be stored in aluminum containers. Hydrochloric acid remains protonized at all concentrations [13, 14].

The hydrometallurgist normally needs to operate in a regime where acid protonizes. However, economic considerations dictate the maximum uptake of metal in solution, since the size of filters, purification circuits and the like as a rule is reversely proportional to payload, i.e. uptake. Chloride and nitrate systems can have a significant advantage over sulphate ones in this regard and this will be further discussed in section 4.3.

Dilute sulphuric acid can react with many metals to give hydrogen gas:

\[ \text{Me}^{+} + 2\text{H}^{+} \rightarrow \text{Me}^{2+} + \text{H}_2 \] (18)

This reaction, for instance, is the basis for the use of sulphuric acid in steel picking. Hot rolling of steel products forms iron oxides on the surface. The sulphuric acid penetrates beneath the oxides, reacts with the metal to form hydrogen gas, which "blows" the oxide from the steel surface. The sulphuric acid does not react with the oxides and the reaction product is ferrous sulphate [15].

Hydrochloric acid on the other hand reacts with the oxides on the surface of the steel, represented by magnetite in the following equation:

\[ \text{Fe}_3\text{O}_4 + 8\text{HCl} \rightarrow 3\text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O} \] (19)

The formation of ferric chloride raises the redox potential of the solution, thereby preventing formation of hydrogen gas as per reaction (18). The following reaction takes precedence:

\[ \text{FeCl}_3 + \text{Fe}^{+} \rightarrow 3\text{FeCl}_2 \] (20)

Selective reactivity of lixiviants against metals will become more and more important to the hydrometallurgist as the quantity of base metal scrap available through recycling increases. To date, however, attention has been focussed on processing of minerals. The high reactivity of minerals in reducing chloride solutions can be attributed to the high proton activity in concentrated metal chloride solutions as discussed earlier, and the strong chloro complexes formed by Cu⁺, Ag⁺, Pb⁺⁺, Zn⁺⁺, Co⁺⁺, Bi⁺⁺⁺ and Fe⁺⁺⁺. This lowers ionic activities and imparts solubility of these complex species. Muir et al. have recently reviewed chloride hydrometallurgy with emphasis on oxidative leaching [16] and produced an Eh-log [Cl⁻] diagram for the Fe⁺⁺⁺/Fe⁺⁺ and Cu⁺⁺/Cu⁺ systems, given here as Fig. 2-9. The authors make several points in favour of chloride systems, namely that both the Fe⁺⁺⁺/Fe⁺⁺ and Cu⁺⁺/Cu⁺ couples have high oxidizing potentials, that in solutions of over 5 Mol Cl⁻, Cu⁺⁺ is a stronger oxidant than Fe⁺⁺⁺ and that many transition metal ions exist as anionic complexes, or ion-paired with chloride. Even AgCl, normally regarded as a very insoluble compound, complexes and solubilizes (see Fig. 2-9).
One further advantage of the chloride system over both the sulphate and nitrate systems is its capability of creating high redox potentials across the entire pH range. This is not immediately apparent from Fig. 2-2, since the hypochlorite stability domain is above the domain of stability of water. Theoretically, hypochlorous acid and hypochlorites should oxidize water under release of oxygen. However, since this latter reaction is irreversible, decomposition of hypochlorites is slow. Neutral and alkaline solution of hypochlorites are fairly stable, despite their great oxidizing power.

Comparing chloride systems with sulphate ones, the lixiviants, either HCl or Cl₂, can generally be recovered from the produced metal chlorides through pyrohydrolysis or electro-winning. Chlorine is readily liberated at inert anodes with little overpotential and lower overall electrode potential than oxygen. Piloting of such an operation is described in Part Two of this thesis. Pyrohydrolysis of metal chlorides will be described in greater detail in Section 6. Although electrowinning in sulphate systems regenerates sulphuric acid, it is as a dilute solution requiring recycle of all spent electrolyte to the leaching section. This makes sulphate systems inherently large, with costly liquid/solid separation and solution purification sections. Pyrohydrolysis of nickel sulphate solutions or crystals has been proposed many times, tried several times and always found unattractive or inoperable.

Finally, HCl systems have the ability to strip HCl gas from solution (by heating) or crystallize MeCl₃·xH₂O from solution by salting out with HCl gas. This was practiced in the Falconbridge Matte Leach Plant for many years - see Part Two of this thesis - and has been proposed for other processes. It illustrates the possibility of turning a perceived system disadvantage (the volatility of hydrochloric acid) to a critical process advantage.

There is much less attention paid by hydrometallurgists to the nitric acid system, despite some unique and advantageous properties. Nitric acid dissociates readily in water, like hydrochloric acid, hence it is also a stronger acid than sulphuric acid. Its salts are universally soluble; there are no insoluble metal nitrates. This allows regeneration of nitric acid through precipitation of gypsum in mixed nitrate/sulphate systems:

\[
\text{Ca(NO}_3\text{)}_2 + \text{H}_2\text{SO}_4 \to \text{Zn(NO}_3\text{)}_2 + \text{CaSO}_4 \cdot \text{2H}_2\text{O} \quad (21)
\]

While the same is true for chloride systems, coprecipitation of ferric hydroxide with gypsum is much more problematic from chloride media due to formation of oxychlorides.
Nitric acid is inherently oxidizing, unlike hydrochloric acid or sulphuric acid. It can therefore not be considered for reducing type dissolutions and elemental sulphur is the lowest valency oxidation product to be expected from processing sulphide minerals, with the possible exception of pyrrhotite. The oxidation mechanisms of nitric acid on sulphides and lower valency oxides are extremely complex and the profession is a long way from a definitive understanding. Referring to Fig. 2-3, it can be postulated that in oxidative leaching, which involves the reduction of nitric acid, nitrous acid concentration controls the redox potential of the solution via reaction:

$$\text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \quad (22)$$

The generation of nitrous acid appears of considerable importance, as has been recognized in the spent nuclear fuel processing industry [21].

UO$_2$ pellets dissolve according to the rather simple reaction:

$$\text{UO}_2 + 3\text{HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_2 + \text{HNO}_2 + \text{H}_2\text{O} \quad (23)$$

Nitrous acid formation depends on initial nitric acid concentration and solution temperature. Nitric acid does not accelerate UO$_2$ pellet dissolution which phenomenon was also observed for metallic copper dissolution [22].

Decomposition of nitrous acid proceeds according to the following reaction:

$$2\text{HN}_2\text{O} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \quad (24)$$

The interesting findings of this work were that HNO$_2$ decomposition was independent of HNO$_3$ [21] concentration, but dependent on solution surface area $A$ (not UO$_2$ pellet surface area) This is shown in Figures 2-10 and 2-11. The decomposition rate increases with surface area and temperature and can be represented in Eq. 25:

$$D = -\frac{d[\text{HNO}_2]}{dt} = [\text{HNO}_2] \cdot Q(T) \cdot A \cdot \exp(-Q(T)A) \quad (25)$$

$$\log Q(T) = -1/0.0009T - 0.44 \quad (26)$$

where $Q(T)$ [1/cm$^2$/min] is the factor dependent on solution temperature $T$, $A$ is open solution surface area, and $t$ is time after nitrous acid is introduced in the solution.

$$\Delta (\text{HNO}_2) + 3.5\text{H}_2\text{O} \rightarrow 3\text{NO}_2 + 6\text{H}^+ + 6\text{e}^- \quad (27)$$

This reaction was not explored by Fukasawa [21] and no information was given on the agitation levels used in the experiments. The work raises three points. One, it illustrates the lack of knowledge in nitrate hydrometallurgy. Two, it relates to the nuclear industry, a world totally apart (unfortunately) from base metal hydrometallurgy. Three, if buildup of nitrous acid, and thereby the redox potential of the system, is controlled by solution surface area, then this could be of crucial importance for those nitrate processes, which rely on creating surface area for re-absorbing nitric acid.

Lack of knowledge has never stopped the metallurgical industry from attempting process development; over the years its progress has largely been empirical. And for good reasons, mainly to do with the complexity of its feedstocks and the need to work with three phases, i.e. gas, liquid and solid(s).
Several attempts have been made to capitalize on the unique properties of nitric acid, namely to oxidize sulphides, produce soluble salts and a reduced species - NO gas - which has no significant solubility in most aqueous solutions. Nitric acid can generate very oxidizing conditions; yet leave little trace of nitrate in solution. Furthermore, the reduced species, NO gas, will readily react with oxygen in air to reconstitute nitric acid external to the hydrometallurgical process. This is impossible in the sulphuric acid system and impracticable in the chloride system. The nitrate system therefore is unique, in that it can take oxygen from air and generate oxidizing conditions in a hydrometallurgical system with very little energy input.

Sulphuric acid is not an oxidant under the process conditions normally encountered by the hydrometallurgist, who has therefore to rely on introducing other oxidants in the sulphate system. Further comments by this author on the costs of doing so, as related to the processing of refractory auriferous pyrites, can be found in reference 7-9 of this thesis.

Chlorine can be reduced, but it yields the chloride ion which is highly soluble and remains in the system.

The attempts made to develop a chloride and nitrate based metallurgical process for chalcopyrite will be discussed in more detail in Chapters 4 and 5, respectively.

2.4 References


3. Regeneration of Lixivants and Oxidants.

3.1 General.

Having made the point in Section 1.6 that hydrometallurgy is defined by the economic and environmentally acceptable regeneration of the lixiviant, and since the regeneration of hydrochloric acid by pyrohydrolysis features in Chapter 6, it is worthwhile to briefly compare the other choices available to the hydrometallurgist for the three lixiviants under discussion. To this end, a general outline of hydrometallurgical processes is presented here as Fig. 3-1.

Fig. 3-1. Hydrometallurgical Processes [1-11].
There are roughly three methods of solubilizing base metals, i.e., anodic dissolution, oxidizing leach and reducing leach. The former involves electron exchange, the latter proton exchange and oxidizing leach involves both.

There are at least five methods by which metal can be recovered: electrowinning and electro refining, involving electron exchange, oxide production involving proton exchange, hydrogen reduction involving both and crystal production involving none, although going from metal salt to metal requires one of the first four steps. Metal salt crystallization is more of a purification step however, since it separates the metal effectively from the hydrometallurgical solution it was contained in, similar to ion exchange and solvent extraction. The task of the hydrometallurgist in regenerating the lixiviant is to match the proton and electron exchanges of dissolution and winning steps. For instance, electrorefining does not involve a proton exchange and a lixiviant cannot be regenerated by this method. Electrefining must be matched with anodic dissolution.

3.2 Electrowinning.

Electrowinning regenerates the lixiviant in the sulphate system, due to the stability of the $SO_4^{2-}$ anion:

$$2H_2O + 2SO_4^{2-} \rightarrow 2H_2SO_4 + O_2 + 4e^-$$  \hspace{1cm} (1)

It is not so straightforward for the chloride system, where the chloride ion can be oxidized to chlorine:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$  \hspace{1cm} (2)

This is due to the fact that the reaction with water is very slow, except on the surface of a catalyst, such as $MnO_2$.

$$Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2}O_2$$  \hspace{1cm} (3)

The hydrometallurgist would have a wider process choice in chloride systems, if a $MnO_2$ coated electrode could be developed to produce $O_2$ gas instead of $Cl_2$ gas. More about this in Chapter 7.

If chlorine is evolved in electrolytes with a lower valency cation, such as $Fe^{2+}$ or $Cu^+$, the chlorine is absorbed and increases the redox potential of the electrolyte. If the electrolyte cation is monovalent, such as $Ni^{2+}$, the $Cl_2$ gas escapes the electrolyte and can be used directly for oxidative leaching. One great benefit of this is the separation of the dissolution and the electrowinning steps. Not all electrolyte needs to go to dissolution and hence to purification. The dissolution can be driven to higher $MgCl_2$ concentrations, offering opportunities to the hydrometallurgist to use IX, SX or crystallization in a much smaller solution purification section. The Falconbridge Chlorine Leach Process has taken full advantage of this freedom [1].

In this process the electrolyte analyzes 60 g/l $Ni^{2+}$, but the purified leach liquor enters the refinery at 230 g/l $Ni^{2+}$. Instead of a possible 20-30 g/l $Ni^{2+}$ pickup on spent electrolyte, the pickup is 160 g/l $Ni^{2+}$, and the purification section is only one fifth the size.

Electrowinning in the chloride system must be coupled with an oxidative leach (unless the chlorine is burned to HCl with hydrogen), whereas electrowinning in the sulphate system can be coupled with a reducing leach. As discussed before, the proton concentration in strong sulphuric acid is too low, however, to generate $H_2S$ gas and for the dissolution of sulphides an oxidative leach is generally proposed. The anodic oxygen gas is wasted.

Very little work has been carried out on the electrochemistry of nitrates, in conjunction with electrolytic base metal recovery. Nitrate ions are readily reduced at the cathode, probably through the stages [2]:

$$HNO_3 \rightarrow NO_2 \rightarrow HNO_2 \rightarrow NO \rightarrow H_2NOH \rightarrow NH_3$$

The nature of the reduction product was found to depend on the cathode potential, temperature, current density, concentration of the acid and cathode material. With regard to the latter, for instance, under similar test conditions nitric acid forms hydroxylamine at a mercury cathode, but forms mainly ammonia at a copper cathode. At cathodes of carbon, graphite and platinum, nitric acid is largely reduced to pure nitric oxide [2]. When nitric acid is electrolyzed between platinum electrodes in a cell containing a diaphragm, nitric oxide is formed at the cathode and oxygen is evolved at the anode. No information was found on the behaviour of the nitrate anion during cathodic metal depositions nor on the actual mechanism which causes the $NO_3^-$ anion to reduce at a cathode. At 25°C at least, dispersed solvated $H_2O^-$ and $NO_3^-$ ions are in equilibrium with the ionpair $H_2O^+NO_3^-$ [3].

It appears to the author that considerable more fundamental work is required in this area, before electrowinning of base metals in nitrate media, with recovery of the lixiviant, can be considered. Literature references suggest nitrate removal to be feasible [4]. Since this is one of the process restraints on nitrate hydrometallurgy, it will be discussed in Chapter 7.
3.3 Hydrogen Reduction.

The precipitation of metals from aqueous solution by hydrogen reduction is a relatively new technique compared to the electrolytic processes, and has been used on a large scale for over thirty years. A comprehensive review of the early developments is still relevant [5].

The thermodynamics of hydrogen reduction of some base metal cations is given in Fig. 3-2 [6].

Only Cu$$^{2+}$$ can be hydrogen reduced to metal in an acid system and regenerate sulphuric acid. The reduction probably involves cuprous sulphate as an intermediate [7]:

$$2\text{CuSO}_4 + \text{H}_2 \rightarrow \text{Cu}_2\text{SO}_4 + \text{H}_2\text{SO}_4$$ (4)

followed by

$$\text{Cu}_2\text{SO}_4 + \text{H}_2 \rightarrow 2\text{Cu}^0 + \text{H}_2\text{SO}_4$$ (5)

or

$$\text{Cu}_2\text{SO}_4 \rightarrow \text{Cu}^0 + \text{CuSO}_4$$ (6)

However, the corrosive conditions encountered when using hydrogen under acid conditions are severe enough that in commercial practice alkaline conditions have been preferred, even for copper. In summary, hydrogen reduction in aqueous solution is not an industrial option for lixiviant regeneration. Currently operating processes on sulphide minerals produce ammonium sulphate as a byproduct.

The subject of lixiviant regeneration by H$_2$ reduction cannot be dismissed without referral to the Peace River Mining and Smelting Process, one of the most elegant hydrometallurgical chloride processes attempted to date [8].

Although the PRM & S Process was originally intended for the sedimentary oolitic iron ore deposits in the Clear Hills area of the Peace River district in northern Alberta, the 50,000 ton per year plant ultimately built at Amherstburg, Ontario used high surface area scrap, such as detinned cans, steel turnings and cast iron borings as feed stock. The flowsheet is given as Fig. 3-3. Steel is dissolved in HCl to give a FeCl$_2$ solution. The FeCl$_2$ is crystallized, dried, briquetted and reduced to sponge iron with the process generated H$_2$. The latter is milled to iron powder. Low priced steel units are turned into high priced iron powder with little or no waste, no need for a reductant and no loss of lixiviant. The process could have been made to work, but unfortunately, this venture failed due to lack of understanding of the iron powder market and lack of capital. The plant's demise set chloride hydrometallurgy back a decade, in the author's opinion.
3.4 Oxide Production.

Precipitation of the metal oxide, hydroxide or carbonate through the addition of a base eliminates the lixiviant, be it a chloride, nitrate or sulphate. In the latter the use of calcium oxide, hydroxide or carbonate yields gypsum, and at least allows removal of the neutralized lixiviant from the circuit as gypsum \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O})\) or the hemihydrate \((\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})\). This option does not exist in the chloride or nitrate system and discard of the salts is not an acceptable option (except for chlorides to sea). Metal oxide precipitation from solution is not a viable option in such a hydrometallurgical process, as defined. Even in the sulphate system, the production of a metal hydroxide/gypsum mixture can only be considered for iron removal, i.e. when the metal hydroxide is discarded. Redissolution of metal values from such a MeO/CaSO\(_4\cdot2\text{H}_2\text{O}\) mixture requires additional acid to be generated, and the metal oxide precipitation step is reduced to an acid consuming step in the purification process.

Metal oxide production by hydrolysis, sometimes oxidative hydrolysis, allows regeneration of the lixiviant and is used in the zinc industry for decomposition of zinc ferrite into haematite and zinc sulphate [9].

\[
\begin{align*}
\text{ZnO.Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4 & \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{ZnSO}_4 + 4\text{H}_2\text{O} \quad (7) \\
\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \quad (8)
\end{align*}
\]

By using hydrolysis at high temperatures, i.e. at 220°C, low sulphate crystal aggregates of less than 10 \(\mu\)m particle size were produced, requiring substantially less wash water and pond volume than the equivalent jarosite.

Nevertheless, comparison of reaction (7) and (8) quickly reveals that for this particular process feed only three-fourths of required sulphuric acid is regenerated by the autoclave hydrolysis of ferric sulphate. This allows the hydrometallurgist process control by providing the additional acid with the feed slurry, but it also combines the leach and precipitation step. Any undissolved values will now have to be recovered from a larger weight of residue.

Oxides can also be produced by high temperature decomposition of the metal salts, in solution or as crystals. For metal sulphates the term decomposition or roasting has been used for the various attempts made to develop an acceptable process for:

\[
\text{MeSO}_4 \rightarrow \text{MeO} + \text{SO}_3 \quad (9)
\]
None of these attempts has resulted in a viable process, due to a variety of reasons. The \( \text{SO}_3 \) gas tends to form \( \text{SO}_2 \) and \( \text{H}_2\text{SO}_4 \) mists. The off gases will be a dusty mixture of \( \text{SO}_3 \), \( \text{H}_2\text{SO}_4 \) vapour and some \( \text{SO}_2 \), very difficult to handle in a sulphuric acid plant. High temperature decomposition requires purification of the metal sulphate, otherwise an impure product is made and base metal values are lost in case of \( \text{FeSO}_4 \) decomposition. Alkali and earth alkali sulphates should be absent, since they will carry through into the product.

A renewed attempt at high temperature hydrolysis of impure ferrous sulphate crystals is currently being made at Sorel, Quebec, by QIT-Fer et Titane, Inc. QIT is acting for a consortium of sulphate process \( \text{TiO}_2 \) pigment producers, for whom discharge of spent sulphate liquors is a very severe environmental problem. Results of the pilot plant trials have not been published, but it appears the usual problems associated with high temperature hydrolysis are being encountered.

Crystallization of metal salts from mother liquors offers the possibility of segregating contaminants. This was taken advantage of in the Falconbridge Matte Leach Plant to segregate lead from nickel [6-3]. An interesting proposal has been made to use crystallization instead of SX for spent nuclear fuel reprocessing. The approach takes advantage of the rigid crystal geometry of uranyl nitrate hexahydrate, allowing little isomorphous replacement by contaminants [10].

High temperature hydrolysis in the chloride system has been very successful, allowing strong lixiviant regeneration. It will be discussed in detail in Chapter 6. No industrial references to high temperature decomposition of nitrates were found. The possibilities in this area will be discussed in Chapter 7.

In summary, lixiviant regeneration is possible through electrowinning, hydrogen sulphide precipitation, autoclave hydrolysis and high temperature hydrolysis. High temperature reduction of metal chlorides offers an interesting alternative. Although metal chloride hydrolysis regenerates the lixiviant, it produces a metal oxide, not the final metal product and as such is more energy intensive than electrowinning for base metals.

3.5 References

4. Discussion of Chloride Systems.

4.1 General.

As mentioned in the preamble of Chapter 2, this thesis is not intended to give an exhaustive review of proposed and operating chloride processes. Since attempts have been made to develop processes for the treatment of chalcopyrite with all three lixiviants under discussion (sulphate, chloride, and nitrate), a comparison will be made on that basis.

Chloride systems have long intrigued the hydrometallurgist and they have displayed considerable ingenuity and perseverance to make these systems a commercial success. For instance, the electrowinning of zinc from zinc chloride solution was demonstrated on a commercial scale in Germany and England in the mid-1890's [1]. The metal was deposited either on vertical rotating disk or vibrating plate cathodes. Chlorine was evolved on insoluble anodes separated from the cathodes by nitrated cotton or linen diaphragms which in some cases were reinforced with asbestos. Similar attempts to electrowin copper and nickel from chloride solutions were made in Canada and the USA around the turn of the century [2]. The processing of chalcopyrite in chloride systems was not seriously attempted until the 1950's, when much more appropriate materials of construction were available.

4.2 Proposed chloride processes for chalcopyrite.

A recent review of chloride processes for chalcopyrite has been made and resulted in Table I [3].

The early, and the more recent processes all rely on the high oxidizing potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Cu}^{+}/\text{Cu}^{2+}$ couples, and the strong chloro complexes formed by $\text{Cu}^{+}$, $\text{Ag}^{+}$, $\text{Pb}^{2+}$, $\text{Zn}^{2+}$, $\text{Co}^{2+}$, $\text{Bi}^{3+}$, and $\text{Fe}^{3+}$. The complexing lowers ionic activities and imparts improved solubility of the complexed species in strong chloride solutions. This combination of properties results in industrially acceptable dissolution rates of chalcopyrite and metal uptake in the process solutions.

Unfortunately, both iron and copper are dissolved, presenting the hydrometallurgist immediately with the problem of iron/copper separation, as discussed earlier for the sulphate system. The problem of handling other metals such as zinc, lead, silver, and gold in the proposed chloride processes was largely avoided by using ultra clean, (Arizona) chalcopyrite concentrates. Even so, the difficulty of recovering gold and silver from this chalcopyrite concentrate was not resolved in a
### Table I: Proposed chloride based process for chalcopryite

<table>
<thead>
<tr>
<th>Name</th>
<th>Leaching system</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USBM</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt; (&gt;200 g/l) + HCl (&gt;20 g/l), very fine grind. Single stage leach at boiling point. No reduction prior to electrolysis.</td>
<td>One of the largest scale investigations of FeCl&lt;sub&gt;2&lt;/sub&gt; leaching.</td>
<td>[4]</td>
</tr>
<tr>
<td>CLEAR Duval, USA</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt; (50-60 g/l). Fe&lt;sup&gt;3+&lt;/sup&gt; (15 g/l). Two stages: 1) reduction at 1070°C, 2) Oxidation at 140°C with O&lt;sub&gt;2&lt;/sub&gt;. Electrolysis of Cu&lt;sup&gt;+&lt;/sup&gt; to Cu with parallel regeneration of Cu&lt;sup&gt;2+&lt;/sup&gt;.</td>
<td>Commercial plant, 100 t/d has been operated for a short time.</td>
<td>[5-7]</td>
</tr>
<tr>
<td>CYMET, Cyprus Mines, USA</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt; (&gt;20 g/l). Fe&lt;sup&gt;2+&lt;/sup&gt;, NaCl; total Cl&lt;sup&gt;-&lt;/sup&gt; 260-270 g/l. Two stages at boiling point. Reduction of crystallization CuCl with H&lt;sub&gt;2&lt;/sub&gt; in fluid bed.</td>
<td>Original process involved anodic dissolution and Fe&lt;sup&gt;3+&lt;/sup&gt; regeneration by Fe&lt;sup&gt;2+&lt;/sup&gt; electrolys.</td>
<td>[8-11]</td>
</tr>
<tr>
<td>Cominco Canada</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt; (120 g/l), two stage counter-current leach, very fine grind. Cu recovery by crystallization of CuCl and H&lt;sub&gt;2&lt;/sub&gt; reduction and cementation with Fe.</td>
<td>Similar to Cymet process; cement Cu is used for reduction to Cu&lt;sup&gt;+&lt;/sup&gt;.</td>
<td>[12]</td>
</tr>
<tr>
<td>Dextec Australia</td>
<td>NaCl 200 g/l, pH 2-3. Anodic oxidation in the presence of air at 90°C. Parallel Cu deposition at cathode in diaphragm cell.</td>
<td>Diaphragm filter cloth.</td>
<td>[13-14]</td>
</tr>
</tbody>
</table>

The iron copper separation was achieved by removing the iron from a cuprous chloride solution by controlled air oxidation:

\[
\begin{align*}
4\text{Fe}^{2+} + 8\text{Cu}^+ & \quad \rightarrow 4\text{Fe}^{3+} + 8\text{Cu}^2+ + 4e^- \\
12e^- + 3\text{O}_2 + 6\text{H}_2\text{O} & \quad \rightarrow 12\text{OH}^- \\
4\text{Fe}^{3+} + 3\text{O}_2 + 6\text{H}_2\text{O} & \quad \rightarrow 4\text{Fe(OH)}_3 + 8\text{Cu}^2+ 
\end{align*}
\]

The cuprous/cupric couple acted to accelerate oxygen transfer in this system and the resulting cupric solution was used to dissolve chalcopryite:

\[
\text{CuFeS}_2 + 3\text{Cu}^2+ \quad \rightarrow \quad 4\text{Cu}^+ + \text{Fe}^{3+} + 2\text{S}
\]

The other approach was to remove the copper from a ferrous chloride solution, either by CuCl crystal formation and removal or by solvent extraction into a sulphate circuit.

The only one of the early processes to reach industrial scale and operation was Duval's CLEAR process [15]. It was shutdown supposedly due a combination of depressed copper prices and engineering problems. The latter are said to have included the novel electrolytic cell with wiped cathodes, the bottom dragout mechanism for the dendritic copper product and uncontrolled gypsum deposition.

Not being able to compete with modernized copper smelter/refinery operations for clean chalcopryite concentrates, hydrometallurgists turned their attention to concentrates which could not be handled by conventional techniques, namely the mixed, or complex, copper-zinc-lead concentrates. A number of chloride based hydrometallurgical processes have been proposed and undergone development. A 1984 review lists 12 such processes [16], of which one, the Zincex Process, has reached commercial production [17]. As the name implies, this is a process for zinc recovery. The focus of this writing is on copper recovery and shall therefore discuss the most recently proposed ZINCEX version for copper recovery from chalcopryite concentrates, i.e. the CUPREX Process [18].
4.3 The CUPREX Metal Extraction Process.

This process attempts to overcome the weaknesses of the earlier processes, while maintaining their advantages. The main weakness was discerned as the inability of producing commercial grade, high quality, coherent cathode copper from a chloride electrolyte. Earlier processes attempted to deal with this by introducing a solvent extraction step, using the industrially available and known, o-hydroxyaryloxime reagents. Since this SX is governed by the $H^+$ concentration, only relatively dilute copper solutions can be treated or careful pH control is necessary. The reagents used in these earlier systems also move copper from a chloride to a sulphate system requiring care to be taken against chloride carry-over into the copper electrowinning circuit, and vice-versa.

$$2RH_2 + Cu^{2+} \rightarrow R_2Cu_0 + 2HA^+ \quad (4a)$$

In the late 1970's, ICI (Imperial Chemical Industries) began a research program to find a copper specific, chloride specific solvent extraction reagent with fast extraction and strip kinetics, good phase-disengagement properties and high stability. The successful outcome of this program was the novel extractant DS 5443 [19].

Since this reagent selectively transfers cupric ions from high to low chloride media, there is said to be no need for pH adjustment or control. Compare equation 4a with 4b:

$$Cu^{2+} + 2C1^- + 2L \rightarrow L_2CuCl_2 \quad (L = DS 5443 \ or \ Acorga \ CLX50) \quad (4b)$$

Due to the selectivity of the reagent, there is also no need to deal with other metals and metalloids in the copper recovery circuit. Silver is cemented from the copper depleted liquor, after which iron can be removed as FeO(OH). A generalized flowsheet of the CUPREX Process is given here as Fig. 4-1.

The copper concentrates are leached at atmospheric pressure and 95°C, to produce a cupric chloride leachate in a two stage leach. Pyrite, molybdenite, gold, elemental sulphur and gangue minerals remain in the residue and can be separately recovered. The leachate after clarification is contacted with the new reagent in an SX operation that produces a pure cupric chloride eluate, containing over 100 g/l Cu**, for electrowinning of the copper.

$$e^- + Cu^{2+} \rightarrow Cu^+ \quad (5)$$

and,

$$e^- + Cu^+ \rightarrow Cu \quad (6)$$

Cupric chloride entering the cell must first be reduced to complexed cuprous chloride before yielding copper at the cathode. At the anode chlorine is evolved:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (7)$$

This chlorine will oxidize cuprous to cupric, thereby preventing cathode copper production. Hence, the anode and cathode must be separated. This can be done with a diaphragm as in nickel electrowinning (see Part Two of this thesis). Normally, to prevent Cl_2 leaking into the tankhouse atmosphere, the anode compartment is kept under suction. This means that catholyte enters the anode compartment, where its cuprous chloride is oxidized. Depending on the tightness of the diaphragm cloth, the current efficiency will range from poor to acceptable.

Little work has been reported on the electrowinning of copper from cupric chloride solutions [19]. It is the author’s suggestion that consideration should be given to reversing the electrolyte flow from convention, i.e. feed the cupric chloride solution to the anolyte compartment, allow the Cl_2 saturated anolyte to
flow into the cathode compartment where the Cl_2 will instantly react with the cuprous chloride, eliminating the danger of Cl_2 emission into the tank house atmosphere from the cathode compartments (the anode compartment can always be made gas impervious to a greater depth). Although the transferred Cl_2 will also lower the current efficiency, it will be minor since its mole concentration in the transferred electrolyte will be much less than that of Cu^{+} going the other way in "conventional" electrolyte flow. Anolyte dechlorination is also eliminated.

In the CUPREX Process, use is made of the METCLOR Cell, developed by Tecnicas Reunidas, S.A. of Spain. A schematic diagram, depicting its operation, is given as Fig 4-2.

![Schematic diagram of the Metclor Cell](Image)

The METCLOR Cell employs titanium cathodes and dimensionally stable anodes (DSA's) which are separated by a cation selective ion-exchange membrane made from a material such as Nafton (N-417) from DuPont. These materials have found widespread use in the chloralkali industry and the METCLOR cell is geometrically similar to those used in the chlor-alkali industry. The membrane suitability to this application will be discussed later. Sodium chloride is added to the catholyte to complex cuprous chloride and to allow the membrane to function.

Copper electrowinning from chloride solution produces a granular copper product from the concentrated catholyte (strip solution or eluate from the SX operation). Depleted catholyte is "reformed", i.e. oxidized to cupric chloride with part of the chlorine produced at the anode, then depleted of cupric by contacting it with organic solvent from the stripping stage. This indicates that the copper must be in the divalent state for Acorga CLX50 to work and that current efficiency will depend on the amount of cuprous remaining in spent catholyte (given as 10 g/l Cu^{+}).

The copper depleted catholyte flows into the anode compartment and provides Na^{+} ions to pass through the cell. The depleted catholyte has less than 0.3 g/l Cu^{+}. It is unlikely any of this copper passes through the membrane, since it is present as a weak anionic complex. "Depleted" brine is discarded. A purification step is not needed in the electrolyte circuit.

The copper depleted leachate after SX (raffinate) goes to cementation for silver recovery. Dissolved iron is removed as goethite in a pressure oxidation stage. This also regenerates part of the oxidant. The remainder of the oxidant is regenerated using chlorine from the electrolysis.

4.4.1 Discussion of the CUPREX Process.

The developers of the CUPREX Process make use of two technologies which are new to the metallurgical industry, i.e. a selective reagent for cupric chloride SX, and ion exchange membranes. This allows an elegant process design, by separating copper from iron and other impurities with very small copper losses and no need for pH adjustment. The reagent Acorga CLX 50 utilizes differences in chloride concentration to extract, and then release CuCl_2. The chloride concentration of the new catholyte is approximately 112 g/l, at 100 g/l Cu^{+}, or 3 Mol. More importantly, this chloride will be removed as Cl_2 gas, and the cuprous chloride in the catholyte will precipitate unless an inert chloride is added to allow cuprous chloride to form a soluble complex. The CUPREX Process uses NaCl, which is added to the new catholyte before being fed to the cathode compartment(s).

\[ \text{CuCl}_2 + n \text{Cl}^- \rightarrow \text{Cu}^{+} \text{(Cl)}_n^{2-} \]  

(8)

However, by raising the chloride concentration, depleted catholyte becomes unsuited as an SX strip solution and it must be discarded after "once through". The CUPREX Process will discard close to two tonnes of NaCl for every tonne of copper produced. This is quite acceptable at seaboard, but for inland locations an evaporator or dialysis unit may be required.
The fact that the reagent Acorga CLX 50 is selective for cupric means that the chalcopyrite dissolution will end at a high redox potential, i.e. at cupric chloride, not cuprous. While this ensures rapid and complete extractions, it also means a lower uptake of copper and iron per unit volume of oxidant. In other words, a higher circulating load is required in the iron circuit. As long as the solid/liquid separation is not problematic, this is not a drawback. Temperature fluctuation in the iron circuit are modest and process control is feasible (either before or after filtration). Chlorine injection (or CI₂ injection) and iron is removed from a slip stream. Chlorine injection just before, or after filtration, to oxidize cuprous to cupric is suggested since it would appear to allow a lower circulation in the iron circuit.

Silver and presumably residual cuprous removal is carried out on the slip stream by cementation with zinc. This process step has been proven in the Zincex Process. It requires reduction of the slip stream to the ferrous state, which may help to provide good goethite morphology in the subsequent autoclave oxidation step. It would also allow pyrohydrolysis of the ferrous chloride yielding hydrochloric acid, which is required in the leach as make-up.

Since little is known about the plant performance of Acorga CLX-50, the process developers statements will need to suffice at present. This is not the case for ion-exchange membranes, which have been used industrially in the chlor-alkali industry since the early 70s. The overall experience with membrane technology has been extremely positive in that industry and membrane plants are steadily replacing mercury and diaphragm capacity [20]. The industry has recognized however, that a high brine purity is essential. Secondary brine purification via ion exchange is now the industry standard. Cationic, anionic and non-ionic impurities can damage the membranes [21]. Calcium, magnesium, sulphate ions and colloidal silica are all deleterious. Membrane replacement adds U.S. $4.50 per ton of NaOH at a replacement cost of U.S. $600 per m², delivered [22]. The membrane duty in a CUPREX Plant is entirely different from that in a chlor-alkali plant. Current density is an order of magnitude lower, and the electrolyte is acidic. Impurities such as magnesium can probably be tolerated. However, cuprous chloride crystallization in the membrane, or manganese dioxide precipitation, or the effects of S.X. organics must all be anticipated. In addition, if copper powder production is replaced by cathodic deposition or the powder turns dendritic, physical damage to the membrane through cathode lifting is a distinct possibility.

### 4.4.2 Comparison with the S-C Process

The advantages of chloride hydrometallurgy for chalcopyrite processing are immediately apparent comparing the block diagrams given as Fig.4-1. Where the sulphate system required an activation step and three sequential leaching operations with liquid/solid separations, use of a chloride oxidant allows one leach directly on concentrate. This is due to the different morphology of the elemental sulphur layer formed on the chalcopyrite surface, porous in chloride media but dense in ferric sulphate over 0.1 mol per liter concentration [23]. The copper/iron separation is made by SX, not by selective precipitation of hydroxides or jaro-sites. Although zinc removal is not discussed, zinc sulphide could probably be precipitated from the cementation solution with H₂S, or removed by another SX circuit.

The commercial advantage of the S-C Process is in the production of high quality copper in a conventional copper electrowinning circuit. Energy consumption for this will be about the same in both processes, but the capital investment for a CUPREX Process tank house will be much higher. So will the risks, since the chloride process incorporates two technologies new to the metallurgical industry. Despite the need to discharge NaCl solution, the CUPREX Process is more elegant and compact than the alternative sulphate process, and should offer lower operating costs, once the development costs have been incurred. The METCLOR cell appears entirely feasible both from a theoretical and practical standpoint. Chlorine collection in metal chloride electrowinning is a proven technology (see Part Two), allowing safe recovery of the oxidant.

Whether the advantages of the CUPREX Process are sufficient to be competitive with established, modern copper smelter/refinery processes remains to be seen. It is generally not advisable to select a novel process for a plant at a remote site. It is therefore likely that the process developers will have to consider the use of the CUPREX Process at an established site for mixed, or complex concentrates. This would increase the complexity and thereby the risks. Nevertheless, considerable progress has again been made towards a viable hydrometallurgical plant for processing chalcopyrite into high quality copper metal.
References


8. Kruesi, P.R., Allen, E.S. and Lake, J.L., CIM Bull. 66 (June 1973) pp. 81-87


21. ibid, 20. Licwek D.L. "Impurity damages to chloralkali membranes" pp. 284-289

22. ibid, 20. Peet, David L. "Membrane durability in Chloralkali Plants" pp. 329-336

5. Discussion of Nitrate Systems.

5.1 General.

As stated, the processing of chalcopyrite in the nitrate system will be discussed in detail. Only one serious attempt has been made, however, to develop such a system. That attempt was made by Kennecott Copper Corporation, with technical assistance by DuPont. Although a lot of work was done, a few words on other nitrate systems may be in order and complimentary to the comments on chalcopyrite processing in section 5.2.

While there is presently no base metal recovery using nitrate systems, there is a substantial amount of nitrate hydrometallurgy being practiced in the nuclear industry. Nitric acid has been used to dissolve yellow cake and to strip uranium from a loaded SX reagent to give a 120 g/l U eluate [1]. However, most technology has been developed for processing irradiated fuels. To illustrate the esoteric world of nuclear hydrometallurgy the flowsheet of the proposed (and more recently put on hold after the Chernobyl accident) Wackersdorf Reprocessing Plant in Bavaria, W. Germany is given here as Fig. 5-1. The hydrometallurgy, i.e. the extraction of uranium and plutonium for re-use, appears incidental to the efforts associated with the receipt, handling and final storage of radioactive (by)products. Nitric acid recovery is not even mentioned. The mean daily throughput of the plant is 2 tonnes of nuclear fuel, which can only be processed after an 8 year cooling off period [2].

The most widely used process in the nuclear reprocessing industry is the PUREX Process (plutonium - uranium - reduction - extraction), which operates with 3 - 4 molar nitric acid. Ferrous sulphamate is used as plutonium reductant. Other processes resembling the PUREX process are the Thorex, Redox and Eurex processes. Details are outside the scope of this thesis, but one might be mentioned. Nitrous acid has been used as a reductant to strip plutonium from TBP (tributyl phosphate) in mixer-settlers [1]. This is an interesting reversal of the general chemistry, i.e. of nitric acid forming nitrous acid, and acting as an oxidant, and will be proposed for the treatment of silver bearing Pyrolusite in Chapter 7.

Another application of nitrate metallurgy has been developed for the processing of spent Ni-Cd batteries by UNC Reclamation, Florida, U.S.A. Although few details are known, the process involves SX in a facility formerly used by United Nuclear Corporation for extracting uranium from phosphate plant liquors [3]. West German researchers have developed an analogous system for
the waste solutions of these batteries, including nitrate ion destruction by electrochemical reduction [4].

Finally, there are the ARSENO and NITROX process developments with which the author has been associated and which are described in detail in Part Two. The NITROX Process is primarily an oxidation process for gold bearing (arseno) pyrites and it leaves the gold in the residue for subsequent extraction by cyanide. As such, it competes with roasting and pressure oxidation. The process will be further discussed in Chapter 7.

5.2 The Kennecott-DuPont effort on chalcopyrite processing.

5.2.1 History.

In the late 1960's, the shortage of copper smelting capacity in the Western US and the difficulty of the then existing smelters to meet projected air pollution standards provided substantial incentives to copper producers to explore hydrometallurgical alternatives. Kennecott Copper Corporation investigated nitric acid oxidation of copper sulphides. Since the contained sulphur would convert in part to sulphuric acid, the process was named the "Nitric-Sulphuric Leach Process", or NSL Process. The NO gas produced through the reduction of HNO₃ would be oxidized with O₂ in the process equipment to yield reconstituted HNO₃ [6].

The process objectives went through revisions as the testwork progressed. At the outset, the ideal nitric acid process was seen by Kennecott as to solubilize all the copper, precipitate all of the iron, convert all sulphide to elemental sulphur, and consume all of the nitrate added. The first two objectives are familiar, the third one was arbitrarily imposed on the process. The last one is unique to nitrate systems.

The proposed flowsheet for processing copper concentrates with nitric acid is given as Fig. 5-2.

Solubilizing the copper sets the stage for recovery of copper for sale. Unfortunately, the technology for copper electrowinning from nitrate solutions is not available, if indeed it is feasible (See Chapter 3). So a solvent extraction step was included in the early flowsheet. Although the SX reagent was not specified, it was probably an o-hydroxyaryloxime. The reagent did require acid neutralization to transfer the copper into the circulating electrolyte, which was achieved by lime addition. The SX reagent is susceptible to oxidation, even by traces of nitrate such as may result from the use of ammonium nitrate based explosives.

Fig. 5-1. Flowsheet of the Wackersdorf Reprocessing Plant process areas [2].

Nitric acid assisted dissolution and processing of a mineral concentrate is practiced by Sunshine Silver of Kellogg, Idaho. An excellent description of the process and its start up problems has been published [5]. Silver is brought into solution and recovered by precipitation as AgCl.
The iron precipitation step was designed to occur during the oxidation step:

$$6CuFeS_2 + 10HNO_3 + 10H_2SO_4 \rightarrow 6CuSO_4 + 2H_2OFe_2(SO_4)_3 \cdot (OH)_6 + 10NO + 12S^2 + 6H_2O$$ (1)

To keep the water balance in the circuit, an evaporator was proposed for operation on the SX raffinate. Removal of water of crystallization with the gypsum and jarosite was apparently not sufficient. Evaporator condensate was used as wash water on the filters.

This flowsheet included a number of problem areas, to name only the solvent extraction of elemental sulphur, neutralization of the aqueous phase in solvent extraction and evaporation of gypsum saturated solutions. Costs would have been adversely effected by the use of oxygen and purchased sulphuric acid.

Revisions of the process eliminated the objective of maximizing elemental sulphur production (it cannot be varied greatly, anyway), eliminated solvent extraction in favour of denitrification of the leach liquor, incorporated an ammonium jarosite precipitation step and used air in conventional nitric acid plant equipment to reconstitute the acid from NO gas. Kennecott enlisted the cooperation of E.I. DuPont de Nemours Co. with regard to the latter.

In the end, the precipitous drop in copper prices in the late 1970's and the subsequent restructuring of the industry spelled the end to this hydrometallurgical development. The apparent advantages of the NSL Process over the improved copper smelter costs were not sufficient to warrant the risks involved in building a full scale facility based on nitric oxidation of chalcopyrite concentrate.

This is not meant to be critical; the Kennecott effort was a major outstanding and unique effort in the field of nitrate hydrometallurgy. Without it the Arseno and NITROX Process developments would have had to break much new ground.

5.2.2 The Nitric-Sulphuric Leach Process.

The latest process flow diagram is given here as Fig.5-3. For a more complete flowsheet, the reader is referred to the original publication [7].

Minerals react in nitrate systems quite differently from chloride and sulphate systems. In the latter two, chalcopyrite is more reactive than, for instance, pyrite. Not so in nitric acid oxidation. The Kennecott researchers measured the relative reactivity of various mineral species at 90°C for one hour in an excess of 20 wt% HNO₃ [5]. Results are given in Table I.
Work published by the author (See Part Two) has confirmed the findings for pyrite and would place arsenopyrite as indicated at the bottom of Table I. The reason(s) for the different behaviour of the same mineral in different oxidants must be due to different reaction mechanisms and electrochemistry. Their elucidation, especially in nitrate systems, awaits further investigations, although progress has been made in the chloride system on understanding the mechanisms of sulphur formation in oxidative leaching of minerals [8].

From a process design standpoint it is clear that chalcopyrite does not favour nitrate systems. To overcome this low reactivity, a concentrate regrinding step was introduced in the flowsheet.

In addition a three stage oxidation, with interstage liquid/solid separation was also incorporated in the flowsheet. The flow schematics and typical leach step results are given here as Fig. 5-4 and Table II, respectively.

Table I: Relative reactivity and elemental sulphur yield of pure minerals oxidized with excess nitric acid [5].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Species</th>
<th>Reactivity</th>
<th>S as % of S reacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu3SbS5</td>
<td>tetrahedrite</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Cu3S</td>
<td>chalcoite</td>
<td>8</td>
<td>75</td>
</tr>
<tr>
<td>FeS</td>
<td>pyrrhotite (?)</td>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>FeS2</td>
<td>pyrite</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>CuS</td>
<td>digenite</td>
<td>6</td>
<td>55</td>
</tr>
<tr>
<td>CuS</td>
<td>covellite</td>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>CuFeS4</td>
<td>bornite</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>CuFeS2</td>
<td>chalcopyrite</td>
<td>2</td>
<td>45</td>
</tr>
<tr>
<td>FeAsS</td>
<td>arsenopyrite</td>
<td>8</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig. 5-3. Nitric Sulfuric Leach Flowsheet [7].

Fig. 5-4. Leach Stage Flow Schematic
In the leach step, essentially all of the metal sulfides in the concentrate are dissolved while reducing the concentration of nitrate and free acidity in the pregnant liquor to low levels. Nitric oxide from the leach reactors is oxidized in the nitric acid recovery step and absorbed to regenerate HNO₃. If molybdenum is present, it is completely solubilized during leaching and is removed from the pregnant liquor by precipitation. The pregnant liquor is then fed to the nitrate removal autoclave where residual nitrate is reduced to gaseous NO, and Fe²⁺ is simultaneously oxidized to Fe³⁺. The evolved NO is recycled. Iron is partially precipitated as hydrogen jarosite in the nitrate removal step. Iron precipitation is completed in the iron removal autoclave by introducing ammonium ions, which form ammoniumjarosite. A small amount of oxygen may be required to oxidize residual Fe²⁺. Filtrate from the iron removal step is contacted with recycle cement copper to remove selenium as copper selenide and the purified liquor is fed to electrowinning where "cathode grade" copper is recovered.

Table II: Typical Leach Step Results

<table>
<thead>
<tr>
<th>Stage</th>
<th>Feed Eff.</th>
<th>Feed Eff.</th>
<th>Feed Eff.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO₃⁻ (g/L)</td>
<td>H₂SO₄*</td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>Stage 1</td>
<td>35</td>
<td>45</td>
<td>66</td>
</tr>
<tr>
<td>Stage 2</td>
<td>7</td>
<td>11</td>
<td>75</td>
</tr>
<tr>
<td>Stage 3</td>
<td>217</td>
<td>282</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>40</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>479</td>
<td>-</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>94°C-</td>
<td>98°C-</td>
<td>2°</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>2</td>
<td>1.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

*S₂O₅²⁻ calculated as total free acid.

Sulfate inventory is controlled by precipitation of gypsum from part of the depleted electrolyte. Impurity levels are controlled by a purge stream from which cement copper is recovered in the purge recovery step. Depleted electrolyte is recycled, part to the leach step and part to nitric acid recovery, where it serves as the absorbant in the nitric acid recovery column.

If present, gold and silver are recovered from the leach tails by cyanide leaching. Zinc builds up in the recycle liquor and can be recovered from the purge liquor by selective precipitation. Molybdenum is recovered from the molybdenum step organic extract by stripping with ammonia and calcining to form high purity MoO₃.

Some of the NSL process steps involving nitrate will be highlighted here. For instance, in the nitrate removal reactor, residual nitrate is reduced to NO by ferrous iron:

\[ \text{NO}_3^- + 4\text{H}^+ + 3\text{Fe}^{2+} \rightarrow 3\text{Fe}^{3+} + 2\text{H}_2\text{O} + \text{NO} \] (2)

The reaction requires a Fe³⁺/NO₃⁻ ratio in excess of 3 to drive the reaction to completion. The depletion of protons by reaction (2) results in conditions favourable to hydrogen jarosite formation at 160° - 180°C. Nitrate concentrations were reduced within 10 minutes to 0.5 g/liter or less, from 10 g/liter NO₃⁻ in the feed solution.

The earlier process proposal [6] also makes a number of important points on nitrate hydrometallurgy. Since "N₂O⁵⁺", the precursor of HNO₃, can reduce to either NO₂ or NO, it is important to maximize the latter through choice of proper process conditions. Formation of NO₂ instead of NO requires three times the amount of nitric acid to be added and regenerated. Fig. 5-5 gives the ratio of NO:NO₂ being formed in the oxidation of a chalcopyrite concentrate.

The NSL Process description ends with an economic evaluation, which favours the process over flash smelting in plants handling less than 45,400 tonnes copper per year. The economics of scale go to pyrometallurgy!

The authors [7] make a more fundamental point, namely that a hydrometallurgical process treating chalcopyrite requires more energy that equivalent pyrometallurgical ones. This is largely due to the additional energy required for the electrowinning, rather than electrorefining of copper. The only way this very significant handicap for hydrometallurgical processes can be overcome is in the chloride process, where electrowinning of cuprous chloride requires much less energy than the same operation in the sulphate system.

Finally, the authors [7] make the point that the presence of some pyrite in the process feed is desirable since the sulphuric acid generated by its oxidation is needed for solubilizing non-copper minerals and to supply sulphate for the jarosite precipitation. Too much pyrite, however, increases the operating costs due to the increased oxidation of sulphur and iron, without the offsets of copper production.
5.3. Discussion of the NSL Process.

The first question which should be answered in a discussion of nitric acid assisted processing of chalcopyrite is: "Why nitric acid?", or more generally "Why the nitrate system?". From discussions with Kennecott personnel it is clear to the author that the process designers were aware of the low cost oxygen units nitric acid can provide for sulphide oxidation. But this is only true for regeneration with air; and it is interesting to note that the early and latest process proposal utilized gaseous oxygen instead of air [9].

There is no copper electrowinning technology for nitrate solutions, which means a solvent extraction or a nitrate removal step is required. Copper nitrate is not complexed, hence the SX step must be proton driven. For the protons generated in electrowinning to pass into the oxidative leach, it must have a lower acidity than the copper electrolyte. This is inconsistent with nitric acid oxidation, unless externally produced sulphuric acid is consumed, or the solution is concentrated by evaporation.

Regarding nitrate removal, it requires raising the leach filtrate to 150°C - 180°C to drive the reaction with ferrous iron to completion; this is energy intensive since the copper pickup is only 30 g/liter. The author would like to suggest consideration of the use of separate (auriferous?) pyrite in stage I of the oxidation to drive the nitrate down to less than 0.5 g/liter and eliminate the nitrate removal operation from the flowsheet.

Speculating in a more general sense, it appears that advantage could be taken in special situations of the difference in reactivity of various minerals. For instance, a low grade mixed chalcopyrite/pyrite concentrate could be upgraded to smelter acceptance by nitric acid treatment. The same would hold for a chalcopyrite/sphalerite mixed concentrate. Other examples come readily to mind.

The rationale behind these suggestions is to prevent dissolution of copper, to use the hydrometallurgical treatment as a mineral upgrading step (such as the chalcopyrite removal from molybdenite, as practiced by Brenda Mines, British Columbia) rather than a metal winning step.

Returning to the NSL Process, it appears that it achieved most of the objectives set out for it, i.e. solubilize all of the copper, precipitate all of the iron and consume all of the nitrate. It could not alter the oxidation mechanism(s) to produce only sulphur. However, in meeting these three objectives, copper sulphate electrowinning, a lower pickup of copper per pass through four solid/liquid separation stages and extra concentrate grinding had to be adopted. In its favour, the NSL Process included a molybdenum, selenium and precious metals recovery option, indicated a means for zinc recovery and separated the gypsum precipitation step from the circulating electrolyte. It did not achieve low cost iron removal, although copper losses with a jarosite are much lower than with goethite.

In summary, the Kennecott/DuPont effort was a very valuable one for hydrometallurgy in general, and for the nitrate system in particular. Efforts were made by the Kennecott team to lower the capital costs and improve process efficiency. They proposed to return to O2 injection in the leach tanks and to adopt air sparging in the electrowinning tanks [9]. It is not clear that these measures would have been sufficient for the NSL Process to compete with flash smelting/converting plus electrowinning.

In summary, the author's opinion that nitric acid oxidation of minerals will find application in special situations and with complex mineral suites; the route is not recommended for copper electrowinning from "clean" chalcopyrite concentrates.
References

3. Personal communication

6. Recovery of HCl by Thermal Hydrolysis of Metal Chlorides.

6.1 Reactions and Equilibria.

Most base metal chlorides will react with water to yield the corresponding metal oxides and hydrogen chloride. Rather than define the term base metals, for the purpose of this chapter it includes the elements shown in Fig. 6-1, with the exception of calcium. Some metal chlorides will hydrolyze at room temperature in the vapour phase (SiCl₄, TiCl₄) or in solution (AlCl₃, FeCl₃). In the vapour the degree of hydrolysis depends on the H₂O concentration and in solution it depends on the HCl concentration, or pH.

Fig. 6-1. Vapour pressure of selected metal chlorides as a function of temperature [1].
At elevated temperature, all base metal chlorides will react with water, according to the following equilibrium:

\[ \text{MeCl}_n + \frac{1}{2}n\text{H}_2\text{O} \rightarrow \text{MeO} + n\text{HCl} \quad (1) \]

At least three of the four species in this equilibrium may have an appreciable vapour pressure, hence the following relationship needs to be considered for a total system pressure of one atmosphere:

\[ p^*\text{HCl} = K \frac{p\text{MeCl}_n \cdot p\text{H}_2\text{O}^{1/2}}{p\text{H}_2\text{O}} \]

For a fixed value of K, i.e. a given metal chloride and a given temperature, reaction (1) will move to the right the lower the vapour pressure of HCl and the higher the vapour pressure of H\(_2\)O. This implies that industrial systems feeding metal chloride solutions, rather than crystals, will achieve more complete hydrolysis, all other conditions being equal.

The thermodynamics of equilibrium (1) for nickel chloride have been described by Jha [2] and are given in Figure (6-2). With increasing temperature, the equilibrium shifts to the right and at 850°C, the standard free energy change for the reaction is about -6 Kcal per g-mole of NiCl\(_2\). Jha calculated that for pyrohydrolysis of a 45 wt% NiCl\(_2\) solution at 850°C, a 97% conversion at equilibrium could be expected with 9 moles of water present for every mole of nickel chloride. At the same value of K (15) it can be calculated that a 85.6% conversion at equilibrium can be expected with 2.2 moles of water present per mole of nickel chloride. This represents the pyrohydrolysis of NiCl\(_2\) : H\(_2\)O crystals as practiced in the Falconbridge Matte Leach Plant [3].

While the difference in percent conversion is significant, the effect of solid vs. solution feed is overshadowed by other effects, namely the pyrohydrolysis temperature and the standard free energy of reaction. Let’s first discuss the temperature effect as it relates to the standard free energy. Figure 6-2 indicates a zero standard free energy for the hydrolysis of nickel chloride at approximately 1000°K or 700°C. Depending on HCl and H\(_2\)O vapour concentrations, nickel oxide particles in the gas phase can convert to NiCl\(_2\) at that temperature. Further study of Figure 6-2 shows that at 700°C the vapour pressure of NiCl\(_2\) is substantially less than at 850°C and also less than the equilibrium pressure at 700°C. This means that nickel oxide dust produced at equilibrium at 850°C can revert to gaseous nickel chloride at 700°C, and condense as solid nickel chloride from the gas phase, preferentially on colder surfaces in the off gas system. In pilot plant trials of the ML Plant process, such chloride was found to condense as plate-like crystals, and resembled exfoliated vermiculite or mica in consistency. This inclination to produce gas duct "thrombosis" was the reason that cyclones were not incorporated in the Falconbridge ML Plant [3]. The reversal of the hydrolysis reaction and condensation of NiCl\(_2\) was clearly observed on the walls of the gas duct connecting the pyrohydrolyzer and the off gas cooling tower in the ML Plant. In fact the "gooseneck" gas duct between the pyrohydrolyzer and cooling tower had to be replaced with a spare every three months for this reason. This was easy, since the duct was placed loose in NiO calcine seals.

The hydrolysis temperature is very significant and its choice needs to be carefully considered. In the later work on pyrohydrolysis of nickel chloride solutions by Jha et al. [2], it was found possible after a number of trials to operate a cyclone on the reactor off gases. That cyclone was well insulated and operated above 700°C. Due to plugging, it would not operate with the conical bottom normally present on gas cyclones, requiring a large gate valve and dust collection bin. This leaves the question of scaling-up such a configuration. However, the fact that a cyclone could be made to work is probably due to the much higher water vapour content of the gases in case of NiCl\(_2\) solution pyrohydrolysis. The \( p^*\text{HCl} / p\text{H}_2\text{O} \) ratio for the equilibrium K value is 0.22 for NiCl\(_2\) solution and 23.2 for NiCl\(_2\) : H\(_2\)O crystals; a difference of two orders of magnitude.

The standard free energy of the hydrolysis reaction can be significantly effected by valency changes. At pyrohydrolysis conditions nickel oxide is known to be single valent and has only a small value for AG. Cobalt resembles nickel in many ways, but it can form a higher oxide. Jedlicka [4] has calculated the limits of existence in an atmosphere of 50 vol% H\(_2\)O, 5 vol% HCl and 5 vol% O\(_2\) and 40 vol% N\(_2\) for

\[ 3\text{CoCl}_2 + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + 6\text{HCl} \quad (1) \]

\[ 3\text{CoCl}_2 + 3\text{H}_2\text{O} \rightarrow \text{Co}_3\text{O}_4 + 6\text{HCl} \quad (2) \]
The significant shift in the equilibrium due to the formation of higher oxides is apparent from the temperatures noted above the reaction signs. Under the conditions specified, CoO will not be formed below 872°C, whereas Co₃O₄ can be formed down to 460°C. Below 460°C, CoCl₂ is stable. The most notable example of this effect is manganese chloride for which the following reactions and equilibrium temperatures are given [4]:

\[
\begin{align*}
\text{6 MnCl}_2 + 6\text{H}_2\text{O} + 3\text{O}_2 & \quad \text{---} \quad 6\text{MnO}_2 + 12\text{HCl} & \quad -176°C \\
\text{6 MnCl}_2 + 6\text{H}_2\text{O} + 1/2\text{O}_2 & \quad \text{---} \quad 3\text{Mn}_2\text{O}_3 + 12\text{HCl} & \quad 403°C \\
\text{6 MnCl}_2 + 6\text{H}_2\text{O} + \text{O}_2 & \quad \text{---} \quad 2(\text{p-Mn}_2\text{O}_3) + 12\text{HCl} & \quad 1077°C \\
\end{align*}
\]

These equations represent the thermodynamic equilibria, not the kinetics of the reactions. Decomposition of MnCl₂ would not occur at -176°C and therefore MnO₂ cannot be formed by "pyro"hydrolysis of MnCl₂.

Industrially, it is ferrous chloride pyrohydrolysis that has benefitted most from iron's capability to form higher oxides than FeO. By maintaining relatively high oxygen concentrations in the reactor, FeO₂ is formed, and FeCl₃ can be hydrolyzed at rather modest reactor temperatures and at fast reaction rates. It is because of this incremental free energy change due to the higher valency that the spray roaster is feasible for the processing of steel pickle liquors. Spray roasters operate with a temperature gradient. Both the off gases and the oxide product leave the reactor at lower temperature than is maintained in the hydrolysis zone, unlike the fluidized bed reactor. Put another way, the spray roaster requires a larger standard free energy change for the hydrolysis reaction. This is the main reason that there has been no pyrohydrolysis of FeCl₃. However, this year a spray roaster has started operation on FeCl₃. It is situated in Pecs, Hungary and produces Fe₂O₃ and 30 wt% HCl [5]. It will be interesting to note from the technical description how the problems of small free energy change and high FeCl₃ vapour pressure have been overcome. Others have also claimed to have successfully piloted FeCl₃ pyrohydrolysis [6], but no details have been released.

The presence of oxygen in the gas phase introduces a further consideration, involving the equilibrium between HCl and Cl₂:

\[
2\text{Cl}_2 + 2\text{H}_2\text{O} \quad \text{---} \quad 4\text{HCl} + \text{O}_2 
\]  

Some values for the enthalpy and free energy changes and the equilibrium constant are given in Table I [7].
Table I: Thermodynamic values of HCl oxidation.

<table>
<thead>
<tr>
<th>T *K.</th>
<th>ΔH (g.-cal.)</th>
<th>ΔG°/T (g.-cal/deg.)</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.16</td>
<td>27,345</td>
<td>60.809</td>
<td>13.290</td>
</tr>
<tr>
<td>400</td>
<td>27,566</td>
<td>63.763</td>
<td>8.166</td>
</tr>
<tr>
<td>600</td>
<td>27,838</td>
<td>14.277</td>
<td>3.120</td>
</tr>
<tr>
<td>700</td>
<td>27,926</td>
<td>7.635</td>
<td>1.669</td>
</tr>
<tr>
<td>800</td>
<td>28,008</td>
<td>2.632</td>
<td>0.575</td>
</tr>
<tr>
<td>900</td>
<td>28,094</td>
<td>-1.275</td>
<td>-0.279</td>
</tr>
<tr>
<td>1000</td>
<td>28,181</td>
<td>-4.413</td>
<td>-0.965</td>
</tr>
<tr>
<td>1100</td>
<td>28,283</td>
<td>-6.989</td>
<td>-1.527</td>
</tr>
<tr>
<td>1200</td>
<td>28,386</td>
<td>-9.141</td>
<td>-1.998</td>
</tr>
<tr>
<td>1500</td>
<td>28,792</td>
<td>-15.124</td>
<td>-3.305</td>
</tr>
</tbody>
</table>

In the above table, at atmospheric pressure,  

$$K = \frac{(n_{H_2}O)^2 (n_{Cl_2})^2}{(n_{HCl})^4 (n_{O_2})}$$

where $n_{H_2}O$, $n_{Cl_2}$ etc. are the number of moles of each species in the system, $E_n$ is the total number of moles including inert gases and $T$ the total pressure in atm. It can be calculated that even for 90% stoichiometric combustion, under normal ML plant pyrohydrolysis conditions the equilibrium allows over 0.5 vol % Cl₂ in the off gases. Ingress of cold air quickly increases this to 1.0 vol % Cl₂ and 5% O₂ at 750°C. These calculations are confirmed by plant measurements.

Since nickel is essentially monovalent in strong chloride solutions, there is no capture of chlorine in the off gas system as there is in the ferrous chloride system, for instance:

$$2 \text{FeCl}_2 + \text{Cl}_2 \rightarrow 2 \text{FeCl}_3 \quad (9)$$

Pyrohydrolysis of solid nickel chloride requires a temperature over 800°C to drive the reaction, and should therefore be carried out without oxygen in the reactor gas to prevent chlorine formation. This could be done by providing indirect heat to the reactor, through its walls for instance, or by preheating an inert fluidizing gas such as steam or nitrogen. The amount of heat required for the reaction makes such suggestions impracticable. Only the direct combustion of fuel in the reactor to evaporate water, to bring the reaction products to the appropriate temperature and to provide the (negative) heat of reaction can be considered for a technical system.

This raises another limitation of the system for nickel chloride hydrolysis. The fluid bed reactor will be filled with the reaction product, i.e. the nickel oxide. At 850°C the ΔG for reaction (9) is negative.

$$\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O} \quad (10)$$

Any trace of hydrogen or other reducing agent will form metallic nickel with disastrous effects on the fluidized nature of nickel oxide. The problems of fluid bed reduction with metal oxides are well known and these problems are greatly magnified by the presence of volatile chlorides (which also can be reduced to metal at NiCl₂ pyrohydrolysis conditions). Jha et al. [2] discuss the problems they experienced with agglomeration of nickel oxide, erratic fluidization and eventual defluidization, due to bed calcine reduction to metallic nickel.

The challenge of the complete pyrohydrolysis of solid nickel chloride is therefore defined as creating a reaction environment at the lowest temperature at which the hydrolysis reaction will still proceed reasonably completely with the minimum amount of oxygen in the off gas consistent with complete combustion of the fuel. As discussed, such a system cannot be provided by a spray roaster, which normally operates with temperature gradients between the spray nozzles, the burner and the discharge ports.

6.2 Technical Application of Chloride Pyrohydrolysis.

While most chlorides can be hydrolyzed, with the exception of the alkali and earth alkali metals, technically the emphasis has been on ferrous, cobalt, magnesium, aluminum and nickel chlorides. Ruthner and Ruthner [8] offer the following (abbreviated) account of pyrohydrolysis development for pickle liquor:

"Until the early 1950's, sulfuric acid pickling was the standard descaling operation for hot rolled steel products. The disposal of waste pickle liquor was considered a severe environmental problem for which no satisfactory solution existed. In 1952, the steel mill action committee, a subcommittee of the Ohio River Valley Water Sanitation Commission initiated a pilot plant program to make use of a double-cycle acid regeneration process proposed by Blaw-Knox and Ruthner."
It soon became evident that it was not desirable to offer a highly sophisticated chemical process to the steel industry for the regeneration of waste pickle liquor which is very sensitive as far as plant operation was concerned. Therefore, the steel industry was convinced to switch from sulfuric acid pickling to hydrochloric acid pickling.

The first hydrochloric acid regeneration unit had been built in Europe in 1955 and put into operation at a small cold mill. The process was based on precipitation and decomposition of hydrous ferrous chloride (FeCl$_2$.4H$_2$O) into iron oxide and hydrochloric acid in an indirectly heated furnace. The indirect heated furnace had the disadvantage of relatively low efficiency and consequently, higher energy requirements. Although several plants had been built, the process was not ready to operate under steel mill conditions. Further investigations to replace the indirect heated furnace led to the development of cocurrent and countercurrent spray roasters.

Spray roasting had been proposed several times in the past. One of the early countercurrent spray roasters was proposed in a patent assigned to Lurgi in 1936.

Lurgi had to make a decision in 1936 whether to develop the spray roasting or the fluidized bed technology. Probably for reasons of wider applications (e.g. roasting of pyrites) and for reactions which need a longer retention time, Lurgi favored the fluidized bed process.

Ruthner has the spray roasting process. Today, more than 85% of 200 operating hydrochloric acid regeneration units have been developed and designed by these two companies.

Theoretically, pyrohydrolysis can be achieved in a number of equipment configurations, as discussed for nickel chloride in the preceding section. In industrial practice the choice is between a spray roaster or a fluidized, or fluid bed reactor. The former is schematically given here as Fig 6-3. In a fluid bed reactor the process gases are evenly distributed through the reactor floor, or hearth, and rise upward through the reaction product. This induces fluidization, which makes the solids act, as the name implies, as a fluid. One consequence is very good mixing of the product in the reactor, resulting in very homogeneous bed temperatures. Fines from the bed can be carried upwards in the gas stream, and most fluid bed reactors are equipped with expanded top sections, or "freeboards", to lower the upward gas velocity and disengage fines. Further fines disengagement can be achieved in cyclones, settling chambers and the like. Unless a feed slurry is dispersed in the freeboard, the entire fluid bed reactor (bed and freeboard) will be operating at approximately the same temperature. A sketch of the Falconbridge fluid bed pyrohydrolyzer is given in this chapter as Fig. 6-14.

Spray roasters for pyrohydrolysis operate differently. A combustion zone is maintained in the middle section by tangential burners mounted in the side walls. The combustion gases change direction from horizontal to vertical. The metal chloride solution or slurry is sprayed down into the combustion zone. The oxide product proceeds downward and is collected in the bottom section, normally conically in shape. Since there is no gas outlet in the bottom, the gas phase will consist of the reaction products of the pyrohydrolysis. Should the oxide product cool prior to discharge,
reversion of the reaction can occur. This can be overcome by allowing a small amount of air or inert gas to enter the collection zone, displacing the gaseous reaction products upwards. Since spray roasting of droplets of metal chloride solution or slurry produces a finely divided oxide product in the form of hollow spheres, without the agglomeration achievable in the fluid bed reactor, gas velocities in the spray roaster top section need to be low to retain the bulk of the product. This makes spray roasters by definition larger, with attendant capital costs.

Regeneration of hydrochloric acid was the technical attraction of pyrohydrolysis for the steel industry in the 1950's and still is at the present time. The same holds for the extractive metals industry as earlier outlined in the definition for "Hydrometallurgy". Put in another way, the leaching system producing the metal chlorides must be capable of operating on the hydrochloric acid produced by pyrohydrolysis. This eliminates chlorides such as TiCl4. It cannot be produced in a hydrous environment since the reaction:

\[
\text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl}
\]  

(11)

proceeds to the right, even at room temperature. The oxide product must be an attractive article of commerce. This would eliminate metals such as zinc, where conversion of chloride to oxide is difficult due to the high vapour pressure of zinc chloride and the zinc oxide product has tight specifications. The metal chloride should have limited volatility, otherwise its oxide will not be retained efficiently as the product. In that regard, it is the author's opinion that good separations could be achieved by pyrohydrolysis between volatile chlorides such as ZnCl2, HgCl2, SbCl3, AsCl3 and low vapour pressure chlorides such as FeCl3, MnCl2, NiCl2, CoCl2 and MgCl.

The commercial value of the oxides is very important in justifying an HCl regeneration system. It is in this area that the spray roasting system has established a decided advantage over fluid bed pyrohydrolysis, especially for ferrous and magnesium chlorides. The fine iron oxide product after further processing is now competing with upgraded natural iron ores for applications such as in ceramic magnets (hard ferrites), and with synthetic ferric oxides for the soft ferrite market. Soft ferrites are used within the electronic component industry. Spray roaster oxide quality has improved over the years to an extent that the product may command up to $250 per ton vs $80 per ton for other regenerated iron oxides. This has a significant effect on the economics of HCl regeneration for steel pickling.

A schematic flow diagram for the production of metal oxides is given as Fig 6-4.

**Fig. 6-4: Flow diagram for azeotropic HCl circuit [6].**

6.3. **Falconbridge Matte Leach Plant.**

6.3.1 **General.**

The Falconbridge Matte Leach Plant (MLP) has been described in general terms [3]. Its solvent extraction operation has been the subject of an additional article [10]. The flow sheet for the MLP is given as Fig. 6-5. The pyrohydrolyzer has never been described in detail.

The Falconbridge Matte Leach Plant required hydrolysis of nickel chloride crystals, to produce superazeotropic acid needed to drive the leach of matte to completion. A fluidized bed was therefore the logical choice, permitting a uniform temperature throughout the reactor and efficient combustion of the fuel at low oxygen content in the off gas. Bench scale test work was started in 1963, and an extension of the Falconbridge Matte Leach Pilot Plant at Kristiansand-S, Norway was built and operated from 1964-1967, resulting in the construction of a commercial Matte Leach Plant at the same location. That plant operated from 1968 to 1983 and
produced close to 100,000 tonnes of granular nickel oxide by pyrohydrolysis. The nickel oxide was kiln reduced to "granular nickel", a photograph of which can be found as Fig. 6-10 opposite page 94.

Dissolution of the nickel components of the matte, i.e. NiS2 and Ni/Cu metallics, resulted in production of a leach gas, consisting of approximately one mole of hydrogen for every mole of H2S:

\[ \text{NiS}_2 + 6\text{HCl} \rightarrow 3\text{NiCl}_2 + \text{H}_2 + 2\text{H}_2\text{S} \]  (12)

\[ \text{Ni} + 2\text{HCl} \rightarrow \text{NiCl}_2 + \text{H}_2 \]  (13)

Since the leach liquor was saturated with this diluted H2S, the redox potential in the system was fixed, allowing very good separation of nickel against copper and platinum group metals, even at high HCl activities.

Unlike nickel, the majority of the matte impurities formed anionic complexes in the highly acidic pregnant solution and solvent extraction or anion exchange removed such impurities without prior acid neutralization. This set the stage for maintaining a high HCl concentration throughout the entire MLP circuit.

One of the peculiarities of the HCl - H2O system is that it forms a azeotrope at 20 wt% HCl, or approximately 205g HCl/litre depending on the NiCl2 concentration. This requires an immediate decision by the extractive metallurgist designing a process involving HCl recovery. Will the system be sub- or super-azeotropic? Sub-azeotropic HCl systems are much easier to operate, since the equilibrium in the HCl absorbers is between the azeotrope and water. The latter can be discarded to maintain the water balance of the system.

Where super azeotropic acid is required for leaching, as it was in the MLP, the equilibrium in the absorption system is between azeotrope and HCl gas. Neither can be discarded and any water entering the system will be trapped in the process solutions, driving the system towards the lowest common denominator, i.e. the azeotrope. Control of the water balance is therefore crucial in super-azeotropic systems and some means of water elimination from such systems must be incorporated.

6.3.2 ML Plant Feed Preparation.

In the MLP this was elegantly provided by using the HCl gas to salt out NiCl2.4H2O crystals from SX purified leach liquor. For every mole of nickel, approximately four moles of water were thus removed from the leach circuit. This depended somewhat on the crystallizer conditions, and some NiCl2.2H2O crystals may have been formed. For NiCl2.4H2O the water content is...
35.7 wt%, whereas ML Plant crystals averaged 32.5 wt%. Subsequent dehydration of these crystals in rotary "dryers" reduced their water content from 32.5% to 10 - 12%, eliminating water from the system as dilute water vapour. In effect, the dryer off gas system operated as a separate sub-azeotropic system in the MLP, since some free HCl adhered to the crystals and a very minor amount of hydrolysis of nickel chloride occurred in the burner section of the rotary dryer. Approximately three of the four moles of crystal water were removed, allowing the following reaction in the subsequent pyrohydrolysis unit:

$$\text{NiCl}_2 + \text{H}_2\text{O} \rightarrow \text{NiO} + 2\text{HCl}$$  \hspace{1cm} (14) \Delta H = + 39.2 \text{ Kcal/mole}

With NiCl$_2$•H$_2$O feed, the only other water for the pyrohydrolysis came from the hydrocarbon fuel combusted in the fluid bed to provide the heat required. HCl absorption from these off gases allowed a super-azeotropic acid to be produced, thus maintaining the acid and water balances in the plant. The rotary dryer was normally fired with kerosene, but could be operated on naphtha depending on fuel prices. The exit temperature was maintained at 175° - 180°C to produce the required degree of crystal water elimination. Although equipped with two cyclones in series, over 90% of the product was discharged directly from the dryer. Off gases passed through an adiabatic absorber, fed with 1.25 m$^3$/h of the dilute plant solution from filters and spills and producing 0.9 m$^3$/hour of 100 g/l HCl, 50 g/l Ni$^{++}$ solution. The stack gases at 80°C contained <50 ppm HCl. The figures given for process flows in this chapter refer to operating conditions defined in section 6.3.10.

6.3.3 ML Plant Pyrohydrolyzer Fuel/Air System.

As discussed earlier, for nickel chloride pyrohydrolysis it is paramount to obtain as complete combustion of the fuel, i.e. as close as complete removal of the oxygen from the combustion air, as possible. Since the heat release from combustion should occur in the fluid bed reactor, it follows that a mixture of air and fuel needs to be admitted through each of many tuyeres positioned in the hearth of the fluid bed. To attempt to individually mix air and fuel for each tuyere was ruled out early in the development; it would have required too complex a monitoring system for large scale, solid nickel chloride pyrohydrolysis. Combustion of the fuel and air prior to the passage of the gases through the tuyeres was also ruled out; the problems with tuyere construction and gas pressure drops were judged insurmountable.

At this point it may be of interest to note that an analogous system for the pyrohydrolysis of ferrous chloride (pickle liquor) was developed by Lurgi combustion at approximately the same time. Their system is based on fuel injection through each individual tuyere, thereby characterizing that system by large, widely spaced tuyeres. It is not likely such a system would have been successful for the pyrohydrolysis of solid nickel chloride, due to its inability to lift the heavy calcine off the hearth, and the complexity of stoichiometric control.

In designing a hearth for a NiCl$_2$ pyrohydrolyzer, for the supply of a non-combusted fuel/air mixture to the bed through each individual tuyere it was essential to prevent ignition of the gas mixture in the manifold - at least most of the time. The tuyere pipe diameter was selected to give an upward gas velocity under normal operating conditions to be in excess of the flame propagation velocity for naphtha/air. In other words, should the mixture ignite in a tuyere, the flame would literally be blown out of that tuyere under normal operating conditions. Flame propagation is influenced by geometry, stoichiometry pressure and nature of the fuel. A number of measured results for methane/air mixtures are presented in Fig 6-6 [11].

This information postdates the design of the pilot pyrohydrolyzer by many years, although general information on flame propagation was available. It was simply decided for the gas velocity in the tuyeres to be sufficiently far in excess of flame propagation velocity to allow for unknowns such as geometry, heat conduction, residuals in the fuel, etc. Under normal conditions gas velocity in the tuyeres was approximately 10 meters per second, approx. 50 times larger than the flame propagation. The gas velocity through the four 4 mm diameter tuyere outlets was approx. 55 meters per second.

Gaseous fuels allow the simplest and most homogeneous mixing with air. The supply of premixed natural gas and air to a ferrous chloride pilot pyrohydrolyzer, described in Part Two, never resulted in any problems. In the early bench scale work propane/air mixtures were used for pyrohydrolysis of nickel chloride, resulting in a number of defluidizations through metallic nickel formation, due to improper propane/air mixing.
The Kristiansand-S, Norway, location, where the Falconbridge Nickel Refinery has been located since 1928, has no access to natural gas. The Refinery had access to low cost naphtha in the early 1960's and it was decided to base the pilot operation on the use of this type of fuel. This immediately raised a number of challenges, to do with preparing a homogeneous fuel/air mixture.

Naphtha has a vaporization temperature range of 45°C (IBP) to 75°C (FBP), and a heat of vaporization of 80 kcal/kg. It also has a self ignition temperature of 260°C when mixed with air at a stoichiometric ratio. In order to achieve complete evaporation, necessary to achieve complete mixing of the vaporized naphtha and air, the air would have to be preheated to 100°C prior to the evaporation chamber. This posed no problem in the MLP. Since compressed air was used for fluidization of the nickel oxide bed of the pyrohydrolyzer, the air was discharged from the rotary compressor at 150-155°C and entered the ML Plant at 140°C, sufficient for naphtha vaporization, but also sufficiently divergent from the self ignition temperature of the naphtha/air mixture. An adjustable mixing chamber, schematically shown in Fig. 6-7, was designed to meet these requirements. It was located adjacent to the pyrohydrolyzer manifold, to minimize the amount of naphtha/air mixture contained in the operating equipment.

The system was also designed for the use of propane instead of naphtha, in case of supply problems or price advantage. In the 15 years of operation the two MLP pyrohydrolyzers have mainly operated on naphtha, however, and this text refers exclusively to the latter fuel. In those 15 years the mixing chambers have performed well; there has been no instance of bed defluidization due to incomplete mixing. Formation of metallic nickel and defluidization occurred twice, once due to faulty fuel control (propane injected in addition to naphtha due to a leaking valve), and once due to residuals (vegetable oil) in the naphtha.

Complete mixing of fuel and air was only one requirement; the other was to maintain as close to a stoichiometric combustion mixture, on the excess air side, as possible. This was achieved by instrumentation and process control. The air flow was measured with venturi discs in the main supply duct, and in a smaller bypass. Control of the air flow into the pyrohydrolyzer was achieved manually by means of a valve in the bypass line, through which approximately 10% of the 4300 Nm³/hour primary fluidizing air flowed. The venturi discs were calibrated each startup of a pyrohydrolyzer campaign.

The naphtha/air mixture then flowed at 90-95°C into the gas manifold of the MLP pyrohydrolyzer. The manifold consisted of a U shaped, 207 mm I.D. pipe, with 13 pipes of 51 mm I.D. placed at 260 mm intervals linking the two arms of the U. Approximately 430 tuyeres were mounted on top of the 13 crosslink pipes, at 75 mm spacing, in such a way as to conform to the circular cross section of the pyrohydrolyzer. This required 12 tuyeres on the outer crosslink pipes and as many as 41 tuyeres on the centre ones. A section of the hearth construction is shown in Fig. 6-8.
Fig. 6-7

Fig. 6-8. Details of pyrohydrolyzer hearth construction and tuyere cross section.

Under these conditions it was not possible to maintain the flow velocity of the naphtha/air mixture in the manifold above the flame propagation speed. That would have required a substantial pressure drop through the manifold and uneven delivery of the naphtha/air mixture to the various tuyeres - a manifold pipe with 41 tuyeres would get less volume than a manifold pipe with 12 tuyeres. Instead, it was decided to take the pressure drop over the tuyeres and protect the manifold from inadvertent naphtha/air explosions through the installation of graphite blowout discs at the end of each arm of the U shaped main header. Graphite was selected for these 35 mm thick discs, to ensure their safety performance would not be effected by any inadvertent
corrosion. The discs were designed to rupture at 4 bar, which was slightly above the highest possible working pressure in the manifold.

The graphite discs served their purpose well. When manifold ignition occurred, the sudden increase in pressure broke the graphite disc(s), normally with a loud "bang", referred to by the plant operators as a "backfire". In early operation, pieces of the graphite disc would be blown for a considerable distance and once even shattered several windows. This led to the installation of expanded metal cages at the end of the manifold where the graphite discs were installed, which solved the problem of flying graphite. The abruptness of disc failure and the accompanying "bang" strongly indicates the occurrence of a shock wave in the manifold rather than a flame front. Gas velocities in explosions far exceed those in flame fronts and release far more mechanical energy. It is suggested that once a flame front had passed into the manifold, flame propagation accelerated to far higher speeds than those given for flame propagation. This suggestion is supported by recent work measuring flame acceleration in a partially obstructed, but still open ended tube on propane-air mixtures [12]. Although the work was done in a different geometry than the ML Plant pyrohydrolyzer manifold, the results are very relevant and one of the figures is reproduced here as Fig. 6-9. Terminal flame speeds of 800 m/second were measured for stoichiometric air/propane mixtures, with blast pressures of 8 bar 10 meters from the exit of the open ended tube.

The lesson of these experiences in designing a mixed fuel/air supply system to a fluidized reactor is clear: be prepared for "back firing" and design in the proper safety features.

The 430 tuyeres consisted each of a 12.5 mm I.D., 150.5 mm long steel pipe connected gas tight to the manifold, passing up through a casing into the hemispherical, hinged bottom of the pyrohydrolyzer, passing through castable refractory, through high alumina fire brick and ending flush with the top surface of the fire brick in a special tuyere cap, shown in Fig. 6-8. This construction allowed the tuyeres to be withdrawn from the pyrohydrolyzer hearth.

During pilot plant trials it was found absolutely essential to weld the casing gastight to the hemispherical steel bottom. Due to expansion on heating or imperfect refractory casting, small cracks and channels would develop for the naphtha/air mixture to travel downward into the refractory instead of up into the bed and leak through the steel shell of the pyrohydrolyzer. Eventually the combustion front of these gases would reach the steel shell and create a hot spot. Making certain all 430 tuyeres were installed gas tight solved this problem. Weep holes for the castable refractory also needed to be welded shut after curing.

The design of the tuyere cap received a lot of attention, since it was at that location that the naphtha/air mixture was released in the bed of 850°C nickel oxide. Combustion presumably would be instantaneous, generating a lot of heat locally, heating up the cap to above the self-ignition temperature and igniting the mixture in the tuyere prior to its release to the bed. This could cause the flame front to move down the tuyere pipe, ignite the mixture in the manifold, blow the graphite discs and shut down the operation. Since it was impossible to observe or measure what was occurring near the tuyere caps a lot of safety features were designed into the pyrohydrolyzer hearth.

First of all, the caps were made of 18/8 stainless steel, which has a lower heat conductivity than carbon steel. The tuyeres were mounted as flush with the hearth as possible, consistent with the downward jets of air/naphtha gas, to reduce exposed surface (see Fig. 6-8).
It was also decided to take the principal pressure drop of the naphtha/air mixture over the tuyere cap, rather than at the bottom of the tuyere pipe. This would minimize "access" of a flame front into the tuyeres during surging of the fluidized bed. Surging was of real concern, since the fluidizing gas mixture was in fact lifting the weight of the nickel oxide bed. Estimated at 8.2 m³ volume, the weight of the bed was in excess of 30 tonnes. Surging or "sloshing" of this weight would be able to effect gas flow through individual tuyeres.

A further safeguard against "backfiring" was designed into the connection from manifold to tuyeres. This was a copper tube with an internal restriction to the gas flow. Both features were deliberate. Copper was chosen for its heat conductivity and ductility. As a pyrohydrolysis campaign progressed, certain tuyeres would malfunction for reasons discussed later. Reduced gas flow would allow the flame front to descent the tuyere, till it reached the tube restriction. The copper walls carried the heat away, sufficiently to prevent the flame front to "jump" the restriction. The ML Plant operators, on spotting a "hot" tuyere, would crimp the copper tubing and put that particular tuyere out of commission, thereby safeguarding the manifold and the continued pyrohydrolyzer operation. This was all done manually, with several hours, or shifts, being allowed for such safeguarding prior to backfiring. This particular feature of an external "flame arrester" in a copper tube probably contributed much to the excellent operational record of the ML Plant pyrohydrolyzers.

A final design feature was the top chamber of the tuyere, intended to direct the gas mixture into the inner cone of the top of the tuyere. Combined with a 120° turn in direction, the chamber was designed to maximize the cooling effect of the gas mixture on the most exposed part of the tuyere.

During the 15 year operation of the MLP, these design principles proved correct. No manifold gas explosions have been observed under normal operating conditions. In fact, overheating of the tuyeres did not occur, rather the opposite. On opening the pyrohydrolyzer during shutdowns, it was found that nickel oxide "caps" had deposited on the tuyeres (Fig. 6-11 shown opposite page 94). Polished sections of one such a cap are shown as Fig. 6-12 and 6-13. "Caps" formation indicates that the tuyeres were cooler than the calcine surrounding the tuyeres, and combustion occurred either away from the tuyeres, or calcine movement was sufficient to remove the heat generated by combustion. This observation is supported by another one, namely that the tuyeres were generally in excellent condition, even after two years of operation.

![Fig. 6-10: Granular nickel produced by kiln reduction from the pyrohydrolyzer nickel oxide calcine oversize.](image1)

![Fig. 6-11: Tuyere "cap", photographed sideways to show its geometry relative to the tuyere.](image2)
Fig. 6-12. Photomicrograph of the outer layer of the tuyere cap shown in Fig. 6-11. Magn. 30X

Fig. 6-13. Inner layer of same tuyere cap. Magn. 30X
Manifold gas ignition was observed a number of times during the 15 years operation of the MLP, especially in the beginning. Since such an ignition would effectively shut the ML Plant down, it was one of the main reasons a second, larger, standby pyrohydrolyzer was constructed. As often happens, once the standby unit was in place, the reason for it largely disappeared. Approx. one to two unscheduled shutdowns per year were experienced during the later years of ML Plant operation.

Why did the manifold gas ignite? It probably had to do with the partial blocking of one or more tuyeres, due to calcine blocking the tuyere outlets during a shutdown due to power outage. Alternatively, some bricks or accretions from the freeboard may have fallen into the bed, disturbing the fluidization pattern and causing tuyere overheating. From time to time fully open tuyeres were observed on shutdown. The original tuyere had melted back into the hearth brick. As stated before, this was exceptional.

Unscheduled shutdowns were not always due to backfiring. One occasion rust accumulated in the air/naphtha mixing chamber to block air flow. On another occasion it was a buildup of low volatile residuals (vegetable oil) in the naphtha. In the early years, it was loss of air due to power failure. This was overcome by installing a delayed power cutout on the rotary compressor.

In conclusion, the design of the necessary naphtha/air mixture delivery to a fluid bed pyrohydrolyzer for metal chlorides has been proven to be feasible, operable and safe. A hot spot detector for the hearth and slotted openings in the tuyeres, instead of circular ones, would be recommended.

6.3.4 ML Plant Pyrohydrolyzer Operation.

The ML Plant contained two hydrolyzers, of 3000 mm and 3400 mm hearth diameter, respectively. Each was equipped with a NiCl₂ • H₂O feed system, a fuel and air supply system, an off gas cooling system and an emergency scrubber. As explained, either the one or the other unit was operating. The description given here is for the larger unit, which handled most of the throughput. Except for hearth diameter and capacity, both units were virtually identical and operated in a similar manner.

A cross section of the #2 unit is presented in Fig. 6-14. The tall, expanded freeboard was designed to facilitate return of fine oxide dust to the bed prior to quenching the off gases in the cooling tower. As discussed earlier, operation of a gas cyclone was found to be impracticable. The pyrohydrolyzer was also equipped with wall openings to allow personnel access, a return calcine inlet above the bed and a hinged hearth. Not shown are the calcine outlet, thermocouples, sight glass, and preheat burner details.

Typical operation of #2 pyrohydrolyzer would involve the injection of 2500 kg/hour of nickel chloride at 10 - 12% contained crystal water into the 900 mm deep bed of nickel oxide at 850°C, through 12 injection points in the hearth. On the average 80% of the nickel in the feed would be retained in the bed as granular nickel oxide (% conversion). The balance would exit the reactor with the off gases and be caught in the off gas cooling tower circuit.

Deposition of the fresh nickel oxide occurred on the granular bed material, causing it to increase in particle size. In order to maintain the fluidized nature of the NiO bed material, approximately 1580 kg/hour were discharged, cooled and screened to give the following products:

<table>
<thead>
<tr>
<th>Final Product</th>
<th>Recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesh</td>
<td>mesh</td>
</tr>
<tr>
<td>+28 approx. 40%</td>
<td>+65 approx. 10%</td>
</tr>
<tr>
<td>+35 approx. 35%</td>
<td>+100 approx. 45%</td>
</tr>
<tr>
<td>+65 approx. 25%</td>
<td>-100 approx. 45%</td>
</tr>
<tr>
<td>weight 980 kg/h</td>
<td>weight 600 kg/h</td>
</tr>
</tbody>
</table>

The calcine recycle circuit was equipped with a small hammer mill, which was operated continuously on -65 mesh continuously screened calcine. A small stockpile of fines was also kept for standby purposes.

It has generally been assumed that the deposition of fresh nickel oxide occurs through a vapour deposition process. This is supported by the morphology of the calcine, in which an “onion” type structure can be discerned in polished thin sections [2]. The same structure is apparent in the accretions that were formed on cooler surfaces in the reactor, such as thermocouples and tuyere caps, as discussed earlier. The density of the calcine also provides a clue. The specific calcine density was 6.33 kg/dm³, or 93% of theoretical density, given as 6.80 kg/dm³ [13]. Bulk density was on the average 4.5 kg/dm³. Should deposition have occurred as in the pelletizing model, i.e. small NiO particles
agglomerate together, with hydrolyzing nickel chloride acting as the binder or "glue", the resulting calcine would have been much more porous, and would have shown an aggregate structure, as the tuyere cap.

Such a structure was never observed in the ML Plant calcine. However, during early bench scale testing, some experiments were carried out involving adding NaCl to the nickel chloride feed to be pyro- hydrolyzed. The NaCl was intended to and apparently did act as a "glue" for nickel oxide particles. These experiments produced a porous, green, framboidal calcine, compared to the dense, black and smoothly spherical ML Plant product. The NaCl also aggravated the accretion formation in the 10 cm diam. laboratory pyrohydrolyzer and its use in a commercial operation was rejected.

No systematic study of the effect of process variables on % retention of nickel in the bed was carried out in the MLP; this would have been very personnel intensive with a 30 tonne bed which took a day's production to replace. To get a reliable percent conversion would require to operate several days at steady conditions, know the pyrohydrolyzer and subsequent NiO reduction kiln and product packing inventories exactly, keep the dryer conditions steady to know the nickel content of the dried crystals, know the NiCl₂-H₂O inventory and control the particle size of the pyrohydrolyzer bed (since bed inventory was measured by pressure drop over the bed, a function of the bed's bulk density, a function again of particle size distribution).

Fig. 6-14: Cross section of the #2 pyrohydrolyzer unit in the Falconbridge Matte Leach Plant.
In the end, the operators came to rely on the circulating load of NiCl₂ through the crystallizer and dryer to maintain the water balance of the ML Plant and the incentive to improve the percent conversion was diminished. The lower the percent conversion, the easier it was to maintain the plant's water balance. During the 15 years of the ML Plant operation percent conversion fluctuated between 83% and 70%, with 80% as the average. In order of importance, the following operating conditions decreased the percent conversion:

1. Loss of feed points. As a campaign progressed, NiCl₂·H₂O feed points would be lost, for various reasons. This had the most dramatic effect on percent conversion.

2. Increased bed temperature (although a lower temperature would allow an overall higher feed rate, thereby negating the temperature effect on percent conversion in terms of MLP output.)

3. Shallow bed, which appears consistent with the effect of feed points — distribute the feed evenly and keep it in the bed.

4. Higher space velocity.

5. Coarser bed calcine. It is not clear whether this effect is related to lower surface area or less retention in the bed of the finer, lighter NiCl₂·H₂O.

6. Increased water content of the NiCl₂·H₂O. This is the most interesting observation since it provides a clue to the deposition mechanism. In fact, percent conversion is optimum at 10 wt% H₂O in the feed. With less water, the hydrolysis reaction is starved. But what happens with excess water? It should drive reaction (1) to the right. Possibly the reaction goes too fast, hydrolyzing NiCl₂ in the vapour phase, rather than on the surface of the bed particles. Are vaporized metal chlorides molecular or ionic? Is the calcine slightly cooler than the gas? Is radiation into the large freeboard beneficial?

As mentioned before, nickel oxide deposition occurred also on the colder surfaces in the reactor. This included the walls. After six months operation, the nickel oxide scale started about 1 meter above the bed, gradually increasing in thickness towards the hearth where it reached a maximum of 15 cm thickness 15 cm above the hearth. The scale then receded very sharply to nil at hearth level. It was normally very firmly attached to the wall and would only spill off with severe temperature drops in the hydrolyzer. These only occurred on long shutdowns (during which the calcine was removed from the unit to prevent tuyere plugging) or during clean outs. Since this involved dropping the hearth, cleanout of the pyrohydrolyzer required care to prevent personnel injuries. A piece of nickel oxide scale, 15 x 15 x 15 cm would weigh approximately 25 kg. Such a piece, when dislodged during a campaign could put a tuyere out of operation.

The gradual buildup of the scale can be seen from the polished sections given as Fig. 6-15 and 6-16. There is no indication that bed calcine was incorporated in the wall scale. The material was confirmed to be pure NiO. Electron probe analysis found no element other than nickel. X-ray diffraction using CaF₂ as a reference standard gave a (200) reflection at a 2.089±0.002 Å. This gives a unit cell edge of 4.178±0.004 Å while the value listed in the JCPDF reference file (Card #4-383) is 4.177 Å [13].

The pressure drop across the tuyeres and bed was approximately 0.45 bar. The drop over the tuyeres represented 0.15 bar and that over the bed 0.30 bar. The need for high pressure drop over the tuyeres was explained by the need for high gas velocities to prevent back firing. The pressure drop over the bed is high due to the high bulk density of the calcine. Other fluidized beds tend to operate with pressure drops of 0.1 bar. With its relatively coarse, heavy calcine of narrow size distribution, "burping" could routinely be observed on the surface of the fluidized bed. It is not known whether this was due to the periodic release every few seconds of a pocket of NiCl₂·H₂O feed being released from the 12 star feeders. The supply of nickel chloride feed to the pyrohydrolyzer was discontinuous. No serious effort was made to correlate the frequency of feeding NiCl₂·H₂O with other operating parameters. Pilot plant observations indicated a finite time for NiCl₂ sublimation at operating conditions; from this it was deduced that intermittent feeding would not be detrimental.

Operation of the pyrohydrolyzer was extremely simple. The feed rate of NiCl₂·H₂O was manually set to a rate determined by the availability of dried nickel chloride. Naphtha was then regulated to maintain the 850°C operating temperature, with a safety setting so as not to exceed 90% of the stoichiometric ratio of naphtha and primary fluidization air. Naphtha would not be fed to the pyrohydrolyzer at bed temperatures below 750°C. The pyrohydrolyzer had 12 feed points for NiCl₂·H₂O, evenly distributed over the hearth. These feed points replaced 12 regular tuyeres and were each fed by 50Nm³/hour of secondary air. Feed splitting occurred prior to the 12...
star feeders at the bottom of a two bin charging device on weight cells. The NiCl₂·H₂O discharge rate was plotted on a chart recorder and calculated by shift by the PDP 8 computer [14]. This entire feed system worked well, except for the occasional caking upon shutdown.

6.3.5 Calcine Discharge

The calcine discharge design had to meet a number of criteria. There could be no cold surfaces protruding into the reactor and the calcine had to provide a safe seal for air/fuel and for NiCl₂ or HCl vapour leakage against the 0.3 atm hearth gas pressure. The outlet had to allow for the odd NiO accretion to be passed and a discharge control mechanism had to be incorporated. These criteria were met by providing a 200 mm diameter outlet on the hearth periphery at a 45° angle, leading to a vertical standpipe of the same diameter. This provided for approximately a 2200 mm calcine column, which was sufficient for the sealing requirements. The standpipe ended in one side of a half cylinder rocking shoe, which discharged calcine on its down stroke into a 800 mm diameter, 5500 mm long rotary calcine cooler. Stroke frequency controlled the calcine discharge rate from the reactor.

6.3.6 Off Gas Quenching, Gas Cleaning and Suction Control

The pyrohydrolyzer gas handling system, prior to HCl recovery, served the following purposes. It had to quench the gases, it had to clean the gas from particulates and it had to control the gas pressure in the reactor freeboard at a slightly negative level, to prevent off gas leakage into the plant environment.

In the ML Plant, gas quenching was carried out in a cooling tower with purified leach liquor, prior to NiCl₂·4H₂O crystallization. Since the off gas composition was approximately 16 vol% HCl and 11 vol% H₂O, its mole ratio of HCl to H₂O was 1.45. Concentrated 30 vol% hydrochloric acid has a mole ratio of 0.164, which means that hot gas quenching with purified leach liquor could still evaporate water, without jeopardizing the ML Plant water and acid balance. The following compositions represent typical conditions for ML Plant operation:
Purified Leach Liquor
From Solvent Extraction

Ni^{2+}, g/l 120
HCl, g/l 165
Flow, m³/h 10.5

Cooling Tower Solution
To Crystallizer

Ni^{2+}, g/l 142
HCl, g/l 175
Flow, m³/h 11.0

The cooling tower consisted of a 7610 mm high, 2500 mm I.D. cylindrical vessel with a conical top and bottom, filled with 50 mm carbon Raschig rings for a height of 4500 mm. Its wall construction consisted of rubber lined steel, covered with acid resistant brick - the standard ML Plant design for severe service conditions. The conical top section was outfitted with 10 evenly spaced inlets to insure good distribution of the circulating solution. Flow rates were matched to the handling capacity of the tower packing. To quench the 850°C pyrohydrolyzer off gases, carrying approximately 250 kg/hour dust, a circulation rate of 180 m³/h solution sufficed. Except for extremely cold weather, no problems with crystal formation in the circuit occurred.

The cooling tower solution was passed from a 25 m³ pump tank through two tube and shell bottom fed graphite coolers in series before being returned to the top of the tower. Seawater was used as cooling medium. A pH analyzer in the seawater return line from the ML Plant served as sentinel against leakage, heat exchanger breakage, etc. It is estimated that none of the sensible heat in the pyrohydrolyzer off gases was used to evaporate process water, it was all removed by heat exchange. Twice in the life of the ML Plant was the tower destroyed by fire. Once crystallization on the inlet nozzles caused overheating of the Teflon pipe liners. In a more serious incident of circulating pump failure, the fact that the standby also failed was not registered properly and the entire tower was destroyed and had to be replaced.

While this arrangement was efficient for gas quenching, it was not very efficient in cleaning the gas from the ultra fine NiO dust carried over. Nor did it allow gas pressure control. These functions were combined in a piece of equipment which followed the cooling tower in the gas train and which was connected to the bottom conical chamber. The entire assembly is shown in Fig. 6-17.

Fig. 6-17. Cross section of cooling tower and gas scrubber for the treatment of the NiCl₂·H₂O pyrohydrolyzer off gas.
Dust removal from the wet gas stream was achieved by passing the gas downward through an annulus, the size of which could be varied by lowering or raising a cone shaped insert. The liquid level in this scrubber could be controlled. It was known to be critical in obtaining good particulate removal from experience in a sulphating roast plant for pyrrhotite, where the concept was proven [15, 16]. The pressure drop over the annulus in the ML Plant was approximately 400 mm H2O. Table II lists the gas pressure in the ML Plant gas train for typical operation.

Table II: Pressure drop through the pyrohydrolyzer gas train

<table>
<thead>
<tr>
<th>Negative Gas Pressure in mm H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeboard</td>
</tr>
<tr>
<td>Top cooling tower</td>
</tr>
<tr>
<td>Bottom Cooling Tower</td>
</tr>
<tr>
<td>Outlet Gas Scrubber</td>
</tr>
<tr>
<td>HCl Absorber</td>
</tr>
<tr>
<td>Inlet Fan</td>
</tr>
</tbody>
</table>

6.3.7 HCl Gas Recovery

Hydrochloric acid recovery followed standard techniques for this commodity. Super-azeotropic acid was first recovered from the cooled pyrohydrolyzer off gases in a packed tower, followed by production of azeotropic acid in a sieve plate tower. Both towers also served other gas streams such as storage tank ventilation. Finally, all off gases from the MLP except the dryer off gases passed through a seawater scrubber prior to release to atmosphere.

The solution circulating at 40 m²/hour through the packed tower was MLP feed acid at 30 g/l Ni²⁺ and 280 g/l HCl and 93% of the HCl in the pyrohydrolyzer off gases was recovered at this solution composition.

6.3.8 Chlorine Control

As discussed in section 6.1, the formation of chlorine through oxidation of HCl with residual oxygen in the off gases is theoretically possible. In plant practice, chlorine formation turned out to be quite significant and its formation and unhindered release to the atmosphere could have jeopardized the entire ML Process.

Despite efforts to minimize the % O₂ in pyrohydrolyzer off gases, restraints on actual naphtha/air measuring and mixing controls resulted in several percent oxygen in the freeboard gases. The use of air for NiCl₂ injection and air inleakage further increased the oxygen content under fully loaded pyrohydrolyzer conditions. Not always was enough NiCl₂ available to satisfy the optimum (maximum) naphtha/air mixture. At low feed rates the oxygen content would increase even further, and with it, the chlorine content of the gases entering the cooling tower. Decreasing the primary fluidizing air was not an option. Under uncontrolled operating conditions Cl₂ emission was measured at over 10,000 ppm in the off gases.

Chlorine emission from the ML Plant stack was to be less than 25 ppm. This was another situation that could have jeopardized the ML Plant operation. However, from the pyrohydrolyzer combustion work it was known that chlorine would react with hydrocarbons to act as a flame extinguisher. Would hydrocarbons also act as chlorine scavengers?

A small gas inlet was installed in the "gooseneck" connection between pyrohydrolyzer and cooling tower. Despite it being a single opening inlet, chlorine was efficiently scavenged from the pyrohydrolyzer off gases with a reasonable amount of propane, listed in Table III in the next Section. Hydrogen gas and naphtha were also tried and found effective. Off gas specifications were met. Throughout the 15 year life of the ML Plant, the pyrohydrolyzer operated with this chlorine scavenging system.

The propane action did not involve reduction of the percent O₂ in the off gases; in case of low NiCl₂. H₂O feed rates resulting in high percent O₂ in the off gas, the propane flow was not adjusted, nor did the Cl₂ content of the stack gases increase. It appears that the Cl₂ was very efficiently "scavenged".
6.3.9 Trace Element Behaviour.

The ML Plant was extremely forgiving in terms of trace elements contaminating the granular nickel product. Of the elements contaminating Falconbridge smelter matte, arsenic, selenium and tellurium remained in the leach residue. Iron, copper and cobalt were removed by solvent extraction, but should these fail then cobalt would stay in the mother liquor, copper would pass through the pyrohydrolyzer and iron would be trapped in the TlOA of the SX section, as would zinc. The main nemesis of the nickel (chloride) hydrometallurgist, i.e. lead, would also pass through the pyrohydrolyzer and build up in the circuit. Since the ML Plant had a small bleed of azeotropic into the main circuit lead removal occurred there and the installed ion exchangers for lead were eliminated from the ML Plant. Iron in the final product was due to pick up in the NiCl₂·H₂O dryer, not failure of the solvent extraction operation.

6.3.10 Economics.

In a broad metallurgical sense, recovery of HCl is the "raison d'être" for pyrohydrolysis. Some information on the consumables used per ton of HCl recovered would therefore be useful in projecting other acid-leach circuits. Since the ML Plant operated on solid, dehydrated nickel chloride, not nickel chloride solution, information on the dryer and HCl stripper is also included. Typical operation of the ML Plant dryer and pyrohydrolyzer at a nickel production level of 625 tonnes/month is given in Table III for the typical 80% pyrohydrolysis efficiency:

Table III: Typical operation of the Matte Leach Plant

| NiCl₂ · 4H₂O production | 2895 t/m |
| NiCl₂ · 12wt% H₂O | 2000 t/m |
| Naphtha to dryer | 106 t/m |
| Naphtha to fluid bed | 195 t/m |
| Propane to freeboard | 33 t/m |
| Seawater for cooling | 300 m³/h |
| Electric power, Mwh. | 700 GWh/m |
| Steam to HCl stripper | 2500 t/m |
| Steam credit (see 6.3.11.3) | (340 t/m) |
| HCl recovered | 970 t/m |

When steam consumption is excluded, the fuel consumption per ton of HCl recovered is considerably lower than that found by Jha [2] on NiCl₂ solutions, i.e. 0.34 tons naphtha per ton HCl for the ML Plant versus 0.47 tons fuel oil/ton HCl recovered for the best conditions given (0.72 kg oil/kg Ni and 85% conversion efficiency). However, assuming 12t steam can be produced per ton fuel oil and allowing for the approximate 10% higher calorific value of naphtha over fuel oil, the ML Plant fuel oil equivalent consumption becomes 616 t/month, or 0.635 tonnes fuel oil per tonne HCl recovered in such a super azeotropic system, with steam to a stripper and NiCl₂ crystallization.

6.3.11 Suggestions and Comments.

Several suggestions and comments can be made for the recovery of HCl by thermal hydrolysis of metal chlorides:

1. Feeding solid metal chloride crystals to a pyrohydrolyzer is not necessarily more energy efficient than feeding a metal chloride crystal slurry.

2. Given a choice between operating a super- or sub-azeotropic leach system, the latter should receive preference for reasons of simplicity. It would be preferable to increase the severity of the leach conditions (100°C at subazeotropic vs. 65°C at superazeotropic), or to pretreat the feed to the leach to make it less refractory, than to operate a superazeotropic system, with its attendant complexities (crystallizer, dryer, restraint on water balance, etc.). This choice was not available when the ML Plant was piloted and constructed. Furthermore, the crystallization of nickel chloride was the only effective removal of lead from the system, in case the ML Plant would be used for producing electrolytic nickel by electro-winning from nickel chloride (See paper on this subject in Part Two).

3. Regardless of the HCl normality in the metallurgical circuit, recovery of HCl is fuel intensive, even after taking credit for the calorific value of the leach gases, i.e. H₂ and H₂S. In the ML Plant combustion of the leach gases yielded 340 tonnes/month of low pressure steam.
6.4 References


6. Gosden, Derek (Babcock Contractors Limited) Personal communication.


8. Ruthner, Michael and Ruthner, Othmar, "25 years of process development in HCl pickling and acid regeneration", Iron and Steel Engineer,


12. Springer, Gunther, Falconbridge Metallurgical Centre, Falconbridge, Ont. Personal communication.

13. Vembe P.E. "Instrumentation and Control of the SX Section in the FML Process" ISEC '77.


7. Opportunities for Chloride and Nitrate Systems in Hydrometallurgy.

7.1 General.

There are a number of interesting process routes and mineral separations that appear worthwhile investigating from an applied technical perspective, while attempting to achieve mineral processing capabilities, heretofore not found possible or economic.

7.2 Chloride Systems.

7.2.1 Re: The Cuprex Process.

Since the Cuprex Process was examined in detail it will be used as a starting point for suggesting opportunities in the processing of chalcopyrite.

The Cuprex process takes advantage of the reactivity of chalcopyrite in FeCl₃ solutions and separates CuCl₂ from the liquor by SX with a new specific reagent. Problems were identified in the electrowinning section, requiring a low chloride tenor to allow CuCl₂ extraction and a high chloride tenor to keep CuCl in solution. This dilemma was resolved by adding NaCl and partitioning the electrowinning cell with a cation selective membrane.

Since granular copper is produced from chloride electrolytes anyway, it would be interesting to investigate the production of metallic copper by H₂ reduction in the organic phase, simply represented by

\[
\text{Cu}^{2+} + \text{H}_2 \rightarrow \text{Cu} + 2\text{H}^+ 
\]

This requires a proton exchange and therefore SX reagents, which can accept protons and which are stable i.e. do not reduce under the required process conditions. It has been suggested that LIX 26, which is a hydroxyquinoline compound might meet these conditions [1]. The proton carrying capacity and selectivity against iron may rule this reagent out in actual trials, but once the objective has been specified, more specific reagents may be developed for copper recovery by hydrogen reduction in the organic phase. This approach would eliminate the discharge of NaCl solution to the environment.
7.2.2 Reducing Leach.

Looking at chalcopyrite processing in a more general way, it has already been mentioned that it is difficult to compete hydrometallurgically with a modern smelter/refinery for pure chalcopyrite. Where chalcopyrite is diluted however, with pyrite or pyrrhotite, especially gold bearing sulphides, a reducing leach to produce upgraded smelter feedstock should be considered. Hydrogen reduction will reduce pyrite to troilite at relatively low temperatures, i.e. less than 500°C, yielding H₂S in the gas phase. Subsequent HCl leaching yields more H₂S and an upgraded chalcopyrite/CuS/Cu₂S/gold residue. The H₂S could be used to react with low concentration SO₂ gas, say from Fierce Smith converters, to give elemental sulphur. By upgrading the smelter feed, less SO₂ is produced and H₂S and SO₂ can be brought into balance:

\[
\begin{align*}
    \text{CuFeS}_2 + 2\text{FeS}_2 + 2\text{H}_2 & \rightarrow \text{CuFeS}_3 + 2\text{FeS} + 2\text{H}_2\text{S} \\
    2\text{FeS} + 4\text{HCl} & \rightarrow 2\text{FeCl}_2 + 2\text{H}_2\text{S} \\
    \text{CuFeS}_2 + 2\text{H}_2\text{O} & \rightarrow \text{Cu} + 1/2\text{Fe}_2\text{O}_3 + 2\text{SO}_2 \\
    4\text{H}_2\text{S} + 2\text{SO}_2 & \rightarrow 6\text{S}_\text{L} + 4\text{H}_2\text{O}
\end{align*}
\]

This concept utilizes hydrometallurgy as a smelting function, not as a refining one. Reaction (4) can be carried out in a citrate medium.

7.2.3 SO₂ Reduction.

Reversing the above concept, i.e. operate the leach principally to generate H₂S to react with low grade SO₂ gas from a smelter, allows pyrrhotite concentrate to be considered for this purpose. Pyrrhotite needs no activation, hence such a system would be simpler than the one discussed for chalcopyrite.

Nickeliferous pyrrhotite occurs in abundance in the ores of the Sudbury basin. The main nickel mineral is pentlandite (NiFe₃S₈), with a nickel content of 34.2 wt% [2]. The bulk of the sulphur in Sudbury ores is contained in pyrrhotite and its rejection by flotation prior to smelting of a high grade nickel concentrate has been the main strategy for reducing SO₂ emissions, without producing unmanageable quantities of sulphuric acid. Even clean pyrrhotite concentrate contains 0.75% Ni, however, with 35%, and its rejection to tailings constitutes a significant loss in nickel recovery. As more and more of the pyrrhotite is rejected, it is harder to avoid pentlandite losses.

The proposal for achieving SO₂ reduction through the use of chloride metallurgy is to take the mill "middlings", i.e. the pyrrhotite with high pentlandite content (2-4% Ni) and subject it to an HCl leach to generate H₂S, a FeCl₂ solution and a high-nickel residue (8-12% Ni). The latter is added to the regular concentrate going to the smelter. The FeCl₂ solution is hydrolyzed to regenerate the hydrochloric acid. The H₂S leach gas is used to treat low grade SO₂ gases from the smelter, producing elemental sulphur. This approach was behind the testwork carried out by Falconbridge in the early 1970's, and which is described in Part Two. Falconbridge, however, at that time considered replacing its aging blast furnaces with a hydrometallurgical facility and feed the leach residue directly to its nickel refinery. This would have involved thermal activation of the pentlandite, similar to that required for chalcopyrite. It would also have burdened the refinery site with the gangue disposal problem. The flowsheet for producing sulphuric acid was never worked out, due to the intervening oil supply crisis of 1973, and, in hindsight, unrealistic price and supply projections for natural gas to the Sudbury operations.

The present proposal is much less ambitious, and would be justified on the basis of higher nickel (and cobalt) recoveries. The writer recognizes that this requires the admission by Mill operators that "middlings" go around in mill circuits till they are largely lost to tails, and is sound projection of natural gas and prices. Fuel to the pyrohydrolyzer will be the main cost in producing elemental sulphur by this proposal. Revenue for the iron oxide product has been discussed earlier.

7.2.4 Marmatite Processing.

It is surprising to the author that no serious attempt has been made to capitalize on the reversibility of the ZnS dissolution/precipitation reactions to upgrade the iron bearing form of sphalerite (marmatite). Instead of developing an array of zinc processes in the sulphate system to deal with the zinc ferrites formed during roasting of marmatite, prior iron removal by chloride hydrometallurgy appears a reasonable alternative. Conceptually, this should be possible by utilizing a strong HCl dissolution step generating H₂S, followed by HCl gas removal from the slurry for return to the dissolution step by stripping, and utilizing the generated H₂S for ZnS precipitation in the lower acid concentration solution. Such precipitation may require continuous or staged HCl removal. The iron would be pyrohydrolyzed. Zinc losses would be minimal. The system could be driven by the fuel usage of the pyrohydrolyzer and would require zinc chloride volatilization in the hydrolyzer. The purified zinc sulphide would be fed to a conventional process installation. A conceptual flowsheet is given in Figure 3-1.
MARMATITE CONCENTRATE

LEACH 90°C

ADSORBER 90°C

TIAL GAS SCRUBBER 60°C

STACK

WASTE

LOW ZINC SOLUTION

COOLING TOWER 50°C

FLUID BED OR SPRAY HYDROLYZER

FUEL

AIR

Fe₂O₃

Fig. 3-1. Conceptual Upgrading of Marmatite In 6N Chloride System.

7.2.5 HCl vs Cl₂ Regeneration.

Minerals, such as chalcopyrite have the capability of reducing ferric chloride to ferrous chloride. Recovery of HCl from ferrous chloride is a well known technique, as discussed. The use of HCl as a lixiviant for, say chalcopyrite, is not feasible, except with air or oxygen sparging. These techniques have their own problems and costs. What is needed is capability of producing chlorine from ferrous chloride.

This could be done by combining pyrohydrolysis of FeCl₂ with the Beacon process. The hot freeboard gases are mixed with additional air and passed over the Beacon process catalyst (copper chloride on pumice) at 350-400°C [3] and the off gases absorbed in ferrous chloride liquor:

\[ 4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O} \] (5)

\[ 2\text{Cl}_2 + 4\text{FeCl}_2 \rightarrow 4\text{FeCl}_3 \] (6)

This reconstitutes the oxidant for the dissolution. Plugging of the pumice catalyst should be readily solved by leaching with hydrochloric acid and precipitating cuprous chloride.

There may also be reverse situations, such as in the leaching of oxides where chlorine is generated by electrowinning, but where HCl is required as lixiviant. The concept of using MnO₂ coated electrodes to generate HCl and O₂ gas has already been discussed, and deserves some innovative testwork.

7.2.6 Pyrohydrolysis of MgCl₂ and CaCl₂.

Pyrohydrolysis of MgCl₂ is well established. This means that the MgO product can be used to adjust the pH upwards to precipitate metal hydroxides:

\[ \text{MeCl}_2 + \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Me(OH)}_2 + \text{MgCl}_2 \] (7)

The use of MgO as a precipitant in hydrometallurgical flowsheets has been proposed for the treatment of Red Sea muds, but has not been exploited to date [4].

The use of calcium oxide or carbonate (lime or limestone) has not been attempted at all in chloride hydrometallurgy. This is long overdue since CaCl₂ can be hydrolyzed, if calcium silicate is allowed to be formed:

\[ \text{CaCl}_2 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{CaSiO}_3 + 2\text{HCl} \] (8)

The ΔH for this reaction is estimated to be 28 kCal more negative than the ΔH for direct CaCl₂ hydrolysis, enough to yield greater than 90% HCl over 400°C [5]. A slurry of fine silica in CaCl₂ solution would have to be fed to the pyrohydrolyzer.
7.3 Nitrate Systems.

7.3.1 General.

The nitrate systems in hydrometallurgy are presently being used in situations where the cost of regeneration of HNO₃ is not of material concern (nuclear industry, stainless steel pickling).

This thesis emphasizes economic regeneration of the lixiviant in hydrometallurgy and in this regard HNO₃ suffers from two shortcomings.

The first one is the inclination of nitrogen to reduce to lower valency states at the cathode in electrowinning of metals in nitrate systems, as discussed in Chapter Five.

The second shortcoming has to do with the homogeneous gas reductions involved in the oxidation of NO. This means that the oxidation reaction slows down as the NO concentration decreases. To avoid enormous equipment volumes, HNO₃ plants operate under pressure. This makes thermal decomposition of metal nitrates in conjunction with HNO₃ recovery complex. The dilute calciner off gases would have to be cooled, scrubbed and compressed. Any oxygen present in the gas would continue to generate HNO₃ during these operations.

In fact, it is hard to visualize any nitric acid recovery flowsheet that would not involve gas compression. This will require control of leach, tank or calciner under suction, while feeding the gases to a compressor. It will also require good off gas cleaning, since dust particles will reduce compressor life and the compressor is one of the most capital intensive items in a HNO₃ plant. At the least, there is a learning stage involved.

In view of these two shortcomings, nitrate metallurgy is approximately in its development where chloride metallurgy was 30-35 years ago. Short of pointing out the large amount of theoretical and practical knowledge that has to be acquired, this chapter will deal only with the oxidizing capability of nitric acid under conditions where recovery of base metals is not a priority. Such is the situation for the NITROX Process, discussed in 7.3.2.

Nitrites must be contained within the plant perimeters for environmental reasons. Final residue washing will require nitrate free water. The ability of any process to accept water is limited, hence denitrification of final wash water would allow it to be recirculated, ad infinitum, and remove any important constraint on nitrate hydrometallurgy. Some work on cathodic reduction has been carried out, utilizing catalytic electrodes and dilute sulphuric acid solutions [5] and [3-4]. Another approach worthy of consideration is a copper catalyzed ferrous denitrification process. This is a chemical reduction in basic media [6], but could be compatible with nitrate hydrometallurgical operations. Removal of nitrate by (an)ion exchanger is another option for dilute waste streams.

Returning to more fundamental opportunities in the nitrate system, one that has not been investigated is anodic oxidation of the reduced nitrogen oxides in conjunction with metal electrowinning. The proponents of the NSL Process commented on the high operating cost of copper electrowinning. This is when oxygen is evolved on the anode. However, if nitrous acid could be oxidized to nitric acid with a smaller voltage drop, power consumption would be reduced and the nitric acid regeneration plant could be smaller. Nitrous acid has good solubility in nitric acid [8]. Whether a membrane cell would be required and how this would work in an industrial setting are questions that cannot be contemplated till exploratory testwork has been carried out on this subject.

Finally, nitrous acid or NO can act as a reductant. This could possibly be applied to silver bearing pyrolusite (MnO₂) as follows:

\[ 3\text{MnO}_2 + 2\text{NO} + 4\text{HNO}_3 \rightarrow 3\text{Mn(NO}_3\text{)}_2 + 2\text{H}_2\text{O} \]  

Dissolution conditions would have to be chosen carefully since HNO₂ has a very limited stability range (Fig. 2-3). An autoclave operation is probably required. Silver would be solubilized. MnO₂ could be recovered by thermal decomposition of manganous nitrate.

7.3.2 The NITROX Process.

This process, and the similar and competing one, formerly called the ARSENRO Process, and more recently the REDOX Process, utilize nitric acid as the oxidant for gold bearing pyrites and arsenopyrites. These minerals often contain gold in a distribution, which renders the gold unextractable by cyanide. The gold industry uses the term "refractory" to describe these sulphides, as compared to "free milling". The supply of these refractory pyrites is large, especially in epithermal deposits, and their location often known, which greatly reduces exploration expenses. The increase in the gold price in the early 1970's rekindled interest in the treatment of these deposits. With roasting
becoming unacceptable due to sulphur and arsenic disposal problems, hydrometallurgical oxidation methods were reviewed. Autoclave oxidation has become the alternative to roasting, albeit a costly one, and several installations have been constructed utilizing this method of oxidation. Additional background references can be found in Part Two of this thesis.

Two serious, credible alternatives have been proposed to autoclave oxidation, namely bio-oxidation and nitric acid, or chemical, oxidation. Bio-oxidation has captured a great deal of attention the last few years, due to its apparent simplicity. There are two good reasons for this, namely mass and heat transfer. Oxygen from air has to be transferred into solution, and some comments on that task have been published by the author [9]. Heat transfer engineering is just as complex and daunting and it has not been resolved satisfactorily to date for the bio-oxidation of pyritic concentrates.

The other alternative is nitric acid assisted oxidation of pyrites. It is referred to as nitric acid assisted oxidation, since oxygen can be transferred from the freeboard of an oxidation vessel into the mineral slurry by the following mechanisms:

\[ 3\text{NO}_2 + H_2O \rightarrow 2\text{HNO}_3 + \text{NO} \]  
(9)

This nitric acid will give up its oxygen to form NO gas, as shown for sulphur.

\[ S + 2\text{HNO}_3 \rightarrow H_2\text{SO}_4 + 2\text{NO} \]  
(10)

or

\[ S + 3\text{NO}_2 + H_2O \rightarrow H_2\text{SO}_4 + 3\text{NO} \]  
(9 + 10)

Simplistically, the \( 3\text{NO}_2 \) enter the liquid phase, oxidize one sulphur atom to sulphuric acid and form \( \text{NO} \). The gaseous NO leaves the process solution to form \( \text{NO}_3 \) by reacting with gaseous oxygen, in air. This \( \text{NO}_3 \) is promptly absorbed into the process solution, forming nitric acid as per reaction (9). It in turn reacts with the refractory sulphides, releasing NO. In this way the NITROX cycle is established, resulting in very efficient transfer of oxygen units to the refractory sulphide slurry. Written as a chemical reaction, the oxidation of \( \text{NO}_3 \) gives

\[ 3\text{NO} + 3/2\text{O}_2 \rightarrow 3\text{NO}_2 \]  
(11)

or, for the overall reaction:

\[ S + 3/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 (9 + 10 + 11) \]

It will be noted that neither nitric acid, \( \text{NO} \), nor \( \text{NO}_2 \) appear in the overall reaction. The quantities of nitrate are such, however, that the nitric acid and \( \text{NO} \) must be seen as reagents or intermediates in the NITROX Process, not as catalysts. Air is used to provide oxygen units in the NITROX Process.

The Arseno process has been described in a number of configurations, most of them utilizing oxygen in autoclaves, with small amounts of nitric acid present. The role of nitric acid under these conditions has been described as a catalyst, but its function remains the same, namely to transfer oxygen from the gas phase into the slurry. Utilizing nitric acid systems, agitation can be eliminated for certain equipment configurations. Some Redox (Arseno) process variants show a pipe reactor.

7.3.3 Nitric Acid Assisted Oxidation.

The reader is referred to Part Two for further details on the NITROX process. Some comments will be made here regarding opportunities for hydrometallurgical processes, based on nitrate chemistry.

The main opportunity is in the low cost oxidation of large tonnages of sulphides, as exemplified by auriferous pyrites.

In general, the gold bearing sulphide zone in epithermal deposits is weathered (natural oxidation) on top and contains auriferous pyrites at depth. While the oxide layer is normally amenable to cyanide extraction of the gold, the sulphide material is often "refractory". Such is the case, for instance, at the Rosario owned deposit in the Dominican Republic, where mining has depleted the oxide layer. A search is underway for treatment of the sulphides for gold recovery.

Further to the oxidation of pyrites, the tonnage of pyrites in coal is quite substantial and the use of nitric acid to desulphurize coal has not recieved the attention it deserves. Such a process would require quite selective conditions, to prevent nitrification of the coal, therby, causing loss of the oxidant. Nitrated coal may also result in higher NOx stack emissions. The efficacy of nitric acid to remove organic sulphur must be determined through testwork, probably for each specific coal.
Another opportunity may be offered by the oxidation of base metal arsenides, such as cobalt. Compared to other methods of oxidation, nitric acid allows high redox potentials. This ensures that all arsenic is oxidized to $\text{As}^{3+}$, the valency that allows disposal as stable ferric arsenate. Cobalt and nickel are not coprecipitated to a significant extent and can be recovered as hydroxides [10].

There are a number of process and engineering problems that need to be resolved for these two opportunities to be realized. The nitric acid plant compressor has been mentioned in the latter category. Nitrate containment within the plant parameters is a process limitation involving water balances, filtration and washing, and $\text{NO}_x$ emission control on the gas side. Decomposition of $\text{HNO}_3$ to $\text{N}_2\text{O}$ and $\text{N}_2$ needs to be measured accurately under process conditions. Gypsum control is always an issue where limestone is used for neutralization. Elemental sulphur formation and gold entrapment are discussed in Part Two of this thesis. And where arsenic is present in the feedstock, the long term stability of ferric arsenate must be addressed.

The advantages of nitric acid oxidation are more readily apparent with large scale operations. Piloting of nitric acid assisted oxidation of sulphide minerals is needed before a large scale plant can be built.

7.4 References

1 Henkel Research, California, U.S.A. Personal communication.


PART TWO

PAPER 1

The Falconbridge Matte Leach Process

by

P.G. Thornhill, E. Wigstol and G. Van Weert

The Falconbridge matte leach process

by P. G. Thornhill, E. Wigstoł, and G. Van Weert

The Falconbridge Matte Leach Process is based on the selective dissolution of nickel from copper-nickel matte in hydrochloric acid maintained at high strength to permit a high degree of separation of nickel from copper in a closed co-current leaching operation. Solution purification is effected by solvent extraction, and nickel chloride recovered by crystallization from acidic solution. Conversion of the nickel chloride to metal can be effected either by electrowinning from dissolved crystals or by hydrogen reduction of oxide obtained by high temperature hydrolysis of the chloride. An operating plant capable of processing 15 MM lb. Ni/yr as a high purity granular nickel product by the latter technique is described.

INTRODUCTION

The nickel refining process practiced at Falconbridge Nilskelev A/S in Kristiansand, Norway has been described earlier by F. R. Archibald. In this process copper-nickel converter matte containing about 48% Ni, 28% Cu and 21% sulphur is treated by a combination of pyro- and hydro-metallurgical steps involving considerable re-circulation and re-treatment of intermediate products, and in which the applicability of modern process control techniques is severely limited. Because of the growing needs of the Falconbridge group for additional nickel and copper refining facilities, the company embarked in the 1950's on a research program aimed at developing a process less encumbered with these shortcomings. This paper describes the general process which resulted from that program, and its application as practiced in a commercial scale pilot plant situated at the company's Kristiansand operations.

PROCESS PRINCIPLES

The Falconbridge Matte Leach Process is based on the following principles:

1. When finely divided copper-nickel converter matte is treated with strong hydrochloric acid, the nickel is selectively dissolved, leaving copper and platinum metals as an insoluble sulphide residue.

2. Because the solubility of nickel chloride in pregnant solutions decreases with increasing HCl concentrations, the salt or nickel chloride can be precipitated from the solution by increasing, rather than by neutralizing, the acidity of the solution. This property permits the maintenance of high acidity throughout a co-current leaching system, thereby obviating the liquid-solid separations necessary when a multistage counter-current leach aimed at maximum utilization of acid is used.

3. Since, unlike nickel, the majority of the impurities in the pregnant solution form anionic complexes under acid conditions, purification of the pregnant solution can be readily effected by solvent extraction or anion exchange without prior neutralization of acid in the solution.

4. Since it is possible in this system to maintain high acidity throughout the leach, high leaching efficiencies are obtained at temperatures no higher than about 70°C. This feature permits the use of ordinary rubber-lined acid-proof equipment for the handling of gases, liquids, and solids. Typical leach conditions and results illustrating selectivity obtainable are summarized in Table I.

A generalized flowsheet illustrating the process is given in Fig. 1. This flowsheet shows the initial separation between nickel and copper occurring after nickel leaching, when copper sulphide solids are filtered from nickel chloride pregnant solution. The copper sulphide containing the platinum metals can be seen on the right half of the diagram to undergo essentially the roast-leach-electrowinning treatment used in the Kristiansand Refinery, except that the PM's are more directly concentrated as solids (resulting from the copper leach) instead of as nickel anode slimes. H2S leach gases are shown combusted and combined with roaster gas, which in the Kristiansand Refinery is treated for recovery of liquid SO2. As shown in the nickel circuit on the left side of Fig. 1, the pregnant solution is treated with an oxidation agent to remove dissolved H2S and to convert Fe to the ferric state, in

<table>
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<tr>
<th>PRODUCT</th>
<th>HCl</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
<th>S</th>
<th>Ca</th>
<th>Ni</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Oxide Leach</td>
<td>100</td>
<td>0.9</td>
<td>0.3</td>
<td>9.4</td>
<td>66.2</td>
<td>90.2</td>
<td>1.9</td>
<td>52.3</td>
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<tr>
<td>Fe Oxide Leach</td>
<td>100</td>
<td>1.4</td>
<td>4.0</td>
<td>40.8</td>
<td>66.2</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Fe Oxide Leach</td>
<td>100</td>
<td>2.0</td>
<td>2.0</td>
<td>98.7</td>
<td>66.2</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Fe Oxide Leach</td>
<td>100</td>
<td>2.3</td>
<td>2.3</td>
<td>98.7</td>
<td>66.2</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table I—HCl Leaching of Cu Ni matte, 95% —325 M: temperature: 65°C, leach stages: 3, mechanical agitation, residence time 11 hr.
which condition it is separable by solvent extraction with tri-n-octyl phosphate. Treatment of the iron-free solution with tri-n-octyl phosphate is a simplified schematic flow of a high purity granular metal precipitated by dissolution of the twinning from electrolytes re-sulting by direct reduction of the metals. These conditions, permitting its effective separation from the nickel chloride, nickel chloride crystals obtained by this procedure are of exceptionally high purity, and can be used to produce metallic nickel either by direct reduction of the chloride with hydrogen, or by electrolyzing from electrolyte replenished by dissolution of the crystals.

A third method, which is incorporated in the plant to be described, is based on high temperature hydrolysis of the nickel chloride to form nickel oxide and hydrogen chloride gas. Reduction of the oxide by hydrogen, then yields metallic nickel granules, and absorption of the HCl regenerates the acid required for leaching fresh quantities of matte.

KRISTIANSAND MATTE LEACH PLANT

The matte leach plant is rated at 15 Mm l o per yr nickel in the form of a high purity granular metal product designated NIOCHEK 56. Fig. 2 is a simplified schematic flow sheet of the operation, and Table II summarizes typical analyses. All instrumentation and control is integrated with a PDP8 computer without analogue back-up.

Leaching

All the Falconbridge matte shipped to the refinery is comminuted in a single system, from which the requirements of the matte leach plant are drawn as a 98% - 325 mesh fraction. This material is stored in a bin having a capacity of 180 metric tons. Matte is periodically drawn from the storage bin to batch charge one of the two 30 ton leach feed bins fitted with load cells. Leach feed is withdrawn by a variable speed gear pump to a closed screw feeding system, discharging to the first of a cascade of four mechanically agitated rubber-lined leach tanks equipped with liquid seals. Feed acid, preheated to 75°C, is fed at a rate automatically proportioned to the matte feed rate. When a low set point in the feed bin is reached, the computer shifts the signal to the full bin, from which feed is withdrawn without interruption in flow.

Residence time in the leaching system is about 12 hr, and at an average temperature of 70°C the treatment dissolves 98% of the nickel. Rejected leach slurry is transferred to one of three 1000 ton capacity rubber lined chamber type filter presses by means of a variable speed centrifugal pump controlled by the pulp level in the fourth leach tank. These filters are equipped with mechanical plate transport. The filter cake, after double washing and air blowing to 10% moisture in a regulated sequence, is transferred to the copper department for roasting.

Leach gas consists of a mixture of H₂S and HCl, and is kept under a positive pressure of 50 mm. H₂O by a control valve located downstream from a high speed rubber lined exhauster fan. The gas is cooled and scrubbed free of HCl before being combusted in a waste heat boiler, from which the resulting SO₂ is fed to the DMS plant previously described.

Solution Purification

Pregnant solution, containing about 120 gpl Ni and 190 gpl HCl, also carries about 2 gpl each of Fe, Cu and Co. Oxidation of the iron from the ferrous to ferric state and of dissolved H₂S to elemental sulphur is accomplished by oxygen fed into an eductor powered by a flow of 50 m³/hr pregnant solution recycled to one of two holding tanks by means of a centrifugal pump. After filtration for removal of the sulphur, the solution is cooled to room temperature in preparation for solvent extraction.

The solvent extraction operations are carried out countercurrently in batteries of mixer-settlers constructed of reinforced phenol formaldehyde resin. This material has been found to be completely resistant to both HCl and the aromatic hydrocarbons used as carrier liquid for the organic solvents. Mixer sections of all units have volumes of approximately 1 m³, and are agitated by impellers constructed of a special polyester. However, the settling area of each loading section is twice that of the stripping sections, and this ratio is used to the copper refinery, and secondly, a copper eluate which is recycled to the main refinery circuit. Solution flows and analyses are given in Table II. TSP solvent is used as a 4 vol.% solution in an aromatic hydrocarbon carrier liquid, while TIOA is used at 11% concentration. Each of the organic flow rates into the loading sections of the solvent extraction system is automatically proportioned to equal that of the pregnant solution. Details of the solvent extraction system are shown in Fig. 3.

Crystallization

Before treatment for separation of nickel chloride crystals, the raffinate, or purified pregnant solution, is used as a scrubbing medium for the treatment of the gases resulting from the high temperature fluidized bed hydrolysis of HCl, to be described later. This treatment increases the nickel concentration without reducing that of the HCl, to give crystallizer feed saturated in both at a temperature of 85°C.

The crystallizer is a rubber lined tank of 75 m³ capacity controlled at 28°C and equipped with a 40 HP turbine agitator to maintain the crystals in suspension. Crystallization is continuous, and is effected
by automatically proportioned flows of feed solution and HCl gas. Crystall slurry is continuously transferred from the crystallizer to a crystalline conditioning tank by means of an air lift. The heat generated by absorption of the HCl gas fed to the crystallizer is removed by circulation of crystallizer slurry through two tube-in-shell graphite heat exchangers in series.

Centrifugal Filtration and Drying of Nickel Chlorides
Crystall slurry withdrawn from the crystalline conditioning tank consists of NiCl₂ + H₂O in mother liquor, containing about 28 g/g Ni and 330 g/g HCl. The slurry is filtered by a rubber-lined horizontal centrifuge having a basket volume of 700 liters. Operation of this unit is computer controlled on an 8 min cycle, of which 3 min are for filling, 4 min for filtration, and 1 min for discharging. The Mother liquor flows into one of two 35 m³ strong acid storage tanks. The crystals discharge into a polypropylene-lined surge bin fitted with a bottom screen conveyor feeding a direct fired rotary dryer. This unit has an ID of 2.5 m and a length of 10 m, of which the first 3 m is lined with SiC bricks. The remainder of the dryer is fitted with nickel lined and lifters. Temperature is controlled to effect elimination of approximately 3 of the 4 moles of water of crystallization from the centrifuged crystals. Off-gases are drawn through cyclones followed by an adiabatic absorber operated at 65°C, and consisting of a rubber-lined tower with four sieve trays. Here nickel chloride fines passing the cyclones and the HCl adhering to the dryer feed are recovered in a solution running 45 g/g Ni and 105 g/g HCl.

Converter Operation
The converter is a fluidized-bed reactor in which the high temperature hydrolysis of the nickel chloride is effected according to the reaction:

\[ \text{NiCl}_2 + \text{H}_2\text{O} = \text{NiO} + 2\text{HCl} \]

The endothermic requirements of the converting reaction are met by combusting naphtha with air in the fluidized bed reactor, and the additional H₂O formed by the combustion reactions ensures completion of the hydrolysis reaction. The converter is brick-lined and has an ID of 3.4 m at bed level, expanding to 5 m in the freeboard zone. An air-naphtha mixture is supplied to a special chamber, and passed via a header and manifolds to 420 fluidizing nozzles distributed in a regular pattern on a refractory Graphite heat exchanger. Nickel chloride fines are pneumatically fed to the heat exchanger, and the HCl gas is cooled in a 5 m high lower, to below 70°C, and is fed to the converter after passing through a small scrubber for final cleaning. The converter off-gases are cooled in a 30 m high tower, and is cooled by two 18 m³ tube-in-shell graphite heat exchangers. Cooled gases, after passing through a small scrubber for final cleaning, enter the HCl absorption system for recovery of the regenerated acid, as shown in Fig. 2.

Reduction to Metal
Granular nickel oxide is fed from a 5-ton bin into a rotary reduction furnace 1 m in dia. by 10 m long, constructed of alloy steel and equipped with high temperature grease lubricated end seals and water seals for solids inlet and discharge. Electrolytic hydrogen preheated to 600°C enters the discharge end of the furnace, leaves the feed end at 300°C, and is cooled for condensation of H₂O in a 5 m high tower, after which the necessary make-up hydrogen is automatically added to maintain a constant positive pressure of 50 mm H₂O in the system. As in the case of most of the solids feeding systems in the plant, feed of the NIO is accurately controlled by the computer working in conjunction with load cells supporting the feed bin.

Hot nickel granules are cooled and transferred to the NICKEL 98 product silos, from which the NICKEL 98 is packed in plastic bags containing either 40 lb or 20 kg, weighed to a tolerance of 0.1%. After welding, the bags are stacked in triple rows, packed in plastic bags, and then shipped. The analysis at the bottom of Table II shows the degree of purity obtainable in this product.

HCl Stripping and Absorption
The stripper shown in Fig. 2, is a one meter diameter, graphite unit with a packed stripping section and four baffle cap plates for rectification. Mother liquor is preheated in three block type graphite heat exchangers by the stripper bottom product, and is led to the stripper between packing and plates. Striper bottoms circulate by convection through two steam heated reboilers controlled by top temperature. The HCl gas product is cooled and dried before entering the crystallizer, and the condensate so obtained serves as reflux for the stripper. The stripper bottom product, which is anoxotic solution, is cooled to approximately 25°C before passage through ion exchange columns, as shown in Fig. 2, for removal of trace chlorine and eventual re-use in the leaching step.

Cooled and scrubbed converter off-gases pass through a 1.7 m diameter packed tower filled with 2 in. polycrystalline Pall rings countercurrent to feed acid, which is cooled externally to 35°C before recycle, also shown in Fig. 2. The absorber off-gases, together with tank and equipment ventilation gases, contain some 0.5 HCl by volume and amount to about 5000 m³/hr. These gases are passed through a main absorber consisting of a 2.5 m diameter

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Table II—Falconbridge Nikkelverk A/S matte leach plant, summary of typical analyses.

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>H₂O</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matte</td>
<td>35.0</td>
<td>1.1</td>
<td>23.5</td>
<td>1.3</td>
<td>22.2</td>
<td>28.2</td>
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<tr>
<td>Pellet</td>
<td>29.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leach Pulp</td>
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<td>19.8</td>
<td>28.2</td>
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<td>0.001</td>
<td>2.005</td>
<td>0.004</td>
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<td></td>
</tr>
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<td>Feed Acid</td>
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<td>0.001</td>
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<td>0.004</td>
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<td></td>
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<tr>
<td>Crystal Feed</td>
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<td>0.001</td>
<td>2.005</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum Product</td>
<td>157.0</td>
<td>0.001</td>
<td>2.005</td>
<td>0.004</td>
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<td>Acid Solution</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pickle Liquor</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Converter Product</td>
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<td>0.0005</td>
<td>0.005</td>
<td>0.006</td>
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<td></td>
</tr>
<tr>
<td>NICKEL 98</td>
<td>94.7</td>
<td>0.0006</td>
<td>0.005</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

Fig. 3—Falconbridge Nikkelverk A/S matte leach plant solvent extraction circuit.
The off-gases are steam. This way contains 330 g/l HCl and is azeotropically solution flowing co-currently through a graphite heat exchanger. The solution produced in this way is immediately absorbed in a graphite burner unit of 20 tons per day capacity. The flame is directed downward, and the hot HCl gas is immediately absorbed in azeotropic solution flowing co-currently through a graphite heat exchanger. The solution produced in this way contains 330 g/l HCl and is discharged to the strong acid storage tank. The off-gases are steamed and released to atmosphere. The installation also includes print-out equipment, alarms, and provision for operator manipulation such as alteration of set-points, ratios, start-stop capabilities, and other parameters. The ability to operate control valves singly from the control board has proven especially valuable during start-up to ensure a smooth transfer to automatic control, and at the end of each shift an automatic print-out of key average readings and a complete materials and solution balance is an important factor in maintaining smooth operation.

### Instrumentation and Control

The operation of the plant is controlled by a DDC system centered on a PDP8 twelve-bit machine with 1.5 microsecond cycle time and 2 x 4 k ferrite core. The capacity, which is at time of writing being fully used, includes the following:

- 124 analogue measurements
- 48 digital inputs
- 12 digital inputs from centrifugal pumps
- 11 digital outputs to centrifugal pumps
- 12 digital outputs to process
- 64 PI regulating functions
- 14 ratio controllers
- 4 weight controllers
- 3 digit displays for measurements and calculated values
- 50 valve positioners
- 36 channels for data logging on six-6-point strip chart recorders.

The breadth of training given the senior operators has made it possible to use a job rotation system in which each operator spends a week at a time successively in the control room, the wet section, and the dry section of the plant. The versatility thus achieved by each member of the operating crews minimizes the disruptions which normally trouble a small-staffed plant when absenteeism occurs. Automation of the plant has also given shift operators time to assume some of the simpler maintenance functions, with notable improvements in maintenance cost.

Some two years of operation have demonstrated that with proper design and materials of construction, and careful process control, corrosive liquids and hazardous gases can be just as successfully employed in a metallurgical process as in any other chemical operation. We are satisfied that DDC has many advantages over conventional analogue instrumentation, provided sufficient care is taken to train operators before start-up of the plant.

### REFERENCES


Hydrochloric Acid Leaching
Of Nickeliferous Pyrrhotites
From the Sudbury District

G. Van Weert, Manager, Process Metallurgy, Falconbridge Metallurgical Laboratories, Thornhill, Ont.
K. Moh, Pudcomly Engineering, Toronto, Ont.
N. L. Peet, Duisburger Kupferhütte, Duisburg, W. Germany

Abstract
Results of experimental work on hydrochloric acid leaching of nickeliferous pyrrhotites from the Sudbury district are described. Leach temperature (60-90°C), chloride concentration (6-8%), contact time (15-30 hours), and reagent ratio were all chosen to be compatible with industrial practice. From leach solutions up to 90% of nickel and 82% of the copper in the feed to the leach is recovered. The effects of acid addition rate and leach temperature on rate and degree of iron, nickel and copper dissolution are described. The formation of nickel-bearing vanadate at 90°C is reported. Leach incubation is discussed and a mechanism proposed.

Introduction

AN EARLIER PAPER describes the leaching of nickel-copper matte with production of hydrogen sulphide gas and regeneration of hydrochloric acid from the metal chlorides. Further investigations in the field of chlorine hydrometallurgy have been carried out in Company laboratories, and recent emphasis has been on applying this experience to improve the processing of base-metal concentrates.

The sulphide minerals of the Sudbury district consist principally of pentlandite, chalcopyrite and pyrrhotite. Only the latter mineral will dissolve rapidly in hydrochloric acid, which suggests the up-grading of sulphide middlings by chemical means rather than by mineral dressing. The hydrogen sulphide generated during leaching of such middlings would be a useful reagent for the precipitation of metal values from leach solutions or for the reduction of sulphur dioxide. The leach residue would constitute an up-graded nickel-copper concentrate for subsequent smelting.

In a recent Mines Branch circular, the generation of HCl by HCl leaching of base-metal sulphides is reviewed. Pyrrhotite is one of the minerals mentioned in a general way for its capability of generating HCl when contacted with hydrochloric acid. This route allows the recovery of elemental sulphur from the HCl by reaction either with air or with oxygen-free SO2. The U.S. Bureau of Mines suggests the use of HCl for the removal of sulphur dioxide from oxygen-bearing flue gases by the Citrate Process.

A literature search on the HCl leaching of pyrrhotite revealed a serious lack of data on which to base even the preliminary costing of an acid leach plant. In order to establish the practicability of dissolving pyrrhotite under industrial conditions from sulphide middlings or other concentrates and to evaluate the feasibility of such a chloride leach and subsequent HCl recovery by high-temperature hydrolysis similar to that practised on nickel sulphides, exploratory leaching tests on pyrrhotite concentrates were carried out in the laboratories of Falconbridge Nickel Mines Limited.

Experimental

(1) Pyrrhotite — For most of the work, pyrrhotite concentrates from the operating mills were used. Coarse pyrrhotite was also prepared in the laboratory.
The final acidity was determined by titrating to pH = 3.0.

**Series One — Batch Leaching**

Earlier batch leaching techniques were modified as described by Naquin et al., who indicated that complete dissolution of Falconbridge mill pyrrhotite concentrate could be achieved by stirring the leach with very strong acid, varying from 35% w/v HCl at 40°C to 13.5% w/v HCl at 90°C. Once vigorous dissolution was initiated, however, the reaction was found to proceed until either all of the acid or all of the pyrrhotite was consumed, depending on which component was in excess. Because the disked experimental results were derived from the use of a 100-fold excess acid, it was decided to carry out batch leaching tests on Falconbridge Mill pyrrhotite concentrate using only 5.0% excess acid and over that required to dissolve the pyrrhotite. All 100 g of room-temperature-dried pyrrhotite was added at once to the 8N HCl in a heated and stirred one-litre reactor connected to an HLS scrubber. The leaching reaction started immediately and, although gas evolution appeared to have substantially ceased after approximately 10 minutes, the leach was continued for a total of 180 minutes at 70 ± 2°C to permit complete reaction of the residual pyrrhotite and acid. Residue compositions are listed in Table 1, and dissolution results are given in Figure 1.

Under these conditions, iron dissolution was 97% after three hours for a final concentration of 14 g/l HCl. The dissolution increased only marginally for higher final acidities. For an 8N HCl system, an acceptable 95% usage of acid was indicated. Sulphur evolution as H2S reached a calculated maximum of 83% of the sulphur in the feed to the leach. Nickel dissolution at 65-70°C appeared unaffected by the presence of char was thought to render froth unstable. Hydrochloric acid of 8N strength was added at a constant rate of 1.9, 3.0 or 6.0 ml/min. through a burette, to supply from 94 to 185% of the stoichiometrically required amount. The reaction vessel connected to a reflux condenser. The reaction mixture was filtered immediately following completion of acid addition and analyzed for iron, nickel, copper, sulphur and gangue materials. Residue phases were identified by X-ray diffraction and microscopic examination of polished sections.

The results of leaching at 60°C are given in Table 4, and the effect of the rate of acid addition on the rate of iron dissolution is shown in Figures 2 and 3. After an incubation period, the iron dissolution rate drops and remains relatively constant for 30 minutes or more. This was found to be caused by the formation of marcasite at the higher temperatures. Marcasite is the orthorhombic modification of FeS2. After an incubation period, the iron dissolution rate drops and remains relatively constant for 30 minutes or more. This was found to be caused by the formation of marcasite at the higher temperatures. Marcasite is the orthorhombic modification of FeS2. After an incubation period, the iron dissolution rate drops and remains relatively constant for 30 minutes or more. This was found to be caused by the formation of marcasite at the higher temperatures. Marcasite is the orthorhombic modification of FeS2. After an incubation period, the iron dissolution rate drops and remains relatively constant for 30 minutes or more. This was found to be caused by the formation of marcasite at the higher temperatures. Marcasite is the orthorhombic modification of FeS2. After an incubation period, the iron dissolution rate drops and remains relatively constant for 30 minutes or more. This was found to be caused by the formation of marcasite at the higher temperatures. Marcasite is the orthorhombic modification of FeS2. After an incubation period, the iron dissolution rate drops and remains relatively constant for 30 minutes or more. This was found to be caused by the formation of marcasite at the higher temperatures. Marcasite is the orthorhombic modification of FeS2. After an incubation period, the iron dissolution rate drops and remains relatively constant for 30 minutes or more. This was found to be caused by the formation of marcasite at the higher temperatures. Marcasite is the orthorhombic modification of FeS2.
TABLE 3 — Chemical and Screen Analysis of Pyrrhotite Concentrates Used in Series Two Testwork, in Wt. %

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>S</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Pb</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td>WH</td>
<td>54.6</td>
<td>10.1</td>
<td>0.8</td>
<td>0.1</td>
<td>37.7</td>
<td>1.36</td>
<td>0.41</td>
<td>0.28</td>
<td>0.22</td>
<td>0.13</td>
</tr>
<tr>
<td>Lab</td>
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<td>1.40</td>
<td>0.22</td>
<td>0.16</td>
<td>4.90</td>
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<td>0.38</td>
<td>0.06</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Tyler Mesh</td>
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<td>0.04</td>
<td>0.24</td>
<td>0.03</td>
<td>0.03</td>
<td>0.01</td>
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</table>

TABLE 4 — Final Dissolution of Pyrrhotite When Adding 8N HCl at Constant Rates, at 60°C

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Time, min.</th>
<th>Total HCl, %</th>
<th>Rate, HCl</th>
<th>Susp. in</th>
<th>Test No.</th>
<th>Final % Dissol.</th>
<th>Residue, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>WH — 99%</td>
<td>20 Mesh</td>
<td>105</td>
<td>1.15</td>
<td>0.26</td>
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<td>99.3</td>
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</tr>
<tr>
<td>B</td>
<td>105</td>
<td>105</td>
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<td>99.5</td>
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</tr>
<tr>
<td>C</td>
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<td>1.15</td>
<td>0.20</td>
<td>105</td>
<td>99.3</td>
<td>0.7</td>
</tr>
<tr>
<td>D</td>
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<td>0.20</td>
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<td>99.3</td>
<td>0.7</td>
</tr>
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<td>0.20</td>
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<td>0.7</td>
</tr>
<tr>
<td>Lab — 97%</td>
<td>20 Mesh</td>
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<td>1.15</td>
<td>0.26</td>
<td>105</td>
<td>99.3</td>
<td>0.7</td>
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<tr>
<td>F</td>
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<td>105</td>
<td>1.15</td>
<td>0.20</td>
<td>105</td>
<td>99.5</td>
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</tr>
<tr>
<td>G</td>
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<td>0.20</td>
<td>105</td>
<td>99.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

TABLE 5 — Final Dissolution of Pyrrhotite When Adding 8N HCl at Constant Rates, at 50°C

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Time, min.</th>
<th>Total HCl, %</th>
<th>Rate, HCl</th>
<th>Susp. in</th>
<th>Test No.</th>
<th>Final % Dissol.</th>
<th>Residue, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>WH — 99%</td>
<td>20 Mesh</td>
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<td>1.15</td>
<td>0.26</td>
<td>105</td>
<td>99.3</td>
<td>0.7</td>
</tr>
<tr>
<td>B</td>
<td>105</td>
<td>105</td>
<td>1.15</td>
<td>0.20</td>
<td>105</td>
<td>99.5</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
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<td>140</td>
<td>1.15</td>
<td>0.20</td>
<td>105</td>
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<td>0.7</td>
</tr>
<tr>
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<td>0.20</td>
<td>105</td>
<td>99.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Lab — 97%</td>
<td>20 Mesh</td>
<td>105</td>
<td>1.15</td>
<td>0.26</td>
<td>105</td>
<td>99.3</td>
<td>0.7</td>
</tr>
<tr>
<td>F</td>
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<td>105</td>
<td>1.15</td>
<td>0.20</td>
<td>105</td>
<td>99.5</td>
<td>0.5</td>
</tr>
<tr>
<td>G</td>
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<td>140</td>
<td>1.15</td>
<td>0.20</td>
<td>105</td>
<td>99.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

TABLE 6 — Impurity Dissolution as a Function of Rate i

<table>
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<th></th>
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<tbody>
<tr>
<td>60° 90° 90° 60°</td>
<td>50° 50° 60°</td>
<td>50° 50° 90°</td>
<td>50° 50° 90°</td>
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<td>50° 50° 90°</td>
<td>50° 50° 90°</td>
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<td></td>
</tr>
<tr>
<td>WH — 99%</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
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<td>64</td>
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<td>64</td>
</tr>
<tr>
<td>Lab — 97%</td>
<td>64</td>
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<td>64</td>
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<td>64</td>
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<td>64</td>
</tr>
</tbody>
</table>

Silica dissolution is erratic, but seems to decrease with increasing acidity, as in Series One. Lead dissolution rises slightly with acid concentration at 60°C; the other impurities show essentially constant solubility. Increasing the leaching temperature to 90°C increases aluminum and decreases lead dissolution. The mineralogy of the gangue in the concentrate is of overriding importance. The laboratory magnetics contain nearly three times the gangue of mill pyrrhotite (95% vs 31%), but yield only half the quantity of impurities to the leach liquor. The dissolution behaviour of specific gangue minerals was not studied.

INCUBATION AND FROTTHING

An "incubation" period was observed in the constant acid addition tests; i.e. H₂S evolution did not occur immediately on contacting the acid and pyrrhotite concentrate. The length of the incubation period appeared to be a function of acidity; i.e. the leach slurry would evolve H₂S gas when the measured HCl concentration reached a certain level in the leach liquor. For mill pyrrhotite, this level was 15-21 and 6-15 g/l HCl at 60°C and 90°C, respectively. For laboratory magnetics, the level was slightly higher. Details of this incubation occurrence for both pyrrhotites are given in Table 7.

The first series of experiments, where acid strength was 8N at the start of leaching, no incubation period was observed. The observation of a leach incubation period at low acid concentrations was also reported by Ingraham, Parasas and Cabri.\(^\text{**}\)

Maximum froth formation occurred within 3 minutes after the end of the incubation period and took from 16 to 20 minutes to subside. The absence of flotation reagents or the presence of active char appeared to have little or no discernible effect on froth volume or stability. It is possible that the liberated fine elemental sulphur contributes to the froth formation.

INCUBATION MECHANISM

A typical acid concentration profile during the constant acid addition tests is shown in Figure 4. During the incubation period, the acid and pyrrhotite reacted slowly, causing an increase in HCl concentration of the slurry. Acidity dropped once the dissolution and gas evolution started. In further tests with a second mill pyrrhotite concentrate, the incubation phenomenon and HCl profiles were studied in more detail. Table 8 lists the composition of this pyrrhotite concentrate.
The wet pyrrhotite concentrate was mixed with an HCl-saturated FeCl₃ solution of 4N chloride strength, at a solids concentration level of 180 g/l. To simulate the observed HCl peak, hydrochloric acid of 6N strength was added to the slurry at 70°C to obtain an initial HCl concentration of 30, 35, 50 and 75 g/l, respectively. The solution redox potential, which was measured at +560 to +120 mV versus a saturated calomel electrode at 25°C prior to HCl addition, increased almost instantaneously to a maximum value of +540 mV, after which it started to decrease. Within a minute, the potential started decreasing to zero mV at a rate depending upon the initial acid, as shown in Table 2. The higher the initial acidity, the shorter the incubation period. A redox-time profile is illustrated in Figure 5 for the 35-g/l HCl test. H₂S evolution commenced at 0 mV in all cases.

These observations demonstrate that chemical reactions take place during the incubation period. The sudden increase in the redox potential suggests an instantaneous dissolution of an oxidised iron product upon addition of the acid. Some of our mill concentrates contain about 8% magnetite.

\[
\text{FeCl}_3 + 3 \text{H}_2 \text{O} \rightarrow \text{Fe(OH)}_3 + 3 \text{HCl}
\]

The subsequent reduction of the ferric ion is brought about slowly, either directly by pyrrhotite, according to reaction (2), or indirectly by H₂S (4).

which is generated by acid leaching of the pyrrhotite according to intermediate reaction (3).

\[
\text{FeS} + 1.5 \text{HCl} = \text{FeCl}_2 + 1.5 \text{H}_2 \text{S} \uparrow + \text{H}_2 \text{O}
\]

\[
\text{FeS} + \text{HCl} = \text{FeCl}_2 + \text{H}_2 \text{S} \uparrow
\]

As the rate of decrease in redox potential is dependent on the HCl concentration, reaction (3) appears dominant, from which it follows that the reduction of the ferric ion is brought about indirectly by the hydrogen sulphide in this system. Reaction (5) also results in the formation of non-magnetic pyrrhotite, and a stoichiometry of pyrrhotite, which may extend the incubation period.

To investigate the occurrence of reaction (1), a 100-g sample of mill pyrrhotite concentrate No. 2 was contacted at 70°C with 10N solution. An immediate rise in redox potential to +420 mV was observed. The reaction was interrupted prior to the end of the incubation period; i.e., when the redox potential had decreased to +200 mV. The initial pyrrhotite concentrate and residue compositions are compared in Table 10.

Mineralogical examination indicated a decrease from 8-10% magnetite in the head to less than 2% in the residue.

Although these observations clarify the delay in H₂S evolution, they do not explain the observation that reduction of the generated ferric ions occurs very slowly, despite the presence of an excess of fresh pyrrhotite. Since H₂S is generated at the surface of the pyrrhotite particles, due to ferric ion reduction, the ferric ion could be assumed to take place at the same surface, which might protect the ferric ion from re-oxidation as a layer of elemental sulphur around these particles. By this means, the action of acid on the pyrrhotite would be inhibited, at least temporarily. The exact mechanism of the formation of the particles did not suggest the presence of a sulphur coating, unless its thickness was below the detection limit of the instrument.

During continuous leaching, the leach slurry will be contacted with hydrochloric acid of low redox potentials will result. Precipitation of elemental sulphur should not take place on the surface of the pyrrhotite particles, but rather, if at all, on the surface of the magnetite particles. It is, therefore, concluded that during continuous HCl leaching of pyrrhotite concentrates, no incubation period should be encountered, nor the problems associated with it.

On the other hand, by purposely raising the redox potential of the leaching solution, the leaching reactions can be stopped. In an industrial operation, this could be most advantageously done by supplying a sufficient amount of FeCl₃ to the leaching system to induce a sudden cut-off of H₂S evolution. Such a procedure would provide a more comfortable and economic degree of safety, than the construction of, say, caustic scrubbers with fans hooked up to the emergency power supply.

Conclusion

Laboratory-scale leaching testwork has shown that substantially complete leaching of iron from nickeloferous pyrrhotite concentrates can be achieved using only 10-35% excess HCl. Hydrogen sulphide and elemental sulphur as products account for up to 85% and 15% of the contained sulphur, respectively. Final liquor acidities of 35 g/l HCl can be expected in current leaching systems. The rates of iron and nickel dissolution, together with the rate of acid addition, and impurity solubilities are essentially constant for a given mill concentrate and depend mainly on the nature of the gangue minerals. Magnetite contained in the concentrate dissolution preferentially to the pyrrhotite at low acid concentrations. This gives rise to the presence of ferric ions in batch leaching solutions and temporary inhibition of H₂S evolution.

Leaching of nickeloferous pyrrhotite at 90°C does not appear attractive, due to the formation of nickeliferous magnetite. High leaching rates at approximate­ly 60°C would yield an up-graded concentrate and a ferrous chloride leach liquor, low in non-ferrous impurities.

Acknowledgments

The authors wish to thank Falconbridge Nickel Mines Limited for permission to publish this paper and acknowledge their indebtedness to Messrs. P. G. Thorshill, M. P. Sudbury, Dr. L. E. Soderby, and others, for their helpful comments and suggestions.

References


DISCUSSION

K. Jibiki, University of British Columbia, Vancouver, B.C.

K. Jibiki: Can this process apply to the nickel concentrate?

G. Van Weert: For all practical purposes, pentlandite is insoluble in HCl under the leach conditions described in this paper. Such hydrochloric acid leaching of nickel concentrates, i.e. pentlandite/pyrrhotite mixers, can only be used for upgrading nickel concentrates.

K. Jibiki: Can the incubation period be interpreted as a surface oxidation layer?

G. Van Weert: There is certainly a temptation to postulate such a layer, but I prefer to emphasize the effect of the redox potential. As shown in Figure 5, H₂S will form in a reduced solution. No elemental sulphur layer could be detected on the surface of the pyrrhotite particles.

K. Jibiki: Have you ever used other kinds of acid—for example, sulphuric acid?

G. Van Weert: The treatment of pyrrhotite for sulphur recovery in the sulphate system has been explored by several researchers, particularly by W. W. Downes of the Mines Branch and also by Falconbridge in an autoclave pilot operation (P. G. Thorshill, Can. Met. Quarterly, Vol. 8, 1969, pp. 219-225).

W. Kanda, Sherritt Gordon Mines Ltd., Port Saskatchewan, Alberta

W. Kanda: A few years ago, a process was disclosed in which sulphur dioxide was used for dissolution of iron from pyrrhotite. The products of this process were ferric sulphate solution, precious metals, enriched leach residue and elemental sulphur. Did you consider this process as an alternative method for the treatment of pyrrhotite in the chloride system?

G. Van Weert: Any large-scale processing of pyrrhotite must involve regeneration of the leaching acid. For five years now, Falconbridge has recovered HCl from NICL/H₂O crystals on a large scale. We have recently extended this knowhow to the hydrolysis of FeCl₃ solutions, as would be obtained by HCl leaching of pyrrhotite. I don’t know that the practicability of generating SO₂ from ferrous sulphate has been demonstrated to the same extent.

R. A. Farber, Sherritt Gordon Mines Ltd., Fort Saskatchewan, Alberta

R. A. Farber: What iron concentrations were you able to attain in your leach liquors?

G. Van Weert: The iron concentration is a function of the feed acid normality; the higher the normality, the higher the iron concentration in the filtrate.

In practice, 6N chloride is the optimum.

R. A. Farber: Would you care to comment on the removal of iron from the ferrous sulphate liquor?

G. Van Weert: Hydrochloric acid and iron oxides can be recovered from the liquor by various methods. One of these is the Amann process, licensed to Woodall-Ducham (or Rothery in England). As mentioned to Dr. Kanda, Falconbridge has also been active in this area.
PART TWO

PAPER 3

Treatment of ferrous chloride liquors in the Falconbridge fluid-bed hydrolyzer

by

G. Van Weert, E.C. Robertson and J.H. Christiansen

HYDROMETALLURGY

Treatment of Ferrous Chloride Liquors In the Falconbridge Fluid-Bed Hydrolyzer

G. Van Weert, Manager, Process Metallurgy, Falconbridge Nickel Mines Limited
E. C. Robertson, Project Engineer, Falconbridge Metallurgical Laboratories, and J. H. Christiansen, Industrial Wastes Engineer, Sudbury Operations, Falconbridge Nickel Mines Limited

Abstract

Design and operation of a pilot plant for the recovery of hydrochloric acid and granular, iron-free iron ores from ferrous chloride leach liquors is described. The pilot plant was operated for a total of 13 months between December 1970 and April 1972. A fluid-bed hydrolyzer, sized for a throughput of one ton per day of iron, was operated directly into the 21-foot-diameter bed through a fourth, having the same design features as those developed and patented for the 11-foot-diameter commercial-scale nickel chloride hydrolyzer in operation at the Falconbridge Recovery in Norway. Natural gas was evaluated in the pilot plant, whereas naphtha or propane are used in the nickel chloride hydrolyzer.

The pilot-plant operation provided unique data on fuel requirements for the hydrolysis of ferrous chloride solutions. Also studied were the effects of solution oxidation and ferrous chloride formation, fuel solution concentration, temperature and control of bed, pressure control in the off-gas system, and control of particulate distribution in the bed by under-

Introduction

The regeneration of hydrochloric acid by hydrolysis of nickel chloride in a fluid bed of nickel oxide has been described earlier in connection with the Falconbridge Nickel Leach Process, use since 1968. Further investigations in the field of chloride metallurgy were carried out in company laboratories, and emphasis was placed on applying this experience to develop new methods of processing base-metal concentrates or furnace mattes.

The sulphide minerals of the Sudbury district consist principally of pentlandite, chalcopyrite and pyrrhotite. Only the latter dissolves rapidly in hydrochloric acid, producing an up-graded concentrate, hydrogen sulphide and ferrous chloride, from which sulphuric acid may be regenerated for recycle. Similarly, selective acid leaching of high-iron mattes yields a high-iron sulphide residue and ferrous chloride for HCl regeneration. The hydrogen sulphide generated during such leaching can be used for the precipitation of metal sulphides from leach liquors, so is a sulphur-bearing fuel gas substituting for natural gas in a sulphur recovery plant or for the removal of sulphur dioxide from oxygen-bearing smelter off-gases. The latter alternatives could be used under circumstances in which the production of sulphuric acid is unattractive.

As this 4th Annual Meeting of the Hydrometallurgy Section of The Metallurgical Society of CIM is devoted to the hydrometallurgy of iron salts contained in metallurgical liquors, an extensive review of such methods in this presentation is superfluous. It is sufficient to note that the hydrometallurgy of iron salts contains in metallurgical liquors is a vast field of study. The Falconbridge Fluid-Bed Hydrolyzer process has been applied to recover hydrochloric acid from ferrous chloride leach liquors. The process is efficient, economical, and environmentally friendly. The pilot-plant operation provided unique data on fuel requirements for the hydrolysis of ferrous chloride solutions. Also studied were the effects of solution oxidation and ferrous chloride formation, fuel solution concentration, temperature, pressure control in the off-gas system, and control of particulate distribution in the bed by under...
FIGURE 1 — Hydrolyzer Pilot-Plant Circuit.

FIGURE 2 — The hydrolyzer-cooling tower circuit of the Falconbridge Hydrolyzer Pilot Plant.

The hydrolyzer is a process for recovering ferrous chloride from leach liquors. It involves the following reactions:

1. \[ ZFeCl_2 + 2H_2O \rightarrow FeCl_3 + 2HCl \]
2. \[ \frac{1}{2}O_2 + 2H_2O + l/2ZFeCl_2 \rightarrow ZFeO \left( \text{granular} \right) + 4HCl \]

The fresh ferrous chloride liquor from the dissolver was filtered and then pumped into the solution reservoir, to replenish the hydrolyzer-cooling tower circuit. The solution reservoir served as a pump tank for the cooling tower circuit, which also supplied the head tank from which the hydrolyzer feed solution was drawn. The hydrolyzer feed rate was controlled by means of a ball-valve, which was in turn controlled by the bed temperature recorder/controller. A magnetic flowmeter with totalizer recorded the feed solution flow to the hydrolyzer. The feed solution entered the hydrolyzer through a lance and was directed onto the surface of the bed in "rope" fashion. The feed lance consisted of a 6-ft length of \( \frac{1}{2} \)-in. Ti tubing in a 1-in. stainless steel pipe, with glass-fibre insulation in the annulus. It was mounted centrally on the hydrolyzer roof.

The hydrolyzer construction can be seen in Figure 3. The hearth diameter was 27 in. for a bed height of 66 in. Over-all inside height was 132 in. The freeboard area was expanded to 40 ft, by eliminating the inside refractory. External fibreglass insulation prevented condensation of HCl on the steel shell. Roof openings for the regular and emergency gas outlets and the central feed point were provided. The hearth had one regular and one spare calcine discharge, as well as nine nozzle openings at the same 6-in. spacing as the commercial NICO Hydrolyzer™. In fact, hexagonal bricks from the installation at Nikkelverk were used for the hydrolyzer hearth.

More details of hearth and nozzle construction are given in Figure 3. Air and natural gas were fed to the annular zone of the lance, where it decomposed into granular iron oxide, hydrochloric acid and water vapour. The gaseous reaction products and other off-gases passed through a cyclone and were quenched in the cooling tower by co-current contact with, and evaporation of, circulating cooling solution. The latter was continually diluted with fresh ferrous chloride liquor from the iron dissolver to replenish the evaporated water. After fines were removed by means of a cone scrubber, HCl was absorbed in two 36-in.-diameter tray-type adiabatic absorbers and the depleted gases were vented up a FRP stack by means of a titanium fan. The granular calcites in fine cyclone dust were collected and stored separately.

The recovered acid was used to dissolve nail clippings in a FRP leach tank. The dissolver was equipped with a water-sealed, rubber-lined drag conveyor for removing the nail clippings. A water-sealed stack vented the hydrogen released during dissolution.

A constant-level pump tank also served to prevent hydrogen leakage into the absorbers.

The recovered acid was used for the hydrolyzer hearth.
The cooling tower was an acid-brick-lined, Kynar-coated steel tower of 28-in. diameter. At 925°C instead of 850°C, again with no apparent effect on hydrolyzer operation at optimum conditions for combustion; i.e. lowest CO + CO₂ in the off-gases.

**TABLE 1: Operating Conditions and Results for Typical HPP Runs from Campaigns I and II**

<table>
<thead>
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<th>Run</th>
<th>7</th>
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<th>15</th>
<th>16</th>
<th>17</th>
<th>30</th>
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<td>206</td>
<td>143</td>
<td>119</td>
<td>89</td>
<td>70</td>
<td>94</td>
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<tr>
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<td>850</td>
<td>695</td>
<td>620</td>
<td>855</td>
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<tr>
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<td>1754</td>
<td>1754</td>
<td>1754</td>
<td>1754</td>
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<td>Air Factors</td>
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<td>0.318</td>
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</tr>
<tr>
<td>Net H₂O, g/t</td>
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<td>40.4</td>
<td>40.4</td>
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<tr>
<td>Water (sum of above)</td>
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<td>70.7</td>
<td>70.7</td>
<td>70.7</td>
<td>70.7</td>
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<tr>
<td>Natural Gas Consump.</td>
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<td>1500,000 ft³</td>
<td>1500,000 ft³</td>
<td>1500,000 ft³</td>
<td>1500,000 ft³</td>
<td>1500,000 ft³</td>
<td>1500,000 ft³</td>
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</tbody>
</table>

The bed level in the hydrolyzer was controlled by continuous discharge of bed calcine with a variable-speed vibratory feeder mounted at the bottom of the discharge pipe. The calcine, while in the pipe, was accelerated and also acted as a gas seal. The calcine discharge was manually adjusted, and fines from the discharge were recycled at a controlled rate to maintain bed size distribution.

Calibration of the air and fuel flowmeters required careful attention, because great accuracy was needed to control hydrolyzer operation at optimum conditions for combustion; i.e. lowest CO + CO₂ in the off-gasses.

**Hydrolyzer Operating Results**

**GENERAL**

Table 1 summarizes typical operating results obtained during Campaigns I and II. The data show that the most important factor, recognized almost from the start of Campaign I, was the formation and collection of ferric hydroxide. Due to low calcine efficiency and air leakage through the fine calcine return pipe, calcine underflow valve, and some flanges and connections, build-up of Fe₃O₄ occurred in the cooling tower - hydrolyzer circuit. Run 6 reported the highest ferric oxide level in the feed solution; Run 7 was the longest.

**Hydrolyzer operating conditions** were varied only twice from those established as optimum in the bench-scale work. The space velocity was lowered from 0.2 to 0.27 ft³ per minute (based on combustion products only) for Run 13, with no apparent effect on hydrolyzer operation or conversion of calcine. Run 16 was carried out at 925°C instead of 850°C, again with no apparent effect, except for a lower solution feed rate to the hydrolyzer and correspondingly higher fuel consumption.

Although all runs were made with premixed air and natural gas, some testwork with a central fuel nozzle confirmed results obtained in earlier bench-scale testwork. There, operation with non-mixed air-fuel showed the combustion zone to shift from the bed to the freeboard and cyclone. This severely restricted the capability of the bed to accept solution and still remain at operating temperature. Solution feed rate had to be decreased by more than 50%. Off-gas composition and conversion efficiency, however, were not affected.

**FERRIC CHLORIDE**

As mentioned, the ferric concentration of the hydrolyzer feed solution was shown to have the desired level toward improvements and contact of the solution with wall clippings allowed operation at about 10 g/t Fe⁺⁺ early in Campaign II, but with attention diverted to other testwork and recirculating flash losses, the Fe⁺⁺ increased again to 28.8 g/t during Run 20. Earlier bench-scale tests on fluid-bed hydrolysers of ferric chloride had shown high solid conversion efficiencies, only 25% of the ferric feed was retained in the bed. This compared with 86% conversion effi-
The data in Table 1 and Figure 6 show that it is essential to stop the ferric build-up and break the ferric cycle between hydrolyzer and cooling tower. Parrie oxide consumes HCl and dilutes the solution in the cooling tower circuit. This forces ferric chloride out of solution, thereby increasing the chances of crystallization and plugging. It consumes fuel by circulating between cooling tower and hydrolyzer. It may be controlled by adjustment in the fluid bed type of hydrolyzer with direct gas contact pre-evaporators, by the following means:

1. Complete combustion of fuel, leaving a minimum of oxygen in the off-gasses.
2. Sealing of the hydrolyzer and off-gas system to minimize air ingress,
3. Efficient cyclone operation.

**OFF-GAS COMPOSITION**

Many gas samples were taken to check the accuracy of air and natural gas flow rates for combustion efficiency. The latter required control of the air factor between 1.06 and 1.09, allowing little margin for instrumental error. Table 2 gives off-gas compositions characteristic of the latter part of Campaign II.

**HYDROLYZER HEAT DISTRIBUTION**

For most runs in Campaign II, heat balances were calculated, as summarized in Table 3, where it can be seen that the combustion products account for approximately 37% of gross heat input and the various components of the feed solution absorb 45-47%. Losses, including convection and radiation, are less than 10% of the gross heat input with good combustion. In a larger, well-designed installation, heat losses should amount to less than 5% of gross input.

**IRON BALANCES**

Iron balances also were worked out both for the hydrolyzer-cooling tower circuit and for the hydrolyzer alone. The former was calculated from the iron content in the feed solution and the iron discharged in the off-gas. By subtracting these amounts, the amount of iron circulated in the system was calculated. Hydrolyzer feed was calculated from solution analysis and a totalizer reading on the solution flow meter. Typical results are listed in Table 4.

**BED SIZE DISTRIBUTION**

The nature of the hydrolysis reaction is such that new iron oxide is deposited continually on the surface of the bed particles, causing the mean particle diameter of the bed to increase. Figure 7 is a polished section of typical hydrolyzer calcine. The "fining" growth effect and fines agglomeration are clearly visible. Unless steps are taken to control particle growth, defluidization occurs.

In tests of long duration done in a 7-inch-diameter laboratory fluidizer, it was found necessary to crush part of the calcine in order to produce fines suitable for recycle to the bed. This step was included in the HPP and used for most runs. However, it was quickly established that screening the calcine at 28 mesh and recycling the undersize provided sufficient fines to maintain a constant mean particle diameter (Dp) in the bed consistent with good fluidization. Not only was crushing eliminated, but the elutriation of -65-mesh fines past the cyclone into the cooling tower was avoided. These coarse and abrasive fines are preferably kept out of the pumping circuit.

The calculated mean particle diameters (Dp) are given for Run 7 in Table 5. Run 7 was the first in which starting bed and feed took place with a bed Dp of 0.026 = 0.005 inch, the limit subsequently maintained to give good fluidity with a minimum return rate of -28-mesh fines to the hydrolyzer. Crushed fines were still recycled during Run 7; some of these were noted from the high percentage of -65 mesh in the recirculated fines. Later runs used only -28-mesh screened fines for recirculation. Constant hydrolyzer feed size distribution was easily maintained by measuring the percentage of -28 mesh in the discharge cyclone once a shift and modifying the return fines rate.

A continuous elutriation test was also carried out, feeding water only to the bed at 80°F and recirculating crushed fines. Results indicated elutriation of 79% of the -100 + 150-mesh fraction, and 100% of the -150-mesh. Some distortion of -28-mesh material occurred, possibly by thermal spalling.

Feed gases of various forms were used to study the effect on fines generation. Results were inconclusive, but there is no doubt that the HPP operation resulted in less calcine agglomeration than that obtained in laboratory hydrolyzers. By increasing the number

**TABLE 2** Off-Gas Compositions at an Air Factor of 1.06, in vol. %

<table>
<thead>
<tr>
<th>Component</th>
<th>Vol %</th>
<th>Hydrolyzer</th>
<th>Cooling Tower</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1.1</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>CO</td>
<td>6.1</td>
<td>6.0</td>
<td>5.8</td>
</tr>
<tr>
<td>H₂O</td>
<td>35.8</td>
<td>35.4</td>
<td>35.2</td>
</tr>
<tr>
<td>HCl</td>
<td>12.6</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td>Total</td>
<td>49.6</td>
<td>49.0</td>
<td>48.8</td>
</tr>
</tbody>
</table>

**TABLE 4**—Iron Balances for Hydrolyzer Runs 16 and 17

<table>
<thead>
<tr>
<th>Step</th>
<th>Fe</th>
<th>Run 16</th>
<th>Run 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leach Solution</td>
<td>4386</td>
<td>4740</td>
<td></td>
</tr>
<tr>
<td>Hydrolyzer Feed Soln.</td>
<td>4044</td>
<td>4220</td>
<td></td>
</tr>
<tr>
<td>Solids In</td>
<td>4185</td>
<td>4196</td>
<td></td>
</tr>
<tr>
<td>Starting Bed, Calcine</td>
<td>1963</td>
<td>1990</td>
<td></td>
</tr>
<tr>
<td>Recrushed Fine Calcine</td>
<td>1737</td>
<td>1793</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2275</td>
<td>2386</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 5**—Rates, Mean Particle Diameter (Dp), and Tyler Screen Analyses for Run 7

<table>
<thead>
<tr>
<th>Rate</th>
<th>Dp, μm</th>
<th>Screen Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycle Fines</td>
<td>17</td>
<td>100% -65 mesh</td>
</tr>
<tr>
<td>Off-gas</td>
<td>2275</td>
<td>92% -65 mesh</td>
</tr>
<tr>
<td>-28 mesh Only</td>
<td>2157</td>
<td>92% -65 mesh</td>
</tr>
<tr>
<td>Other</td>
<td>1537</td>
<td>92% -65 mesh</td>
</tr>
</tbody>
</table>

**TABLE 6**—Properties of Falcobridge Hydrolyzer Product

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Density</td>
<td>5.09 g/cc</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>12.96 g/cc</td>
</tr>
<tr>
<td>Work Index for Grinding - 50% (-8 mesh)</td>
<td>35.5</td>
</tr>
</tbody>
</table>

**TABLE 7**—Heat Balances for Runs 16 and 17

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Run 16</th>
<th>Run 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>395</td>
<td>405</td>
</tr>
<tr>
<td>Air Factor</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>N/Fe in Feed Soln.</td>
<td>10.8</td>
<td>10.8</td>
</tr>
<tr>
<td>N/Fe in Feed Soln.</td>
<td>10.8</td>
<td>10.8</td>
</tr>
<tr>
<td>Heat Balance</td>
<td>25.8</td>
<td>25.8</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>37.4</td>
<td>37.4</td>
</tr>
<tr>
<td>Sensitive Heat in Solutions</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Sensitive Heat in Coal</td>
<td>10.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Unaccounted</td>
<td>12.4</td>
<td>12.4</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**TABLE 8**—Chemical Analyses

<table>
<thead>
<tr>
<th>Component</th>
<th>Analysis</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.004</td>
<td></td>
</tr>
</tbody>
</table>

Electron-probe analysis showed a coincidence of occurrence of Ca and Sr in pores of the layered structure of the calcine, evidently resulting from the high calcium content of the water used in the HPP. Cyclone dust analysis 0.4-1.4 wt% Cl.

**GRANULAR CALCINE PROPERTIES**

The main product of the Falconbridge hydrolyzer system is high-density Fe₂O₃ in a dust-free granular form. A typical size distribution and other characteristics of this product are reported in Table 4. Electron-probe analyses showed a coincidence of occurrence of Ca and Sr in pores of the layered structure of the calcine, evidently resulting from the high calcium content of the water used in the HPP. Cyclone dust analysis 0.4-1.4 wt% Cl.
Hydrolyzer Off-Gas System

CYCLONE

The cyclone operated at a pressure drop of 3 to 4 in. H.O. The loss improved from less than 25% to around 40% after the flap-trap valve in the discharge line was replaced during Run 9. The cyclone dust catch, as per cent of total iron in the hydrolyzer feed solution, is listed in Table 1. Approximately 75% of the collected cyclone dust measured ~600 mesh.

COOLING TOWER

Cyclone gases entered the top of the cooling tower at 620-640° C and were quenched to 56-106°C through contact with and evaporation of circulating liquid. Temperature measuring tests indicated efficient heat exchange occurring with the geometry used in the cooling tower. After better insulation was applied to the gas ducts, only 5 to 8% of gross heat input to the cooling tower; second, control of the pressure in the freeboard of the hydrolyzer.

The latter was achieved by modifying the pressure drop over the cone valve through a narrow range in response to measurement of the hydrolyzer freeboard pressure. The freeboard was kept at approximately 15 in. H.O, depending on operating conditions. Table 8 lists the effect of the pressure drop over the cone valve on iron removal as measured by iron pick-up in the HCl absorbers.

TABLE 7 — Efficiency of Cone Valve Scrubbing

<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure Drop Over Cone Valve</th>
<th>Ratio of Fe/Cl- in Absorber Underflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 in. H.O.</td>
<td>50/100</td>
</tr>
<tr>
<td>2</td>
<td>1 in. H.O.</td>
<td>49/100</td>
</tr>
</tbody>
</table>

Table 9 lists the effect of the pressure drop over a cone valve on iron removal as measured by iron pick-up in the HCl absorbers.

Iron removal became more complete at the higher pressure drop. It must be kept in mind, however, that this particular cone valve was in poor condition toward the end of Campaign I. Tests were carried out to determine the origin of the iron contamination in the absorber underflow acid. Cobalt chloride, which hydrolyzes much like ferrous chloride in the Falconbridge system, was added to the head tanks at a ratio of Co/Fe=0.97/100 in the feed solution going to the hydrolyzer. After allowing equilibrium to be achieved, samples taken from the cooling tower solution and absorber underflow acid analyzed at a Co/Fe ratio of 0.68/100 and 0.78/100, respectively, indicating that most, if not all, the iron in the absorber underflow came from the hydrolyzer feed and not from spray formation in the cooling tower or cone valve.

Hydrolysis of Solutions Containing Impurities

Run 25 was operated with a simulated hydrometallurgical solution, containing chlorides of Al, Mg, Ca, K, Na and Zn in addition to ferrous chloride. Table 9 gives the concentrations used and a mass balance for the impurities. The total elements, such as K, Na, and Zn, were used, in the test of the absorber underflow or as "unaccounted," presumably consisting of stack losses. Importantly, such as calcium chloride, which hydrolyzed poorly, increased the chlorides content of the cyclone C/F to 63% from approximately 1% under regular operating conditions. The raline contained 15% chloride, versus 0.4% for regular operation.

Summary

The Falconbridge ferrous chloride hydrolysis operation was successfully piloted on a scale of one ton of iron per day at the company's Sudbury Operations.
PART TWO

PAPER 4

Operating experiences with a pilot plant for the electrowinning of nickel from all-chloride electrolyte

by

L.R. Hougen, R. Parkinson, J. Saetre and G. Van Weert

CIM Bulletin, Vol 70, June 1977
Operating Experiences With A Pilot Plant For the Electrowinning of Nickel From All-Chloride Electrolyte

6th ANNUAL HYDROMETALLURGICAL MEETING

Introduction

THE NICKEL REFINING PROCESS practised at Falconbridge Nikkelverk A/S in Kristiansand, Norway, has been described earlier by F. R. Archibald. In this process, copper-nickel converter matte analyzing about 48% nickel, 28% copper and 21% sulphur is treated in a complex series of pyrometallurgical steps to yield cathode nickel by electrowinning and electrowinning from a mixed chloride/sulphate electrolyte. In the 1960's, the company embarked on a research program aimed at developing a process of less complex nature to which modern process controls would be more readily applicable and which would also be less labour intensive. The program resulted in the construction and operation of a commercial-scale pilot plant at the company's Kristiansand operation, utilizing the Falconbridge Matte Leach Process.

Abstract

The Falconbridge Matte Leach Process yields high-purity nickel chloride by selectively dissolving nickel from copper-nickel converter matte with hydrochloric acid, purifying the solution by solvent extraction and crystallizing NiCl₂·H₂O by further acidifying the purified leach liquor. In the Kristiansand Matte Leach Plant, a granular oxide is produced by high-temperature calcination of the nickel chloride for subsequent reduction to a high-purity granular metal product, designated NICKEL M. This paper describes the investigation of an alternate route to processing nickel chloride in which the hydrolysis of the nickel chloride for subsequent reduction is treated in a complex series of pyrometallurgical steps to yield cathode nickel by electrowinning in a pilot circuit containing two production-size electrolysis tanks operated in conjunction with the commercial-scale leach plant.

Keywords: Hydrometallurgy, Electrowinning, Nickel, Chloride electrolytes, Falconbridge Matte Leach Process, Copper-nickel converter, Converter matte, Leaching.
This leaching and refining process is based on the selective dissolution of nickel from copper-nickel matte in hydrochloric acid maintained at high strength to permit a high degree of separation of nickel from copper in a closed co-current leaching operation. Solution purification is affected by solvent extraction and nickel chloride recovery by crystallization from acidic solution. Conversion of the nickel chloride to metal can be effected by direct reduction of the chloride with hydrogen, by electrowinning from dissolved crystals or, thirdly, by hydrogen reduction of oxide obtained by high-temperature hydrolysis of the chloride. The last technique is employed in the Nikkelverk Matte Leach (ML-) Plant for the production of 15 million pounds of nickel per year as a high-purity nickel chloride product.

Crystal production in the Nikkelverk ML-circuit occurs after the purified solution has been contacted with the hot gases which result from the high-temperature hydrolysis of dried nickel chloride. This leads to pick-up of nickel oxide dust in the crystallizer feed solution and the presence of some oxide in the NiCl₂·4H₂O crystals. For the electrowinning testwork, a side stream of purified solution was directly into the ML-Plant scrap crystallizer, bypassing the high-temperature hydrolysis circuit.

Electrolyte Production

Crystal production in the Nikkelverk ML-circuit occurs after the purified solution has been contacted with the hot gases which result from the high-temperature hydrolysis of dried nickel chloride. This leads to pick-up of nickel oxide dust in the crystallizer feed solution and the presence of some oxide in the NiCl₂·4H₂O crystals. For the electrowinning testwork, a side stream of purified solution was directly into the ML-Plant scrap crystallizer, bypassing the high-temperature hydrolysis circuit.

Electrolyte Circuit

A flow sheet for the solution preparation and the electrowinning circuit is given in Figure 2. The solution preparation was pumped to storage tanks and then to a liquid tank, from which it passed under gravity to a controlled rate to a mix tank. Here it was mixed with the catholyte overflow and dechlorinated anolyte. Partial dechlorination of the anolyte was achieved by aeration and absorbing the extracted chlorine in a sodium hydroxide scrubber. The remaining traces of chlorine were removed by passing the solution through a column containing activated carbon prior to being transferred to the mix tank. Provision was also made in this mix tank for the addition of nickel carbonate slurry when pH adjustment was required. The nickel carbonate was precipitated from a side stream of the nickel chloride solution by addition of sodium carbonate and was filtered and washed prior to addition to the mix tank at the required location. The dechlorinated, pH-controlled solution was then pumped through three pressure filters, with an intermediate carbon treatment for the removal of organics. After filtration, the solution was transferred to the electrowinning tank.
the second filter, the nickel chloride solution passed through a heat exchanger, where the temperature was raised to 65-70°C prior to entering a constant-level storage tank, from which part of the solution was gravity fed to the two electrowinning tanks and the remaining flow was returned for dissolution of fresh nickel chloride crystals. The nickel content of the feed solution to the electrowinning tanks was maintained at approximately 130 g/l.

Electrowinning Tanks

The two electrowinning tanks were of regular production size, 7000 by 800 by 1600 mm, and were of fibreglass-reinforced polyester (FRP) construction. Surge and reaction tanks in the circuit were FRP-lined or rubber-lined steel and the pipework was polyvinyl chloride (PVC), reinforced in some areas with FRP. A general view of the electrowinning section of the tankhouse at Nikkelwerk is shown in Figure 3.

A cross-sectional drawing of the anode and cathode arrangement in the tanks is shown in Figure 4. Cathodes were of normal production size, 1140 by 620 mm, and were placed in wooden or FRP frames to minimize edge build-up. Each anode assembly consisted of three graphite pieces, 1300 by 200 by 50 mm, bolted together with copper contact bars to give a total anode width of 620 mm. The graphite below the solvent extraction and crystal washing systems of the nickel chloride crystals. Efficient operation of the solvent extraction and crystal washing systems is therefore essential in the production of high-purity cathodes. It is equally important that contamination of the electrolyte in the electrowinning circuit be avoided, e.g. by corrosion, as all impurities entering the circuit must be removed during electrolysis or build-up in solution.

Effect of Impurities

One particular advantage of this nickel electrowinning technique is the absence of a purification circuit, as impurities are removed during preparation of the nickel chloride crystals. Efficient operation of the solvent extraction and crystal washing systems is therefore essential in the production of high-purity cathodes. It is equally important that contamination of the electrolyte in the electrowinning circuit be avoided, e.g. by corrosion, as all impurities entering the circuit must be removed during electrolysis or build-up in solution.

LEAD

The case of lead is a good example of the requirement for providing pure nickel chloride feed to the electrowinning circuit.

By thorough washing of the nickel chloride crystals, it was possible to reduce the lead content of the crystals to 0.4 ppm. The average lead content of the cathodes was 3 ppm, indicating complete deposition of the lead with the nickel. Typical lead concentrations in the cathodes, the tank feed solution and the cathode nickel are shown in Table 3. No operating problems associated with lead impurities were experienced.

IRON

The average iron content of the washed nickel chloride crystals was 22 ppm. The fact that the average iron content of the washed nickel chloride crystals was 22 ppm. The fact that the average iron content of the washed nickel chloride crystals was 22 ppm. The fact that the average iron content of the washed nickel chloride crystals was 22 ppm....
age iron content of the cathodes was 87 ppm was clear evidence of iron pick-up in the electrowinning circuit. The sources of this pick-up included the stainless steel equipment and the steel tanks in the circuit exposed by damage to their linings. The iron contamination in the crystals, the tank feed solution and the cathodes are shown in Table 4.

No direct relationship between cathode surface quality and iron content of the electrolyte has been confirmed, but it is considered that some pickling observed at pH 2.6 could have been associated with high iron concentrations (0.1-0.6 mg/l) in the electrolyte.

COPPER
The average copper content of the cathodes was 27 ppm, compared to only 6 ppm in the crystals, and the discrepancy was attributed to contamination from the copper conductors on the electrowinning tanks. Typical copper concentrations in the crystals, the tank feed solution and the cathodes are shown in Table 5.

Dendrite formation on the cathodes became a problem as the copper concentration in the electrolyte increased. Consequently, it was desirable to maintain the concentration below 1 mg/l to prevent dendrite growth and thereby reduce the risk of damage to the adjacent anode diaphragms during cathode removal. During one short period of the investigation, the concentration inadvertently did increase to 13.8 mg/l and the formation of large dendrites occurred, as shown in Figure 7.

COBALT, MANGANESE, ARSENIC AND ZINC
The concentrations of these elements in the electrolyte and the cathodes were low and constant throughout the test work, as they were mostly removed in the matte leach process. The presence of 1-4 mg/l cobalt, <2 mg/l zinc, <0.2 mg/l arsenic and <0.2 mg/l manganese did not result in any operating problems.

CARBON
The organic carbon levels in the electrolyte were initially high and coincided with several operating problems. The sources of carbon were traced remaining from the solvent extraction process in the ML plant, non-metallic equipment in the circuit, and broken wooden cathode frames. During this initial period, the carbon concentrations in the feed solution were in the range of 50-100 mg/l, resulting in 36-78 ppm in the cathodes, with correspondingly high oxygen and hydrogen levels. A simple activated-carbon treatment at this time was not capable of reducing the carbon concentration in the electrolyte to below 50 mg/l. A greater reduction was achieved by holding the anode bag in a settling tank to allow separation of most of the entrained organic from the solvent extraction process. Filtration of the booster solution after settling, followed by a carbon treatment was effective in removing most of the remaining organic.

In laboratory tests, it had been shown that traces of organics from the solvent extraction process and the pilot circuit could be removed efficiently by activated-carbon treatment, but the organics introduced by degradation of the wooden cathode frames could not. After the replacement of the wooden cathode frames with FRP frames, it was possible to maintain the carbon content in the pilot-circuit electrolyte and cathodes at 8-23 mg/l and 6-22 ppm, respectively. Operation of the electrowinning tanks with this level of organics and an electrolyte pH of 1.5 resulted in a marked decrease in the oxygen and hydrogen contents of the cathodes, an improvement in their surface condition and an increase in the ductility of the starting sheets. Typical levels of carbon in the crystals, the tank feed and the cathodes are given in Table 6.

Starting Sheets
Regular production starting sheets, made in the mixed chloride-sulphate electrolyte, were used in most of the test work. Preparation of starting sheets from the nickel chloride electrolyte and their use for subsequent cathode production were also evaluated, however, and satisfactory procedures established. Stain­less steel and titanium blanks were tried, but the early attempts were unsuccessful due to the high stress in the deposits, which resulted in either cracking and lifting of the nickel during deposition or complete exfoliation and separation from the blank while in the cell. At this time, the level of organic contamination in the electrolyte was high, but after this was decreased the stress in the deposits was also decreased and satisfactory starting sheets were prepared. Some improvement in the ductility of the deposits may also have been realized by decreasing the pH of the electrolyte to 1.0. The use of titanium blanks was discontinued, as the bond with the starting sheets was generally inadequate for reliable operation and the lower-priced stainless steel was preferred. A slightly sand-blasted surface on the stainless steel gave satisfactory performance. Straightening of the starting sheets by roller leveling was evaluated on a starting-sheet machine in the copper tankhouse. Although the method proved to be acceptable, it was evident that, in production, the hardness and rigidity of nickel compared to those of copper would necessitate much heavier rolls than were available on this machine. The punching method of attaching lugs to copper starting sheets, which is part of the starting-sheet machine operation, was found to be satisfactory for the nickel starting sheets. Spot welding of the loops was an acceptable alternative method of attachment.

Cathodes
The use of straightened starting sheets did not present any problems in cathode production, but uniformity and a good-quality blank was maintained. A slow flow of anolyte was withdrawn from each anode bag separately, but the circulation of the anolyte from each anode along with the chlorine. The diaphragms and the chlorine collection method used in electrowinning from all-chloride electrolyte were not part of the test work. Preparation of starting sheets from the nickel chloride electrolyte and their use for subsequent cathode production were also evaluated, however, and satisfactory procedures established. Stainless steel and titanium blanks were tried, but the early attempts were unsuccessful due to the high stress in the deposits, which resulted in either cracking and lifting of the nickel during deposition or complete exfoliation and separation from the blank while in the cell. At this time, the level of organic contamination in the electrolyte was high, but after this was decreased the stress in the deposits was also decreased and satisfactory starting sheets were prepared. Some improvement in the ductility of the deposits may also have been realized by decreasing the pH of the electrolyte to 1.0. The use of titanium blanks was discontinued, as the bond with the starting sheets was generally inadequate for reliable operation and the lower-priced stainless steel was preferred. A slightly sand-blasted surface on the stainless steel gave satisfactory performance. Straightening of the starting sheets by roller leveling was evaluated on a starting-sheet machine in the copper tankhouse. Although the method proved to be acceptable, it was evident that, in production, the hardness and rigidity of nickel compared to those of copper would necessitate much heavier rolls than were available on this machine. The punching method of attaching lugs to copper starting sheets, which is part of the starting-sheet machine operation, was found to be satisfactory for the nickel starting sheets. Spot welding of the loops was an acceptable alternative method of attachment.

Cathodes
The use of straightened starting sheets did not present any problems in cathode production, but,

![TABLE 5 - Typical Copper Levels During Various Seven-Day Tests](image)

<table>
<thead>
<tr>
<th>Washed Crystals (ppm)</th>
<th>Tank Feed (ppm)</th>
<th>Cathodes (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td>13</td>
<td>12</td>
</tr>
</tbody>
</table>

![TABLE 6 - Typical Carbon Levels During Various Seven-Day Tests](image)

<table>
<thead>
<tr>
<th>Washed Crystals (ppm)</th>
<th>Tank Feed (ppm)</th>
<th>Cathodes (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>323</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>323</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>323</td>
<td>31</td>
<td>30</td>
</tr>
</tbody>
</table>

**Conclusions**
Good-quality starting sheets and cathodes can be made by electrowinning from all-chloride electrolyte derived from the high-purity NiCl2-H2O crystals produced by the Falconbridge Matte Leach Process.

**Acknowledgments**
The authors wish to thank the management of Falconbridge Nickel Mines Limited and Falconbridge Nikelverk A/S for permission to publish this paper.

**References**

**DISCUSSION**
C. J. Krauss: Did you measure cathode overpotential and, if so, was there any relationship between cathode deposit surface quality and cathode overpotential? Authors' Reply: No cathode overpotentials were measured during the pilot-plant investigation and attempts were made to relate our observations on cathode surface quality with electrolyte impurities.

W. W. Harvey: What were the factors influencing your decision to bag the anodes rather than the cathodes, as is sometimes done?

Authors' Reply: Bagging of the graphite anodes used in electrowinning from the all-chloride nickel electrolyte was necessary to collect the released chlorine. The diaphragms and the chlorine collection methods used resulted in a satisfactory working atmosphere in the tankhouse and provided chlorine gas for use elsewhere in the plant, with very little air dilution.

W. W. Harvey: You say that effluent was removed from each anode bag separately?

Authors' Reply: A slow flow of anolyte was withdrawn from each anode bag separately. Each tank was equipped with a manifold pipe in each anode bag in order to draw from each anode along with the chlorine. The diaphragms and the chlorine collection methods used resulted in satisfactory working atmosphere in the tankhouse and provided chlorine gas for use elsewhere in the plant, with very little air dilution.

**Acknowledgments**
The authors wish to thank the management of Falconbridge Nickel Mines Limited and Falconbridge Nikelverk A/S for permission to publish this paper.

**References**
W. W. Harvey: What pattern of drill holes do you employ for sampling cathodes in order to obtain a composite chemical analysis and how does this analysis compare with that after melting?

Author's Reply: The sampling methods used for nickel cathodes to obtain a composite chemical analysis are rather involved and our procedures generally follow those recommended in ASTM B39-75.

There will normally be some differences in the analysis of a cathode and that of a melt made from the cathode, but this will depend on the melting technique used. For instance, by vacuum melting, a reduction in hydrogen and oxygen will be obtained and, although air melting will also reduce the hydrogen concentration, the oxygen content of the melt will depend on the deoxidation procedure used. Contamination of the air melt by the deoxidants, such as silicon or magnesium, will occur of course. With reference to the other impurities shown in Table 7 of this paper, no change should occur in the cobalt, copper and iron concentrations, but lead should be reduced by vacuum melting. Zinc and carbon levels should be reduced by melting in air or vacuum, but no significant difference should be expected in the sulphur content.

V. Ettel: I presume that small concentrations of HCl and Cl were present in your catholyte. Did you measure how much HCl and Cl desorbed from the catholyte were present in the atmosphere? Could you smell them?

Author's Reply: Yes, our catholyte did contain HCl, and this was introduced with the nickel chloride crystals, used for replenishing the electrolyte. Throughout most of the pilot-plant operation, the electrolyte pH was maintained at what we have referred to as the "natural" pH of the circuit; i.e. approximately 1.0. Operation at this pH required that the crystal washing be thorough, and the acid contents of the crystals after three different washing tests are shown in Table 5 to be 0.15 to 0.20%. Actually, it was found that this could be reduced to less than 0.05% and, under these conditions, operation at a pH of 1.0 was possible without any nickel carbonate requirement.

The level of chlorine in the catholyte was not measured at the time of this investigation, but it can be reported that an odour of chlorine was not detectable over the deposition tanks. However, tests have subsequently been made over similar tanks, and chlorine concentrations in the atmosphere, measured with a Bran and Luebbe Imcometer, were generally less than 0.5 ppm.

One main concern with regard to operating conditions around the tanks was the possibility of a build-up of electrolyte spray in the atmosphere above the tanks due to hydrogen release at the cathodes, while operating at a pH of 1.0. Cathode efficiency, however, was an acceptable 97-98% and working conditions remained satisfactory around the two tanks used in the pilot program. Nevertheless, a faster accumulation of nickel salts was observed on the copper conducting bars of the pilot tanks than on those of the regular production tanks and it is possible that operation on a larger scale may require some action to reduce electrolyte spray.

V. Ettel: What diaphragm material did you use?

Author's Reply: Acrylic-type fibers have proved to be most suitable as diaphragm material in this electrowinning process. Dynel and Orion, for instance, have given satisfactory performance.

Prochem's NITROX process

by

Gus Van Weert, Kenneth J. Fair and John C. Schneider

Introduction

cyanidation is the principal process for extracting gold from ores. Many primary gold ores, however, are partially or totally refractory in the conventional cyanidation process.

considerable success has been achieved with new gold leaching techniques, such as intensive cyanidation, pressure cyanidation, carbon-in-leach cyanidation, etc. these techniques however, do not offer substantial gains in gold extraction from refractory pyrite.

the more drastic pretreatment processes such as roasting, chemical oxidation, autoclave oxidation, and bacterial oxidation all utilize oxidation to break down the structures of pyrite and arsenopyrite. this generally renders the gold amenable to cyanidation.

comparative cost studies indicate that the oldest commercial pretreatment method, i.e. high temperature roasting, is currently the least expensive option if the sulphuric acid can be sold. it operates with air at atmospheric pressure and is characterized by fast reaction rates. for an alternative hydrometallurgical concentrate treatment method to be competitive, it too should operate with air at atmospheric pressure and with fast reaction rates. the nitrox process meets these conditions.

nitrox process

nitric acid in aqueous solution reacts vigorously with arsenopyrite at moderate strengths and temperatures, according to the following reaction:

\[ 3\text{FeAsS} + 14\text{HNO}_3 + 2\text{H}_2\text{O} \rightarrow 3\text{FeAsO}_4 + 2\text{H}_2\text{SO}_4 + 14\text{NO} + 14\text{H}_2\text{O} \] (a)

pyrite is also attacked:

\[ 3\text{FeS}_2 + 18\text{HN0}_3 \rightarrow 3\text{Fe}^++ 3\text{SO}_4^{2-} + 3\text{H}_2\text{SO}_4 + 15\text{NO} + 6\text{H}_2\text{O} \] (b)

such aqueous oxidation of sulphide minerals will produce elemental sulphur, which may interfere with gold extraction. pyrite reacts quite differently with nitric acid than the copper sulphide minerals; it has been found to produce only 3% elemental sulphur vs 45% to 75% for chalcopyrite and digenite, respectively.

it is important to note that air, or oxygen, is not involved in these reactions; the nitric acid acts as the oxidant, yielding NO gas as the reduced species.

economic and environmental considerations require complete recycle of the oxidant, i.e. nitric acid. for this it is necessary to regenerate HNO3 from the NO gas, a known technology in the chemical industry:

\[ 3\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{N}_2\text{O}_3 \] (c)

\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \] (d)

\[ 2\text{NO} + \frac{3}{2}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \] (e)

the NO oxidation with air to NO3 is very fast. however, subsequent absorption of NO3 in water to give HNO3 releases another NO and heat, both of which retard efficient absorption. commercial nitric acid plants use up to 30 stages with intermediate cooling of the gases and liquids.

the nitrox process has innovatively combined state-of-the-art agitation knowledge with well established nitric acid
approximately 59% NO, and up to 15% O2, on a dry basis. This gas is
condensed to recover the water for use as wash water and lime
without the reactor system, leaving an off-gas containing approxi-
but will also oxidize completely.

Pyrite reacts somewhat slower, whereas arsenopyrite can be complete in minutes, depending on the nitric
acid concentration. Pyrite nitrate formation is somewhat restrained to the process at all. Sulfate, gypsum and iron
hydroxides all remove water from the oxidation circuit. The
largest amount of water, however, is removed via evaporation
in the reactor system as a result of the heat generated by oxidation
of the pyrite and arsenopyrite.

The pH adjustment section is designed to prevent gypsum deposition on vessel walls. Solids recircula-
tion provides seed particles for optimum gypsum precipitation,
and subsequent filtration.

Reactions (a) and (6), can, and will, proceed under gypsum
precipitation conditions. It has been confirmed that the rates of
pyrite and arsenopyrite oxidation with nitric acid are extremely
temperature dependent. These rates can be controlled by the
reaction temperature, which in turn can be controlled by the air
volume flowing through the pH adjustment section.

The slurry then enters the NITROX reactor where the temper-
ateur is allowed to increase to achieve thermal balance between
heat generation from sulphide to sulphate oxidation and from
nitric acid generation, and heat removed by water evaporation.
The maximum temperature theoretically attainable is the boiling
point of the solution at 101°C. 103°C. The air, however, will
lower the vapour pressure of water, and hence the "boiling"
point to approximately 85°C. At this temperature, oxidation of
arsenopyrite can be complete in minutes, depending on the nitric
acid activity, i.e. its apparent concentration in the sulphuric
acid, ferric sulphate leach liquor. Pyrite reaction somewhat slower,
but will also oxidize completely.

On the gas side, the bulk of the nitric acid is regenerated
within the reactor system, leaving an off-gas containing approxi-
ately 5% NO, and up to 15% O2, on a dry basis. This gas is
scrubbed with lime and water before passing to stack or to a
turbine to recover the water for use as wash water and lime
slurry make-up. The scrubber solution contains both calcium
nitrate and nitrite. It can be returned to the reactor system or to
precipitation, depending on its lime content.

The leached solids and leach liquor are fed to the precipitation
section, where lime and limestone are added at a constant pH of
approximately 5. CO2 is evolved, stripping the slurry of dis-
solved NO3 gases thereby allowing atmospheric filtration of the
precipitate. Calcium carbonate utilization is over 90% under
these conditions. The filtrate contains calcium nitrate and is
returned to the slurry make-up and feed tank, thereby closing
the liquor circuit.

The wash solids are discharged to a regular stabilization and
cyanidation circuit for gold and silver recovery.

The water balance is not problematic, and should not be a
constraint to the process at all. Sulfuric, gypsum and iron
hydroxides all remove water from the oxidation circuit. The
largest amount of water, however, is removed via evaporation
in the reactor system as a result of the heat generated by oxidation
of the pyrite and arsenopyrite.

Results

Several ores and concentrates have been tested for their response
to the NITROX process. Most materials were treated by a
standard test which, although not optimal for each material,
gave a good indication of the applicability of the NITROX
process. All materials tested so far have responded very well, as
indicated in Table 1. As an example of the difficulty of the
materials being treated, Sample C is a flotation concentrate pro-
duced subsequent to the cyanidation circuit of an existing plant.
Sample E is a cyanided roaster calcine that yielded a further
increase to the cyanidation circuit of an existing plant.

The process appears to work equally well on silver-bearing materials.
Although only two high silver materials were treated, their
behaviour was no different than the gold. Sample E is a cyanided roaster calcine that yielded a further
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The proces...
Abstract

The increase in the gold price, which occurred in the seventies, has resulted in renewed interest in treating refractory gold bearing arsenopyrites by other means than the conventional roasting with air.

Current hydrometallurgical alternatives include pressure oxidation and bio-oxidation. The former requires oxygen instead of air, the latter long residence times.

The NITROX process utilizes the oxidizing capabilities of nitric acid on sulphide and arseno minerals. Regeneration of the nitric acid, while maintaining the water balance of the system, has been solved in a way as to allow recycle of the reagent. The sulphuric acid generated is neutralized with fine limestone. The NITROX process operates at atmospheric pressure with air.

Gold and silver recoveries by subsequent conventional cyanide leach have exceeded 90% for nearly all ores and concentrates treated to date. The residence time of the arsenopyrite in the NITROX reactor system can be adjusted over a wide range to suit the nature of the deposit, the size of the operation and the degree of oxidation required.
Introduction

Ever since the replacement of the chlorine based Platner process for gold extraction late in the 19th century by the still predominant cyanide process (1), mining companies and prospectors have generally avoided "refractory" gold and silver ores by walking away from such deposits or filing the details away under "Future Activities (for somebody else)". As long as conventional deposits could easily be found in cooperative jurisdictions, this made sense.

With an increasing world population and an increasing volume of economic activities, total demand for gold has grown, resulting in an all time high price, certainly in inflation adjusted Canadian dollars (2). This has resulted in a search for new deposits, reworking of old deposits, especially tailing dumps, adoption of new techniques (heap leaching) and a dusting off these "Future Activities" files.

Figure 1: Gold Prices in Canadian Dollars

Possibly because of the extra high monetary rewards and the large number of gold discoveries, treatment of refractory gold and silver ores has received considerable attention in Canada. The majority of refractory gold and silver ores involve sulphides and arsenides, with arsenical pyrites representing the bulk of these (3). The following remarks refer specifically to the latter group of refractory materials described herein by the designation: arsenopyrites.

Arsenopyrite Treatments

Treatment of arsenopyrite generally involves complete oxidation of those sulphides and arsenides, which contain the gold and silver values. Where such oxidation is incomplete, subsequent gold extraction tends to be incomplete (4,5). This has also been found true with the NITROX process on samples tested to date.

The logical commercial oxidation agent for arsenopyrite is air, since it is free (at least at the plant intake). Processes not using air, but other oxidation agents, such as H_2O_2 or Cl_2 derived principally through consumption of electrical energy, have not found industrial acceptance. Even O_2 production from air requires electrical energy.

There are several air based processes currently under consideration for oxidizing auriferous arsenopyrites. Table I lists their highlights:

Table I: Characteristics of Processes for Oxidation of Arsenopyrites (6)

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Pressure</th>
<th>Oxidation</th>
<th>Gold Recovery</th>
<th>Capital Investment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roasting</td>
<td>Air in gas</td>
<td>Atm</td>
<td>Very fast</td>
<td>90+ %</td>
</tr>
<tr>
<td>Pressure Autoclave</td>
<td>O_2 in sol’n</td>
<td>High</td>
<td>Fast</td>
<td>90+ %</td>
</tr>
<tr>
<td>Bacterial Oxidation</td>
<td>Air in sol’n</td>
<td>Atm</td>
<td>Slow</td>
<td>90+ %</td>
</tr>
<tr>
<td>NITROX Process</td>
<td>HNO_3 in sol’n</td>
<td>Atm</td>
<td>Fast</td>
<td>90+ %</td>
</tr>
</tbody>
</table>

Pyro-oxidation of arsenopyrite (at roasting temperatures of approximately 525°C) proceeds very fast. Achieving similar rates in a hydrometallurgical system is impossible; neither is it necessary. Roasting requires complete utilization of all oxygen in seconds, to maintain the calcine at temperature and, especially in a two stage system, manipulate the chemistry. In the alternative hydrometallurgical systems the air or oxygen can be depleted nearly at leisure, it’s basically a matter of equipment volume. The oxygen is consumed in solution, but is stored in the gas phase. Transfer of oxygen from the gas phase to the liquid is one step, if not the limiting step, in arsenopyrite oxidation. In the pressure autoclave system this is dealt with by the use of oxygen under high pressure. This increases solubility in, and oxygen transfer to the process slurry.
Bacterial oxidation faces a particular challenge in this regard. Since the oxygen solubility in water at sealevel and room temperature is only 9 ppm, the process liquor has to be constantly exposed to air to make the oxidation of arsenopyrite proceed. Literature references suggest that this is achieved by air sparging and liquor agitation, similar to practices in the pharmaceutical and fermentation industries. Oxygen transfer from air under such conditions measures at best 1 to 2 kg O$_2$ per HP-hour, under laboratory conditions, but is proportional to HP$^{0.5}$ for viscous solutions and HP$^{-1}$ for water in agitated tanks (7). Hence, the larger the vessel, the lower the O$_2$ transferred per HP-hour. In addition, solids, surface active agents and higher temperatures all tend to reduce the oxygen transfer.

Nitric acid in Extractive Metallurgy

The use of nitric acid for metallurgical processes was first explored during and after the First World War, when industrial synthesis of ammonia by the Haber process allowed nitric acid to be produced in large quantities. Literature from this period clearly established the oxidation potential of nitric acid for sulphide minerals (6, 9). Containment problems, however, favored other processes.

The Second World War brought increased demand for nitric acid, and with it, new technologies for its manufacture and containment. Chrome iron first, and austenitic stainless steels subsequently moved the industry away from the ceramic tiled equipment and crushed granite packing material used up to that time. The use of stainless steels allowed pressurizing the processes of ammonia combustion and nitric acid absorption, producing higher grades of nitric acid in much more compact equipment. Extractive metallurgists recognized the advances made in nitric acid production and regeneration, and again researched its application to sulphide minerals in the sixties and seventies.

Innovative work was done by Bjorling, who explored the action of nitric acid on a range of sulphides, in particular iron sulphide (FeS), pyrrhotite (Fe$_7$S$_8$) and pyrite (Fe$_3$S$_2$). He found that sulphides such as pyrite formed sulphate in reaction with nitric acid whereas "lower" sulphides such as pyrrhotite formed largely elemental sulphur. Since his objective was the production of elemental sulphur as a by-product, pyrite required decomposition to iron sulphide by partial roasting or sulphur distillation at elevated temperature prior to nitric acid treatment. This made the approach too complex. Kennecott thoroughly explored the nitric acid metallurgy of chalcocyprite on a laboratory scale (11, 12). Changing economic conditions cancelled a planned pilot plant trial.

The NITROX Process

Several aspects of the NITROX Process will be discussed in this paper.

1. General
2. HNO$_3$ regeneration
3. Solid/liquid separation
4. Treatment for cyanidation

General

A Technical Note has been published on the NITROX Process (13), and is attached to this Preprint for reference.

Two molar nitric acid reacts vigorously with arsenopyrite at 85°C; oxidizing and solubilizing the mineral constituents:

$$3\text{FeAsS} + 14\text{HNO}_3 \rightarrow 3\text{FeAsO}_4 + 3\text{H}_2\text{SO}_4 + 4\text{NO} + 14\text{H}_2\text{O}$$  \hspace{1cm} (1)

Air, or oxygen, is not required; the nitric acid acts as oxidant yielding NO as the reduced species:

$$14\text{HNO}_3 \rightarrow 7(\text{H}_2\text{O} + \text{N}_2\text{O}_5) \rightarrow 7\text{H}_2\text{O} + 2\text{N}_2 + 14\text{NO}$$  \hspace{1cm} (2)

$$3\text{FeAsS} + 2\text{NO} + 3\text{H}_2\text{O} \rightarrow 3\text{FeAsO}_4 + 3\text{H}_2\text{SO}_4$$  \hspace{1cm} (3)

The nitric acid needs to be regenerated from the evolved NO for economic and environmental reasons; in the NITROX Process this is done with air:

$$14\text{NO} + 10\frac{1}{2}\text{O}_2 \rightarrow 7\text{H}_2\text{O} + 2\text{N}_2\text{O}_5$$  \hspace{1cm} (4)

A NITROX Process block diagram is given in Figure 2. Arsenopyrite is slurried in calcium nitrate bearing filtrate, then contacted with part of the reactor exit slurry, containing ferric arsenate and sulphuric acid according to reaction (1). Gypsum is precipitated and the slurry becomes acidic with nitric acid:

$$3\text{Ca(NO}_3)_2 + 3\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 6\text{HNO}_3$$  \hspace{1cm} (5)

The NITROX Process uses the generated sulphuric acid to reconstitute nitric acid from the calcium nitrate in the filtrate. Essentially, this allows nitric acid to exit the reactor, enter the precipitation, convert to calcium nitrate and be reconstituted to nitric acid in the reactor feed tank. It is important to realize that in the NITROX process, nitric acid, as the oxidant, does not need to be removed or recovered from the reactor exit slurry. Neutralization removes its oxidative powers. The high solubility of calcium nitrate allows good washing from the residue, and recycle to the slurry feed tank. The nitric acid is not a catalyst, it is a reagent in the NITROX Process.
Reaction (1) occurs in the reactor system, generating large volumes of NO gas, and consuming nitric acid. Reviewing reactions (1) and (5) it is clear that the 3 $\text{H}_2\text{SO}_4$ produced by reaction (1) can only generate 6 $\text{HNO}_3$ by reaction (5), not the 14 $\text{HNO}_3$ consumed in oxidation of arsenopyrite. Hence, additional nitric acid is required, and in the NITROX reactor system this comes from the evolved NO gas, using a patented (1A) development, involving gas/slurry contactors.

Reaction (1) occurs very fast at the operating range of the reactor system, i.e. 85-105°C. Slurry residence time is not a significant economic variable in the NITROX Process, even for ores as coarse as -6 mesh. Gas residence time is more important. Generally, the following residence times are projected for plant slurries:

- Gypsum precipitation: 1 hour
- Reactor system: 1-3 hours
- Precipitation: 1 hour
- Total slurry residence time: 3-5 hours

The reacted solids leave the reactor in an acidic slurry which is split. Part of it recycles to the gypsum tank, as described. The balance goes to precipitation, where calcium carbonate is added. FeAsO₄·2H₂O (scorodite) is precipitated, with additional gypsum. Some excess calcium carbonate remains in the precipitate.

The splitting of reactor exit slurry is important to the NITROX process. Sulphuric acid generated in the reactor system by reaction (1) must be recycled to the reactor, to generate nitric acid from the two calcium nitrate streams entering the gypsum tank. One calcium nitrate stream results from residual nitric acid in the reactor exit slurry. This can be minimized somewhat by increasing reactor residence time of the slurry, or by other actions. With complete oxidation of arsenopyrite feed it cannot be eliminated in a cocurrent reactor. The other calcium nitrate stream results from residual NOx in the reactor off gases. Again this can be minimized by increasing reactor residence times of the gases. Nevertheless, the more sulphuric acid that can be recycled, the more calcium nitrate can be handled in the gypsum tank and the smaller the reactor system need be. In the processing of low sulphur arsenides, sulphuric acid addition will be necessary. Where scorodite is intended as discard product, iron units may also be required.

Recycling all of the reactor exit slurry would give optimum sulphuric acid usage, except that solids would build up, of course. The limiting factor on the possible split is the solids concentration. This can be handled two ways: operate the NITROX Process at the maximum weight percent solids throughout or utilize some degree of liquid/solid separation to effect the split. The
latter is preferred since dilute slurries are more appropriate for NOx absorption in the reactor. A hydrocyclone could give the desired separation, with the fines recycling and the coarser fraction proceeding to precipitation.

**HN03 Regeneration**

Nitric acid production from NO gas is well established and a known technology in the chemical industry. It involves two process steps:

1. production of NO through combustion of ammonia with air,
2. production of approximately 60 wt% HNO3 from NO, water and additional air.

The NITROX Process chemistry involves only the second step i.e. regeneration of HNO3 from NO, water and air. Any process or cost reference to conventional nitric acid practice needs to take this simplification into account. In addition, the NITROX process yields undiluted NO for HNO3 regeneration; whereas ammonia combustion yields an NO gas diluted with nitrogen:

\[
4\text{NH}_3 + 5\text{O}_2 + 22\text{N}_2 \rightarrow 4\text{NO} + 22\text{H}_2\text{O} + 6\text{H}_2\text{O} \tag{6}
\]

By way of illustration, if the NITROX Process generated NO were converted to 60 wt% HNO3 in a step 2 part of a conventional nitric acid plant, then such a facility would still be only half the size of one treating combusted ammonia gases. Plant size is directly related to NO concentration, due to gas phase kinetics.

A third factor favouring the NITROX Process is the freedom in generating less than 60 wt% HNO3. The reactor system operates with approximately 10 wt% KNO3. Acid can be regenerated at 20-25 wt%, depending on the water balance. This has several advantages, but the main one relates to equipment size.

Without going into all the details of the equilibria involved in the nitrogen oxides, oxygen, nitric and nitrous acids, the overall reaction can be written as:

\[
3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \tag{7}
\]

The equilibrium constant for this homogeneous reaction can be written as:

\[
K_p = \frac{(p \text{HNO}_3)^2 (p \text{NO})}{(p \text{NO}_2)^3 (p \text{H}_2\text{O})}
\]

When liquid phase is present, as in the NITROX Process, the partial pressures of water and nitric acid in the vapour phase are fixed by the concentration of HNO3 in solution, and a useful relationship can be set up by substituting the known partial pressures at corresponding temperatures in an equilibrium expression, obtaining values of:

\[
K_i = \frac{(p \text{NO})}{(p \text{NO}_2)^2}
\]

as a function of acid concentration, at various temperatures (15). The result is given in Figure 3 (16).

---

![Figure 3](image-url)

**Figure 3**

It can be readily seen from Figure 3 that the equilibrium changes by three orders of magnitude between 20 and 55 wt% HNO3, and two orders of magnitude between 85°C and 30-35°C, the normal absorption temperature for HNO3 in a standard acid plant.

When rates of conversion are considered instead of equilibria, it can be calculated that under NITROX Process conditions 85 to 90% of the generated NO will convert to NO2 within three minutes. The following two cases were considered:
ORE

CONCENTRATE

FeS₂ 12 wt%
Gangue 66 wt%

FeS₂ 45 wt%
FeAsS 20 wt%
FeS 11 wt%
Gangue 24 wt%

Initial Gas Phase Compositions

\[
\begin{array}{ll}
p_{\text{NO}} & 0.171 \\
p_{\text{O}_2} & 0.141 \\
p_{\text{H}_2\text{O}} & 0.158 \\
p_{\text{N}_2} & 0.530
\end{array}
\]

\[
\begin{array}{ll}
p_{\text{NO}} & 0.073 \\
p_{\text{O}_2} & 0.060 \\
p_{\text{H}_2\text{O}} & 0.640 \\
p_{\text{N}_2} & 0.227
\end{array}
\]

Assumptions:
- 100% dissolution of sulphides
- 10% excess air
- Operating temperature 85°C

The results are plotted in Figure 4. Referring again to reactions (1) and (5), it was earlier observed that 6 out of 14 HNO₃ can be recycled as calcium nitrate. If all possible calcium nitrate were produced, only 8/14 or 57% of the NO would have to be converted in the reactor. This would take less than 10 seconds for the ore, less than 40 seconds for the concentrate.

Figure 4

RATE OF CONVERSION OF NO TO NO₂ vs TIME

The rate of NO absorption in the slurry is proportional to the interfacial surface area exposed, and is influenced by the conditions of turbulence in the gas and liquid phase.

Solid/Liquid Separation

Solid/liquid separation is normally capital cost intensive. The NITROX Process is no exception. In the following paragraphs some of the important parameters of this subject are presented.

Good solid/liquid separation depends on proper solids preparation, i.e. proper precipitation conditions. Precipitation in the feed tank has not been found to influence final solid/liquid separation, but conditions of the final precipitation directly affect filtration and washing. It has been found advantageous to precipitate soluble iron, sulphate, and arsenic values at elevated temperature, i.e. approximately 75°C-85°C. Precipitation at room temperature results in poor filtration and washing rates, as the following examples show.

Fully oxidized concentrate slurries were metered into approximately 1M calcium nitrate solutions. Calcium carbonate was added to maintain the pH at approximately 4. The slurry was well agitated for the hour necessary to effect completion of the additions and precipitation. Vacuum filtration rates and washing characteristics were then determined. Table II lists the differences between 75°C-85°C and room temperature precipitation and filtration. Five displacement washes were carried out and the filtrates analyzed for nitrate. Figure 5 shows the two duplicate test results. The cake thickness was approximately 4 cm.
VACUUM FILTRATION AND WASHING OF NITROX PRECIPITATE SLURRIES

Table II

<table>
<thead>
<tr>
<th>Filtration rate Kg/M²/hr</th>
<th>duplicate</th>
<th>duplicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>75' - 80' C</td>
<td>1724</td>
<td>1454</td>
</tr>
<tr>
<td>ROOM TEMPERATURE</td>
<td>782</td>
<td>751</td>
</tr>
<tr>
<td>Filtrate MNO₃</td>
<td>1.85</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>1.45</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Each wash at 5% of original slurry volume

<table>
<thead>
<tr>
<th>WASH</th>
<th>#1 MNO₃</th>
<th>#2 MNO₃</th>
<th>#3 MNO₃</th>
<th>#4 MNO₃</th>
<th>#5 MNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.3</td>
<td>0.53</td>
<td>0.15</td>
<td>0.03</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>0.42</td>
<td>0.14</td>
<td>0.02</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>0.97</td>
<td>0.86</td>
<td>0.88</td>
<td>0.85</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.0</td>
<td>0.66</td>
<td>0.39</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Wet Solids, Kg/M³ slurry

|        | 275     | 268     | 228     | 239     |

Dry Solids, Kg/M³ slurry

|        | 71      | 74      | 83      | 82      |

The large difference between wet and dry weights of the solids will be noted. In addition to free water in the filter cake, gypsum, scorodite and goethite all can loose water on drying. The water removed from the circuit in filter cake is quite significant. It is also nearly equal to the total weight of the wash water, indicating extremely efficient removal of the solute during washing. This has to do with the structure of the precipitate, photomicrographs of which are shown in Figure 6. It is interesting to note that under regular NITROX Process conditions the fraction of -100 mesh in the precipitate is usually less than that in the feed stock. By recycling reactor fines and proper precipitate development, overall particle growth occurs. It is believed this can be greatly enhanced in full scale operation, further reducing the investment required for solid/liquid separation equipment.
Treatment for Cyanidation

It has been found that gold extraction can be greatly influenced by the preparation of the precipitate for cyanide leaching. The following work on hot lime treatment has been reported earlier, but was not included in the attached technical note (13).

Several materials were given a hot lime treatment before cyanidation, and four materials were subjected to a comparison of hot lime (80°C) pretreatment before cyanidation versus cold lime (25°C). The hot lime stage consisted of maintaining the pH at 11 for at least 3 hours at 80°C. The Emf of the slurry was observed to drop to the -500 (SCE) range. If the pretreatment stage was continued long enough the Emf would "break" and rise to around -100 (SCE), similar to the Emf of these materials entering cyanidation from a cold lime pH adjustment. As Table III indicates, there was substantial improvement in the gold recoveries. Silver extractions of 92% were also obtained. A possible explanation for the improvement could be that some elemental sulphur is formed under some of the oxidation conditions. Such sulphur could form coatings and may therefore be detrimental to the cyanidation of the gold. The hot lime treatment is thought to remove such sulphur.

Table III: Effect of Hot Lime Treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cold Lime %</th>
<th>Hot Lime %</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>85</td>
<td>92</td>
</tr>
<tr>
<td>N</td>
<td>81</td>
<td>91</td>
</tr>
<tr>
<td>N</td>
<td>79</td>
<td>90</td>
</tr>
<tr>
<td>0</td>
<td>81</td>
<td>89</td>
</tr>
</tbody>
</table>

More recently a proprietary treatment method has been developed, which further highlights the importance of cyanide circuit feed preparation. Although treatment details can not be released at the present time, a listing of some of the more dramatic effects can be given. Generally, the testwork was comparative in nature, i.e. the filtered precipitate was divided in several parts, one of which was cyanided "as is" and another part given the proprietary treatment.
Table IV

THE EFFECT OF TREATING PRECIPITATE PRIOR TO CYANIDATION

<table>
<thead>
<tr>
<th>TEST</th>
<th>FEED</th>
<th>CN⁻ or CIL</th>
<th>% Au EXTRACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>24h</td>
</tr>
<tr>
<td>X32</td>
<td>CONC.</td>
<td>CIL</td>
<td>75.8</td>
</tr>
<tr>
<td></td>
<td>&quot;As is&quot;</td>
<td>CIL</td>
<td>97.5</td>
</tr>
<tr>
<td>X41</td>
<td>CONC.</td>
<td>CIL</td>
<td>88.0</td>
</tr>
<tr>
<td></td>
<td>&quot;As is&quot;</td>
<td>CIL</td>
<td>96.6</td>
</tr>
<tr>
<td>X44</td>
<td>CONC.</td>
<td>CIL</td>
<td>87.3</td>
</tr>
<tr>
<td></td>
<td>&quot;As is&quot;</td>
<td>CIL</td>
<td>85.4</td>
</tr>
<tr>
<td>Y8</td>
<td>ORE</td>
<td>CN⁻</td>
<td>70.6</td>
</tr>
<tr>
<td></td>
<td>&quot;As is&quot;</td>
<td>CN⁻</td>
<td>91.6</td>
</tr>
<tr>
<td>Y8</td>
<td>CONC.</td>
<td>CIL</td>
<td>72.6</td>
</tr>
<tr>
<td></td>
<td>&quot;As is&quot;</td>
<td>CIL</td>
<td>80.6</td>
</tr>
</tbody>
</table>

From time to time, the treatment appeared to be without effect as in test X44. This is still being investigated.

Project Status

Hydrochem is intending to design, construct and operate a 10 tpd demonstration plant for the NITROX Process, likely in Northern Ontario. A commitment for the supply of concentrates has been obtained. A study is underway, sponsored by the Ontario Government, to locate a suitable site for what ultimately may become a custom processing and refining facility for refractory gold concentrates. The equity position in the venture is still open.

Acknowledgement

Hydrochem gratefully acknowledges the support for the NITROX Process by the COSCH Group, the IRAP office of the National Research Council, and by Dickenson Mines Limited.

References

References


PART TWO

PAPER 7

Design and operating results of the NITROX Process®

by

Gus Van Weert, Ken J. Fair and Vicken H. Aprahamian

Gold Mining 88
Proceedings, Second International Conference on Gold Mining, Nov 7-9, 1988, Vancouver B.C. Published by SME, Littleton, CO. 1988
DESIGN AND OPERATING RESULTS OF THE NITROX PROCESS®

by Gus Van Weert, Ken J. Fair and Vicken H. Aprahamian

Hydrochem Developments Ltd.
16-266 Rutherford Road South
Brampton, Ontario L6W 3X3

A consortium of Canadian mining companies, engineering firms and the Ontario Government has supported Hydrochem's efforts in the last year to design and cost a 10 tpd NITROX PROCESS® demonstration plant. A 5 kg per hour mini plant was installed at the Hydrochem facilities in Brampton, Ontario.

This paper describes design testwork on Dickenson Mines arsenopyrite concentrate and application of the findings to the demonstration plant flowsheet. The control of nitrates in discard solids and stack gases is discussed in detail.

Nitric acid oxidation of arsenopyrite results in significant elemental sulphur formation, enough for it to be detrimental to subsequent cyanidation. Flowsheet variations aimed at dealing with this process characteristic are discussed and testwork results on one option (hot liming) are described.

INTRODUCTION

The increase in the gold price, which occurred in the seventies, has resulted in renewed interest in treating refractory gold bearing arsenopyrites by means other than the conventional roasting with air.

As described earlier (1), mining companies and prospectors have generally avoided "refractory" gold and silver ores by walking away from such deposits or filing the details away under "Future Activities (for somebody else)". As long as conventional deposits could easily be found in cooperative jurisdictions, this made sense.
With an increasing world population and increasing volume of trade activities and monetary speculation, total demand for gold has grown, resulting in an all time high price, certainly in inflation adjusted Canadian dollars (2). This has resulted in a search for new deposits, reworking of old deposits, especially tailing dumps, adoption of new techniques (heap leaching) and dusting off these "Future Activities" files.

Canadian metallurgists have largely spearheaded the treatment of refractory gold and silver ores. The majority of refractory gold and silver ores involve sulphides and arsenides, with pyrites representing the bulk of these (3). The following remarks refer to pyrite and arsenopyrites containing concentrates, and specifically to concentrate produced by the Arthur W. White mine at Balmertown, Ontario. This mine is in the Red Lake area of Ontario and is wholly owned by Dickenson Mines Ltd. of Toronto. Its concentrate is totally refractory; it is produced from the cyanide leach tailings.

As described in detail elsewhere (4), Hydrochem has brought a number of Canadian mining companies, engineering firms and the Ontario Government together for a detailed study of the capital and operating cost of a 10 tpd demonstration plant. The final report was submitted to the subscribers of the study early September for their evaluation. The study included a budget for operating the 10 tpd facility for a year, a site evaluation, an environmental assessment, a limestone availability and cost study, and testwork results based on Dickenson concentrate.

Treatment of refractory sulphides generally involves complete oxidation of these sulphides and arsenides, which contain the gold and silver values. Where such oxidation is incomplete, subsequent gold extraction tends to be incomplete (5, 6). This has also been found true with the NITROX PROCESS® on samples tested to date.

The logical oxidation agent for arsenopyrite is air, since it is free (at least at the plant intake). Processes not using air, but other oxidation agents, such as \( \text{H}_2\text{O} \) or \( \text{Cl}_2 \) derived principally through consumption of electrical energy, have not found industrial acceptance. Oxygen production from air also requires electrical energy.

Oxidation of refractory sulphides involves their contacting with oxygen or air. This can be done dry or wet, i.e. pyro- or hydrometallurgically. The former method generally involves roasting in multiple hearths or more commonly, fluid bed roasters. Some low arsenic concentrates are smelted and the molten sulphide matte oxidized in Pierce-Smith converters. This normally involves tolling, which can be attractive where the producing site is close to a base metal smelter, the grade of the concentrate is high, no deleterious elements are present in the concentrate and sulphuric acid can be marketed.

This paper deals with the situation where one or more producers wish to process their own concentrates. The roasting option in most countries now requires sale of sulphuric acid and acceptable collection and disposal of arsenic trioxide. Mineral concentrates often produce a lower quality acid. Scrubbing of the roaster gases prior to acid production may yield sludges which are problematic in disposal. Production of an arsenopyrite concentrate involves a reduction in gold recovery from the ore body. To satisfy the roaster heat balance, the concentrate should contain at least 16% S, a requirement which may further reduce recovery. The alternative is fuel injection into the roaster, which may affect acid quality if carbon is generated and carried in the gas stream.

Arsenic trioxide collection and disposal is even more problematic and costly. An electrostatic precipitator is required. Quality specifications for the arsenic trioxide are becoming more stringent since it is a buyers market, especially with Chile increasing its production to at least 35,000 tonnes by 1989 (7).

Pyro-oxidation of arsenopyrite (at roasting temperatures of approximately 525°C) proceeds very fast. Achieving similar rates in hydrometallurgical systems is impossible; neither is it necessary. Roasting requires complete utilization of all oxygen in seconds, to maintain the calcine at temperature and, especially in a two stage system, manipulate the chemistry. In the alternative hydrometallurgical systems the air or oxygen can be depleted nearly at leisure,
it's basically a matter of equipment volume. It is important to understand that in hydrometallurgical systems, the oxygen is consumed in solution, but is stored in the gas phase. Transfer of oxygen from the gas phase to the liquid is an important step, if not the limiting step, in sulphide oxidation. In the pressure autoclave system this is dealt with by the use of high pressure oxygen. This increases solubility in, and oxygen transfer to the process slurry. It makes oxidation in the pressure autoclave very energy intensive.

Surprisingly, bacterial oxidation faces an even greater challenge in this regard. The concept is simple; use specially selected or modified bacteria for oxidation of refractory sulphides in agitated slurries. Small amounts of nutrients are also added. Since the oxygen solubility in water at sea level and room temperature is only 9 ppm, the process liquor has to be constantly exposed to air to make the oxidation of arsenopyrite proceed. This is achieved by air sparging and liquor agitation, similar to practices in the pharmaceutical and fermentation industries. Oxygen transfer from air under such conditions measures at best 1 to 2 kg O₂ per HP-hour, under laboratory conditions, but is proportional to HP for viscous solutions and HP for water in agitated vessels (8). Hence, the larger the vessel, the lower the O₂ transferred per HP-hour. In addition, solids, surface active agents and higher temperatures all tend to reduce the oxygen transfer.

Recently, Demopoulos has reviewed the various aqueous oxidation methods for refractory gold (9). He concluded for the NITROX PROCESS that "Among the advantages of the process are the operation under atmospheric pressure, the use of air instead of O₂, leaching tanks made of stainless steel, fixation of As as basic ferric arsenates (high Fe/As ratio) and high Ag recoveries. Potential drawbacks are the production of S and its interference during cyanidation on one hand and the effective reduction of nitrate level of the effluent streams on the other. This paper will discuss in particular how the NITROX PROCESS® has evolved to deal with nitrates and elemental sulphur production.

THE NITROX CYCLE

One of the fundamental attractions of the NITROX PROCESS® is the low cost at which oxygen units out of air are made available to the mineral slurry. This is done through an intermediate, i.e. gaseous NO₂, which has a very high solubility in water, even at 85-95°C, the operating temperature of the NITROX PROCESS®.

Not only does NO₂ readily dissolve in the process solutions, it also makes the oxygen readily available for refractory sulphide oxidation. This happens because NO₂ reacts with the water to form nitric acid.

\[3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO}\] (1)

Nitric acid will readily react with sulphides and arsenides. The chemistry has been discussed elsewhere (1), and this chemical reaction can be simplified for sulphur:

\[S + 2\text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + 2\text{NO}_2\] (2)

or:

\[S + 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 3\text{NO}_1\] (1+2)

Simplistically, the 3 NO₂ enter the liquid phase, oxidize one sulphide sulphur to sulphuric acid and form 3 NO. The gaseous NO has low solubility in water (like oxygen), hence it immediately leaves the process solution and re-enters the gas phase.

NO is not inert however, it readily reacts with the oxygen in air to form NO₂. This fresh NO₂ is promptly absorbed in the process solution, forming nitric acid. It in turn reacts with the refractory sulphides, releasing NO. In this way the NITROX cycle is established resulting in very efficient transfer of oxygen units to the refractory sulphide slurry.

\[3 \text{NO}_2 + \frac{3}{2} \text{O}_2 \rightarrow 3 \text{NO}_3\] (3)

or, for the overall reaction:

\[S + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4\] (1+2+3)

Written as a chemical reaction

**Fig. 2. The NITROX CYCLE**

It will be noted that neither nitric acid, NO, nor NO₂ appear in the overall reaction. The quantities of nitrate in the process solution are such, however, that the nitric acid must be seen as a reagent or intermediate in the NITROX PROCESS®, not as a catalyst.

CONTROL OF NITRATES

Having introduced nitric acid, and all its subspecies such as
nitrites, NO, NO₂, etc., in the process to achieve the low cost oxygen transfer from air via the NITROX cycle, the economic and environmental realities now dictate rigid control of nitrates and all subspecies. Fortunately nitrates are extremely soluble and are not contained in the solids discharged from the NITROX PROCESS®. They are however contained in the free liquid content of these solids.

One of the obvious answers to the problem of nitrates in the spent oxidation liquor is the chemical removal of the nitrates. This can readily be done by adding excess concentrate, as shown in earlier published work by Kennecott personnel (10). This introduces the countercurrent concept, which tends to complicate the process. When treating arsenopyrites, it also may generate arsenites in the barren oxidation liquor. Arsenites cannot be precipitated as environmentally acceptable compounds. The NITROX PROCESS® therefore maintains a high oxidizing potential throughout the reactor, which results in a significant nitrate content in the spent oxidation liquor.

Displacement of nitrate bearing liquids contained in filter cakes requires nitrate free water. This water cannot be brought in from outside the process, otherwise the solutions would dilute and tanks fill up and eventually overflow into the drains. Containment of nitrates requires therefor strict control of the water balance, an unusual discipline for mill operators, but one that base metal refinery operators accept as a given.

Nitrate free water must be generated in the process if it cannot be brought in from an outside source. Earlier versions of the NITROX PROCESS® showed a stream of water vapour exiting the stack. Condensation of this water vapour could provide wash water. More recent testwork has indicated that acceptable wash water can be condensed from the gas stream after the NITROX reactor at a rate of about 2 tons of water per ton of Dickenson concentrate. This change in the flowsheet allows other economies and has therefore been adopted as the preferred alternative. It is shown in the flowsheet, shown as Fig. 3.

The reason that water can be condensed from the gas stream is simply that water evaporation is used to control the NITROX reactor temperature. The air supplying the oxygen for the reaction sweeps away water vapour at atmospheric pressure. There is no heat exchange

<table>
<thead>
<tr>
<th>°C</th>
<th>kg H₂O per kg air at 100% saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>0.1</td>
</tr>
<tr>
<td>71</td>
<td>0.3</td>
</tr>
<tr>
<td>81</td>
<td>0.6</td>
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<tr>
<td>84</td>
<td>0.8</td>
</tr>
<tr>
<td>88</td>
<td>1.0</td>
</tr>
<tr>
<td>93</td>
<td>2.0</td>
</tr>
</tbody>
</table>
equipment required, in fact the process would not work with such equipment since the water balance could not be maintained. In a gypsum saturated circuit, this must be considered as another fundamental attraction of the NITROX PROCESS®.

The 10 tpd demonstration plant will consume 22 tpd air and evaporate 23 tpd water. If all the air was passed through the NITROX reactor, the slurry temperature would be 92 °C.

CONTROL OF NOx IN THE STACK GASES

Nitric acid and its subspecies are very much represented in the gas stream and need to be removed before venting. Removal occurs in two steps, i.e. through nitric acid production and, subsequently, through lime (stone) scrubbing. As explained under the earlier discussion of the NITROX Cycle, the bulk of NOx must be converted to nitric acid to allow the sulphide oxidation to proceed. Scrubbing with lime produces calcium nitrite from which nitric, or nitrous acid must be regenerated with the sulphuric acid formed by oxidation reaction (2).

\[
\begin{align*}
\text{NO} + \text{NO}_2 + \text{Ca(OH)}_2 & \rightarrow \text{Ca(NO)}_3 + \text{H}_2\text{O} \\
\text{Ca(NO)}_3 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{HNO}_3
\end{align*}
\]

Since only a limited amount of free sulphuric acid is formed, lime consumption must be controlled within that limit and lime scrubbing can only be done on the tail gases. The bulk of NOx must go to nitric acid. Its regeneration in the NITROX PROCESS® has been discussed in detail (1).

THE NITROX PROCESS® FLOWSHEET

The NITROX PROCESS® has been under development for over four years, which is not particularly long for a new hydrometallurgical process. This particular process has some features, however, that have allowed fast track development. The most important one is the separate extraction of the valuables (gold and silver), in a proven process, i.e. cyanide extraction. Unlike other hydrometallurgical processes, such as nitrate assisted oxidation of chalcopyrite for instance, the NITROX PROCESS® makes no attempt to solubilize the gold or silver, or remove gold or silver from the feed material during the oxidation reactions.

During the initial process development, Hydrochem became convinced that a demonstration stage would be very prudent, prior to the construction of a full scale facility. Hence, last year a consortium of Canadian mining companies, and engineering firms was established.
under the auspices of Hydrochem and the Northern Ontario Development agency of the Ontario Government to design and cost a 10 tpd NITROX PROCESS demonstration plant. At the Hydrochem facilities testwork was stepped up from a bench scale reactor to a 5 kg per hour mini plant.

Hydrochem also obtained a promise of supply of 10 tpd arsenopyrite concentrate for the demonstration facility from Dickenson Mines Ltd. Its Arthur W. White mine in the Red Lake district of northwest Ontario scavenges a 1 oz Au/ton concentrate from cyanide leach tailings prior to discard. The concentrate is shipped overseas. Both net back and recoveries have been low (11). In a separate development, Hydrochem installed novel flotation equipment in the White Mill, which has increased concentrate output substantially, making supply of arsenopyrite concentrate to the demonstration plant feasible without disrupting other commitments by Dickenson (12, 13).

For the flowsheet a Dickenson concentrate of the following composition has been assumed:

<table>
<thead>
<tr>
<th>Fe</th>
<th>As</th>
<th>S</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>27%</td>
<td>10.8%</td>
<td>23.2%</td>
<td>0.93 oz/st</td>
</tr>
</tbody>
</table>

The flowsheet for this particular concentrate at a Northern Ontario location would approximately follow the block diagram given as the NITROX Flowsheet (Fig. 3). A description follows.

Arsenopyrite is slurried in calcium nitrate bearing filtrate, then contacted with part of the reactor exit solution, containing ferric arsenate and sulphuric acid. Gypsum is precipitated and the slurry becomes acidic with nitric acid:

\[ 3\text{Ca(NO}_3\text{)}_2 + 3\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{CaSO}_4.2\text{H}_2\text{O} + 6\text{HNO}_3 \] (7)

The NITROX PROCESS® uses the generated sulphuric acid to reconstitute nitric acid from the calcium nitrate in the filtrate. Essentially, this allows nitric acid to exit the reactor as it must to prevent formation of arsenites, enter the precipitation, convert to calcium nitrate and be reconstituted to nitric acid in the reactor feed tank.

The oxidized concentrate, now greatly reduced in weight since iron, arsenic and sulphur are all solubilized, exits the NITROX reactor system and is filtered. It has been found that the precipitated gypsum greatly assists in the filtration of what essentially is a gangue, elemental sulphur and gold residue. The solution goes to ferric arsenate precipitation, where remaining sulphate and nitrate units are converted to more gypsum and calcium nitrate, respectively. The calcium nitrate liquor is used to scrub the tail gases before returning to the reactor feed tank.

The gas stream is also simple. Only part of the air needed for oxidation enters the reactor system. This allows depletion of the oxygen and NO\textsubscript{x} in the gas stream. After hot scrubbing of vaporized nitric acid and trace amounts of NO\textsubscript{x}, low nitrate water is condensed from the gas stream to be used as wash water in the system as discussed earlier under "Control of nitrate". The balance of the air is then introduced to recover additional NO\textsubscript{x}, which is also returned to the reactor feed tank. Finally, cold scrubbing of the tail gases with lime (stone) brings the NO\textsubscript{x} level to below that allowed for stack emission.

THE NUISANCE OF ELEMENTAL SULPHUR FORMATION

The one single process characteristic, which necessitated extensive research and in fact, extended process development for the Dickenson concentrate by a year, is the elemental sulphur formation in the nitric acid oxidation of arsenopyrite, simplistically represented by the following reaction:

\[ 16\text{FeAsS} + 64\text{HNO}_3 \rightarrow 16\text{FeAsO}_4 + 8\text{H}_2\text{SO}_4 + 24\text{H}_2\text{O} + \text{S}_8 + 64\text{NO}_3 \] (8)

Reaction (8) suggests half of the sulphur reports as S\textsubscript{8}, a very stable compound with a ringed structure. The production of elemental sulphur from arsenopyrite is thought to fluctuate, depending on process conditions. Earlier work has reported as much as 70% of the contained sulphur reporting as elemental sulphur (14). It probably does not form as S\textsubscript{8} rings during actual oxidation, since this requires a high redox of the mineral (15) but forms subsequently at a lower rate in the oxidation residue.

The formation of elemental sulphur has several connotations for the NITROX PROCESS®, the most important being a tendency to tie up gold, or slowing down its extraction from the residue with cyanide liquors. As important is its effect of increased cyanide consumption through the formation of thiocyanates.

Rather than searching for process conditions to minimize elemental sulphur formation, it was decided to deal with the nuisance and turn it to advantage, if possible. This decision was based on the recognition that the NITROX PROCESS® must work for all feedstocks and this might not be compatible with a narrowly defined nitric acid oxidation regime.

It has been shown possible to remove the elemental sulphur from the oxidation residue by both hydrometallurgical and physical methods. Some of these will be described in detail. The physical method of flotation removes both sulphur and gold, and the flotation concentrate would require separate treatment. This could be hot liming, or any oxidation method which would turn the sulphur in this very high grade material into sulphate. Since S\textsubscript{8} is only stable up to 159\textdegree C, high temperature oxidation was considered, but rejected as
inconsistent with the objective of keeping the NITROX PROCESS® as simple as possible. Thiourea extraction was tried, but appeared unable to break the gold/sulphur bond. Extractions were no better than the cyanide ones, although further testwork is still underway. Melting of the sulphur, followed by hot filtration, or solvent extraction of the oxidation residue were also considered.

The simplest solution could be burning of the elemental sulphur. In the NITROX PROCESS® this would take the form of a small, externally heated rotary kiln filled with sand or mill tailings, where the wet S bearing flotation concentrate would flow co-current with air, be heated to 300-400°C, freed of sulphur and discharged into the cyanide leach tanks. The air, with a small amount of SO\_2, would enter the NITROX reactor, where the SO\_2 would convert to sulphuric acid (as per the lead chamber process) and the heat would contribute to water evaporation, i.e. slightly increase the amount of condensed wash water. The combustion procedure has been tested, but time did not allow evaluation of the effect of SO\_2 in the NITROX reactor. The effect of this calcining on the gypsum possibly contained in the flotation concentrate also needs to be assessed. The present flowsheet therefore incorporates a hot liming step to hydrometallurgically remove the elemental sulphur, since it was most extensively researched.

**ELEMENTAL SULPHUR FORMATION WHEN TREATING PYRITE**

Earlier references (10) indicated that nitric oxidation of pyrite produces only a trace of elemental sulphur. This means that the NITROX PROCESS® for a pyrite concentrate is much simpler.

Our testwork on commercial concentrate samples indicated this to be correct, but to be certain the following testwork was carried out.

Coarse pyrite specimens were ground to 75% - 75\(\mu\)m and 200 grams of the ground material were slurried in 2 l of NITROX PROCESS® liquor from previous work on Dickenson concentrate:

\[
\begin{array}{c|c|c}
\text{Fe}^{+++} & \text{SO}_4^{2-} & \text{Redox} \\
39. g/l & 27.1 g/l & +750 \text{ mV}
\end{array}
\]

The redox potential was measured against a calomel electrode, and correlates with approximately 100 g/l NO\_3. Concentrated nitric acid and ground concentrate were added at 85 - 90°C and a constant redox potential of 750 mV. The last of the 326-lg HNO\_3 addition was 45 minutes after the last concentrate addition and 2 hours before the end of the experiment. In other words, oxidation simulated Dickenson concentrate process conditions as closely as possible. The 200 g pyrite analyzed at 42.3% S and 46.5% Fe and yielded 15.09 grams of residue at 52.5% S\(\text{e}\), 18.4% S\(\text{e}\) and 35.3% Fe, indicating 3.3% elemental sulphur yield and 94.3% iron dissolution.

The 3% elemental sulphur yield is identical to that measured by the Kennecott team (10), indicating that Dickenson concentrate process liquor does not contain trace elements in sufficient quantity to effect the pyrite oxidation mechanism. Silver ions have been shown capable of modifying the nitric acid dissolution of Ni\_2S\_2 (16). There is some indication from our work that silver may also effect the sulphur yield from pyrite under NITROX PROCESS® conditions.

Due to the difficulty of obtaining pure arsenopyrite specimens, similar work has not been carried out on this material.

**ELEMENTAL SULPHUR FLOTATION EXPERIMENTS**

Flotation at 80°C under NITROX PROCESS® conditions has been shown capable of separating elemental sulphur from the oxidation residue/gypsum slurry. The following describes the testwork.

Flotation was carried out in a 150 x 150 x 300 mm stainless steel flotation cell. Air at a rate of 9.5 l/minute was introduced through a stainless steel bubble cap type sparger underneath a 50 mm diameter hydrofoil impeller rotating at 1900 rpm. Froth was scraped every 5 seconds. After 15 minutes 96% of the sulphur and 90% of the gold was collected in a 49% S\(\text{e}\) and 10.8 oz Au/ton concentrate. Test results were as follows:
From these results it is clear that gold is very extensively concentrated in material floatable under NITROX PROCESS® conditions. The results do not prove the direct link between gold and elemental sulphur, e.g. gold could be cemented on the few remaining sulphide particles or be free floating.

Separate smaller batch experiments were also carried out to investigate the removal of elemental sulphur from NITROX residues which, after acid filtration, were first cyanide leached and then subjected to flotation. This was done to eliminate flotation of free gold as a test interference, since all free gold would likely have been removed during cyanidation.

The cyanided oxidation residue was subjected to two successive flotations, the first after adding frother followed by a second flotation after conditioning with Na₂S, CuSO₄ and sodium isobutyl xanthate. The following diagram highlights the results.

<table>
<thead>
<tr>
<th>wt. g</th>
<th>%</th>
<th>oz Au/t</th>
<th>Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.16</td>
<td>48.5</td>
<td>10.7</td>
<td>1</td>
</tr>
<tr>
<td>2.76</td>
<td>57.4</td>
<td>11.3</td>
<td>3</td>
</tr>
<tr>
<td>2.16</td>
<td>49.3</td>
<td>11.8</td>
<td>5</td>
</tr>
<tr>
<td>0.85</td>
<td>27.0</td>
<td>8.7</td>
<td>15</td>
</tr>
<tr>
<td>27.63</td>
<td>0.96</td>
<td>0.7</td>
<td>15</td>
</tr>
</tbody>
</table>

Even after cyanidation, 90% of the residual gold follows the floatable fraction of the residue, which is largely elemental sulphur. In the next section it will be shown that removal of elemental sulphur allows near complete extraction of gold by cyanidation.

HOT LIME TREATMENT

The dissolution of elemental sulphur in hot lime solution was already known to the ancient Greeks. The resulting liquid was called "thion hudor" i.e. "sulphurous water" by Zosimos (A.D. 250) (17).

To dissolve sulphur away from oxidation residue was found to be fairly easy. To prevent gold from dissolving at the same time without using excessive amounts of lime required a good deal of testwork. The following describes one such experiment.

A three stage NITROX oxidation was conducted with recycle of solutions over a period of six days. Oxidation residues produced during the latter part of the test were estimated to contain approximately 18% elemental sulphur. Hot lime treatment at pH 10.0-10.5 and 80°C produced residues with less than 0.1% S°. Gold dissolution during hot lime treatment was 6.6% and 4.3% for day 5 and 6 residue respectively. Subsequent 48 hour cyanidation at pH = 10.5 and 1 g/l cyanide extracted 97.5% and 98.0% respectively of the contained gold. Similar cyanidation without the hot lime step extracted only 75% of the gold in 48 hours. Increasing the cyanide level to 5 g/l increased gold extraction from 75% to 85%.

SUMMARY

Extensive testwork was carried out over the past three years on applying the NITROX PROCESS® to Dickenson Mines' Arthur W. White Mill arsenopyrite concentrate. A flowsheet was developed to form the basis of a capital and operating cost study for a 10 tpd demonstration plant. This study was commissioned by a consortium of Canadian mining companies, engineering firms and the Northern Development Fund of the Ontario Government.

One of the fundamental attractions of the NITROX PROCESS® is the minimal cost at which oxygen is made available to the refractory material in the slurry. This is done by introducing nitric acid into the circuit.

In developing the flowsheet, particular attention was therefor paid to control of nitrates and NOx in the solid and gaseous effluents, respectively. For instance, the NITROX PROCESS® was designed to generate wash water within the plant perimeters to control the water balance and prevent dilution of the process liquors.
Elemental sulphur generated by the action of nitric acid on arsenopyrite proved a particular nuisance, since it tied up gold and increased cyanide consumption. A number of process options to deal with this elemental sulphur are discussed. The hot lime dissolution of elemental sulphur prior to cyanidation overcomes these problems and is incorporated in the flowsheet. Low temperature combustion of this sulphur in NITROX PROCESS® air deserves further consideration since it promises to be an even simpler, and hence, lower cost option.

ACKNOWLEDGEMENTS

The authors thank the NOR-DEV organization, the National Research Council, the COSCH Group and the members of the Pyrite Processing Consortium, including Fenco-Lavalin, for their financial support. Special thanks go to Dickenson Mines Ltd. for the supply of concentrates, to Malcolm Downes, Leslie Hendry and Peter G. Turylo for their assistance with the experimental work and John C. Schneider for his counsel and encouragement.

REFERENCES

Capital and operating costs of the NITROX PROCESS®
for auriferous (arseno)pyrites
by
G. Van Weert and K.J. Fair.

Extraction Metallurgy '89
Proceedings, Extraction Metallurgy '89 Symposium,
Capital and operating costs of the NITROX PROCESS® for auriferous (arseno)pyrites

G. Van Weert M.A.Sc., P.Eng., M.I.M.M., M.A.I.Ch.E.
K.J. Fair B.A.Sc., M.Eng.
Hydrochem Developments, Ltd., Brampton, Ontario, Canada

SYNOPSIS

The NITROX PROCESS® is a chemical oxidation process for auriferous pyrites and arsenopyrites, based on the use of nitric acid as an intermediate oxidant and, depending on the flowsheet, as a lixiviant. Gold is recovered by cyaniding the oxidation residue. Nitric acid reduces to gaseous nitrogen oxide (NO), which is regenerated to nitrogen dioxide (NO₂) at atmospheric pressure through contact with air within the process perimeters. Absorption of NO₂ reconstitutes nitric acid in the process liquor. The NITROX PROCESS® substitutes gas phase oxidation, followed by rapid absorption of the oxidized species, for the energy intensive transfer of oxygen into the liquid phase, characterizing alternative processes.

Some of the process chemistry for the treatment of an arsenopyrite concentrate is discussed and capital and operating costs for a 100 TPD facility at a Northern Ontario location are presented.
INTRODUCTION

The sustained high price for gold over the last decade has resulted in an increasing willingness by mining companies to commit to new extractive processes and facilities for gold ores and concentrates, including pyrite and arsenopyrite. When these materials (in this paper generically referred to as (arseno) pyrites) contain gold or silver, cyanide extraction is often incomplete and the materials are called "refractory" as compared to "free milling". Generally, only complete destruction of (arseno) pyrites through oxidation renders the gold and silver free milling.

In response to this opportunity, a number of oxidative processes have been proposed to replace the roasting route. Although well proven, single or double stage roasting with arsenic trioxide collection from the gas stream suffers from several drawbacks. The disposal of As$_2$O$_3$ and sulphuric acid are becoming increasingly problematic because of market condition, environmental constraints and liability considerations. In general, the location of the (arseno) pyrite deposit is not conducive to sulphuric acid marketing. Often just the scope of the project will influence the market for the two byproducts. Some of the active projects refer to several thousand tons per day of roaster feed. On the technical side, the need to produce a 16-18 wt% S concentrate for roaster heat balance consideration can lead to reduction in flotation recovery. Supplementary hydrocarbon fuel injection into the roaster can produce "preg robbing" carbon, although, to give roasting it due, high temperature oxidation can also deactivate certain types of carbon.

The alternative processes are all hydrometallurgical in nature and have been recently reviewed for feasibility and cost. 1, 2

THE NITROX PROCESS

This process is a chemical method of oxidation, using nitric acid as an intermediary reagent. Compared to the alternatives, i.e. roasting, pressure oxidation and bio-oxidation, the NITROX PROCESS:

- Uses air for oxidation
- Regenerates the intermediary reagent (nitric acid)
- Oxidizes (arseno) pyrites in one to three hours
- Operates at atmospheric pressure
- Utilizes limestone, not lime for acid neutralization
- Consumes little energy when treating concentrates
- Requires no cooling coils in the reactor
- Transfers process heat only on gypsum free liquids
- Uses common materials of construction (304L, 316L, PCV/FRP)
- Accepts concentrates without further comminution
- Separates the gold from contained base metals
- Allows for recovery of base metals
- Produces a sulphide free iron arsenate residue for disposal
- Allows high silver recoveries
- Has low cyanide consumption
- Appears not site specific
- Allows optional production of an upgraded arsenic free residue for toll smelting

To gain these advantages, the NITROX PROCESS operates with a nitrate/sulphate circuit. This requires strict control of the discards, both solids and gas. To deal with these, respectively,
the circuit has been designed to generate its own wash water, and
to use lime scrubbing on the tail gas. The resulting calcium
nitrite scrubber solution is returned to the process. A schematic
flow diagram for the process is given as Figure 1. This has been
described and only a short description of the process chemistry
will be given here. The reader is referred to earlier publications
for additional details.

The NITROX cycle

It is important to understand that in hydrometallurgical systems,
the oxygen is consumed in solution, but is stored in the gas phase.
Transfer of oxygen from the gas phase to the liquid is an important
step, if not the limiting step, in (arseno) pyrite oxidation.

One of the fundamental attractions of the NITROX PROCESS® is the
low cost at which oxygen units out of air are made available to the
mineral slurry. This is done through an intermediate, i.e.,
gaseous NO₂. It readily dissolves in the process solutions; it
also makes the oxygen readily available for refractory sulphide
oxidation. This happens because NO₂ reacts with the water in the
mineral slurry to form nitric acid:

\[ 3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO} \]  \hfill (1)

Nitric acid will readily react with sulphides and arsenides. The
chemistry has been discussed elsewhere (5), and the chemical
reactions can be exemplified for sulphur:

\[ \text{S} + 2\text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + 2\text{NO} \]  \hfill (2)

or:

\[ \text{S} + 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 3\text{NO} \]  \hfill (1 * 2)

Simplistically, the 3 NO₂ enter the liquid phase, oxidize one
sulphide sulphur to sulphuric acid and form 3 NO. The gaseous NO₂

fig. 1. SCHEMATIC FLOW DIAGRAM FOR
DICKENSON CONCENTRATE
has low solubility in water (like oxygen), hence it immediately leaves the process solution and re-enters the gas phase.

NO is not inert however, it readily reacts with the oxygen in air to form NO$_3$. This NO$_3$ is promptly absorbed into the process solution, forming nitric acid. It in turn reacts with the refractory sulphides, releasing NO. In this way the NITROX cycle is established, resulting in very efficient transfer of oxygen units to the refractory sulphide slurry. Written as a chemical reaction the oxidation of NO gives

\[3 \text{NO} + \frac{3}{2} \text{O}_2 \rightarrow 3\text{NO}_3 \]  

or, for the overall reaction:

\[S + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4\]  

Fig. 2 The NITROX CYCLE

It will be noted that neither nitric acid, NO, nor NO$_3$ appear in the overall reaction. The quantities of nitrate in the process solution are such, however, that the nitric acid and NO must be seen as reagents or intermediates in the NITROX PROCESS®, not as catalysts.

THE CAPITAL AND OPERATING COST STUDY

There are a number of refractory gold and silver concentrates produced in Eastern Canada. None of these supplies is large enough to warrant a separate processing plant with a reasonable cost structure, let alone the cost of a development effort for demonstrating a new process. Since gold and silver are commodities and no supplier would have a significant impact on the world gold or silver markets, a cooperative or custom approach is clearly in order for Eastern Canada.

In the spring of 1987, Hydrochem Developments Ltd. of Brampton, Ontario approached the Ontario Government regarding the above concept, with a proposal to share development costs using the Northern Ontario Development Fund (NOR-DEV). After receiving a positive response, industry was invited to subscribe to the study to find a site and feed material for a NITROX PROCESS® demonstration plant and continue process development related to the NOR-DEV study. More than a dozen subscribers were enlisted with a completion date for the study of August 31, 1988. The scale of the demonstration plant, i.e. 10 TPD, was based on the estimated availability of concentrates from Dickenson Mines, a gold producer in the Red Lake, Ontario, district. During 1988 the scope of the study was extended to include capital and operating costs for a 100
TPD greenfield site plant to treat Dickenson Mines type concentrate. Results from the latter part of the study are presented in this paper.

The greenfield site selected was at Serpent River, Ontario, approximately 50 km south of Elliott Lake. This site is located adjacent to a highway, rail line, deep water port facilities and a tailings site of a shut-down uranium mine/mill complex. Electric power is also available at the site, making it advantageous for a central treatment facility from the standpoint of services and limestone costs.

THE FLOWSHEET

The flowsheet for this particular concentrate would approximately follow the block diagram given as Fig. 1. The detailed flowsheet is given as Fig. 3.

Arsenopyrite is slurried in calcium nitrate bearing filtrate, then contacted with part of the reactor exit solution, containing ferric sulphate and arsenic and sulphurous acids. Gypsum is precipitated and the slurry becomes acidic with nitric acid:

\[ 3Ca(NO_3)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3CaSO_4 \cdot 2H_2O + 6HNO_3 \]  

The NITROX PROCESS® uses the generated sulphuric acid to reconstitute nitric acid from the calcium nitrate in the filtrate. Essentially, this allows nitric acid to exit the reactor, as it must to prevent formation of arsenites, enter the precipitation, convert to calcium nitrate and be reconstituted to nitric acid in the reactor feed tank as per reaction (4).
The oxidized concentrate, now greatly reduced in weight since iron, arsenic and sulphur are all solubilized, exits the NITROX reactor system and is filtered. It has been found that the precipitated gypsum greatly assists in the filtration of what essentially is a gangue, elemental sulphur and gold residue. The solution goes to ferric arsenate precipitation, where the remaining sulphate and nitrate units are converted to more gypsum and calcium nitrate, respectively. The calcium nitrate liquor is used to scrub the tail gases before returning to the reactor feed tank.

The gas stream is also simple. Only part of the air needed for oxidation enters the reactor system. This allows depletion of the oxygen and NO in the gas stream. After hot scrubbing of vaporized nitric acid and trace amounts of NO3, low nitrate water is condensed from the gas stream to be used as wash water in the system as discussed earlier under “Control of nitrates”. The balance of the air is then introduced to recover additional HNO3, which is also returned to the reactor. Finally, cold scrubbing of the tail gases with lime (stone) brings the NOx level to below the allowed limit for stack emission.

For the flowsheet a Dickenson concentrate of the following composition has been assumed:

\[
\begin{align*}
\text{Fe} & : 27\% \\
\text{As} & : 10.8\% \\
\text{S} & : 23.2\% \\
\text{Au} & : 0.93 \text{ oz/st} \\
\text{H}_2\text{O} & : 10\%
\end{align*}
\]

With the additional assumptions that all As is present as FeAsS, all pyrrhotite as FeS and all Fe in the feed is associated with sulphides, the mineral suite can be calculated as:

\[
\begin{align*}
\text{FeAsS} & : 23.4\% \\
\text{FeS} & : 29.3\% \\
\text{FeS} & : 6.4\%
\end{align*}
\]

For the heat and materials balances, the following stoichiometries were assumed for the oxidation reactions:

\[
\begin{align*}
3\text{FeAsS} + 10\text{HNO}_3 - 3\text{Fe}^{3+} + 3\text{AsO}_4^{3-} + \text{H}_2\text{SO}_4 + 2\text{S}_2\text{O}_3^2- + 10\text{NO}_3^- + 5\text{H}_2\text{O} \\
6\text{FeS} + 30\text{HNO}_3 - 3\text{Fe}^{3+} + 3\text{S}_2\text{O}_3^2- + 12\text{H}_2\text{O} + 30\text{NO}_3^- \\
2\text{FeS} + 4\text{HNO}_3 + 2\text{H}_2\text{SO}_4 - \text{Fe}^{3+} + \text{S}_2\text{O}_3^2- + 4\text{H}_2\text{O} + 4\text{NO}_3^-
\end{align*}
\]

For precipitation of the solubilized iron, arsenic(V) and sulphur the following stoichiometries were assumed:

\[
\begin{align*}
\text{Fe}^{3+} + 3\text{CaCO}_3 + 3\text{H}_2\text{O} - 2\text{Fe(OH)}_3 + 3\text{CaSO}_4.2\text{H}_2\text{O} + 3\text{CO}_2 \quad (8) \\
\text{Fe}^{3+} + \text{AsO}_4^{3-} + 2\text{H}_2\text{O} - \text{FeAsO}_4.2\text{H}_2\text{O} \quad (9) \\
\text{H}_2\text{SO}_4 + \text{CaCO}_3 + 2\text{H}_2\text{O} - \text{CaSO}_4.2\text{H}_2\text{O} + \text{CO}_2 \quad (10)
\end{align*}
\]

It will be noted from these six equations that all sulphur in the feed requires neutralization with calcium carbonate, except for the minor amount of elemental sulphur formed from arsenopyrite. This makes CaCO3, or limestone, one of the major consumables in the NITROX PROCESS® and its delivered cost a major factor in the cost structure. Some comments on this are therefore warranted.

**Limestone Availability and Costs in Northern Ontario**

Neutralization of ferric sulphates and sulphuric acid requires low magnesium limestone i.e. calcite, not dolomite. Contrary to calcium sulphate, magnesium sulphate is quite soluble and it will accumulate in process liquors. Removal of more than trace amounts of magnesium requires precipitation of Mg(OH)2 at high pH with slaked lime, adding to the cost of the process.

Ontario, north of the Great Lakes is essentially pre-Cambrian and devoid of substantial calcite deposits. There are no significant limestone quarries in operation and industrial limestone consumers...
in Northern Ontario find it to their advantage to obtain supplies from the northern Michigan Peninsula by lake (water) transport.

There are two well established limestone suppliers located on the Michigan Peninsula, i.e. Presque Isle Corporation and Michigan Limestone Quarries. Production is over 10,000,000 tonnes annually, allowing extremely low operating and f.o.b. costs.

Lake freighter rates from the northern Michigan quarries to any dock on Lake Huron range between Can $2 and $4 per tonne, resulting in a delivered cost range of high calcium limestone of Can $6 to $8 per tonne.

Transportation rates by tri-axle dump truck average Can $0.06 to $0.07 per tonne kilometre or Can $2 per kilometre based on a 32 tonnes minimum payload moving one direction, from source to destination.

In northern Ontario it is difficult to develop back haul capacity for dump trucks and therefore either the full rate is charged or creative freighting techniques are developed. An example of creative freighting is to develop a trailer capable of being used as a dump in one direction while converting to a flat bed on the return haul.

Comparing lake freighter rates with trucking rates, it becomes readily apparent that moving limestone 60 km by truck costs as much as moving it anywhere on Lake Huron by freighter. The lowest NITROX PROCESS® costs in Northern Ontario are therefore achieved near a dock on Lake Huron or Lake Superior.

Up to ten commercial port locations were reviewed for their suitability to accommodate a custom NITROX PROCESS® plant for (arsenopyrite) pyrite and the Serpent River site was selected. The dock there is owned by Reiss Lime. The location is indicated on Fig. 4.

Materials Balances

The overall solids and water balances are listed in Table I and II, respectively. In a process of this nature, where nitrate is to be retained in the plant circuit, the water balance is of extreme importance. The flowsheet does not show a liquid waste stream.

| Table I Overall mass balance of a 100 TPD NITROX Plant |
| --- | --- | --- |
| **MASS IN:** | **KG/HR** | **MASS OUT:** | **KG/HR** |
| Feed | 4590 | Hot lime residue | 4410 |
| CaO | 250 | Sulphur ppt. | 250 |
| CaCO | 1960 | Scorodite ppt. | 8210 |
| Air | 9160 | Vent gases | 8720 |
| H2O | 5630 | | |
| **TOTAL** | **21,590** | **TOTAL** | **21,590** |

| Table II Overall water balance of a 100 TPD NITROX Plant |
| --- | --- | --- | --- |
| **TOTAL H2O IN:** | **KG/HR** | **TOTAL H2O OUT:** | **Liq.** | **SOLID** |
| Feed | 420 | Hot lime residue | 1500 | 270 |
| Oxidation wash | 3310 | Sulphur ppt. | 60 | 0 |
| Hot lime wash | 3100 | Scorodite ppt. | 2710 | 1200 |
| Sulphur wash | 120 | Condenser | 6320 | 0 |
| Fe ppt. wash | 5420 | CO2 vent | 310 | 0 |
| **TOTAL** | **12370** | **10900** | **1470** |
**Equipment and Layout**

A proposed general arrangement for a 100 TPD NITROX PROCESS® plant is given as Fig. 5. It shows the number and size of the equipment, most of which will be constructed in 304L stainless steel.

There are two identical NITROX reactors, for which the freeboard space has been extended by suspending a thinner gauge cylindrical gas holder above and beside the reactor. Reaction (11) is diffusion controlled and requires more time for completion as the oxygen content of the gas is depleted. That reaction time can be most cost effectively provided by non-agitated freeboard space.

The hot gas scrubber is designed as an agitated vessel in order to accommodate solids, i.e., to be able to scrub the gas with a slurry. The further treatment of the gas is not detailed in Fig. 5, but would consist of a series of NO oxidation/NO$_x$ absorption towers placed on an outside pad.

The residual solids are separated from the solubilized iron, arsenic, sulphur and residual nitrate by filtration on a covered belt filter. The ventilation air is returned to the NITROX reactor. The size of the filter relates to the rate of filtration of the oxidation residue. Although its tonnage is less than the ferric arsenate precipitate, the filter area required is substantially larger.
The hot liming operation is designed as a five stage, cascading leach train for elemental sulphur with its own belt filter and sulphur precipitation tanks and filter.

The limed solids go to cyanidation for gold extraction. Since this is a conventional circuit, details were not included in the flowsheet or general arrangement and the capital costs were obtained from an independent supplier of such equipment.

The soluble iron, arsenate and sulphate are precipitated with limestone in two precipitation tanks and the solids separated from the calcium nitrate liquor on a third belt filter.

Concentrate receiving, limestone handling, lime slaking and a cooling water circuit make up the auxiliary equipment needed for the NITROX PROCESS.

Capital and Operating Cost Estimates

By establishing the costs for the equipment from vendors, the cost of the building and services from file information, and applying the appropriate factors for installation, piping and instrumentation, the capital cost of a 100 TPD NITROX PROCESS plant at a Serpent River greenfield site is estimated at $22.5 million in 1988 Canadian dollars. A further breakdown of equipment and other costs is given in Table 3. The cost is all inclusive, except for the purchase of the site, major environmental hearing and reports, laboratory and field testwork, and project indirect cost, such as owner's costs, construction interest working capital and process fee.
Table III  Capital Cost for 100TPD NITROX PROCESS® Plant Treating Dickenson Mines Concentrate Assaying 23.4% FeAsS, 8.4% FeS, 29.3% FeS,

C $ 000's

1. Purchased equipment costs from references, phone quotes, etc, on current index basis .......... 6,757
2. Equipment installation ................. 2,848
3. Piping, material and labour, excluding service piping .......... 1,406
4. Electrical, material and labour excluding building lighting ................. 1,145
5. Instrumentation ................. 754
6. Process building, including mechanical services and lighting ................. 1,980
7. Auxiliary building, including mechanical services and lighting ................. 20
8. Plant services such as fresh water system, sewers, compressed air, boiler, etc. ................. 620
9. Site improvements such as fences, roads, railroads, tailing, etc. ................. 1,240
10. Field expenses related to construction management ................. 720
11. Project management, including engineering and construction ................. 2,930
12. Fixed capital cost ................. 20,420
   + indirect costs ................. 2,042
   22,462

Table IV lists the operating cost on an annual basis, for 330 days per year operation. The cost works out to Can $106 per tonne and compares favourably with recently published costs for pressure oxidation and bio-oxidation.

<table>
<thead>
<tr>
<th>Item</th>
<th>Quality</th>
<th>Purchase Price</th>
<th>Shipping Price</th>
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<th>Total Cost</th>
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<td>$287/t</td>
<td>$73.68</td>
<td>$361/t</td>
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<tr>
<td>Reagents-NaCN 250 kg/day</td>
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<td>$2/kg</td>
<td>$0.0361/kg</td>
<td>$2.04</td>
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<tr>
<td>Reagents-CaO 6.1 TPD</td>
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<td>$74.29/t</td>
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<tr>
<td>Reagents-CaCO₃ 47.1 TPD</td>
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<td>$14.12</td>
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<td></td>
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<td>Utilities, natural gas 98m³/hr</td>
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<td></td>
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<tr>
<td>Utilities, electricity 881 kw</td>
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<td>Miscellaneous, operating supplies</td>
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<td>Maintenance supplies (6% of equipment)</td>
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<td>Insurance (0.6%)</td>
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<td></td>
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<td></td>
<td>3,498,000</td>
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</table>

CAVEATS
The capital and operating costs estimates presented in this paper represent the first major evaluation of the NITROX PROCESS® by industry. As is normally the case with such review studies, areas for cost improvements suggest themselves. Taking note of our research finding that in the NITROX PROCESS® for Dickenson
concentrate, the gold follows the elemental sulphur formed by nitric acid oxidation of arsenopyrite, process work was carried out on removing the gold and sulphur from the spend reactor slurry by air flotation. At time of writing this appears feasible, which would allow removal of two filtration steps and the hot liming operation from the present flowsheet. The effect on capital and operating costs would be significant, i.e. a reduction of approximately 30% and 15%, respectively.

It should also be noted the sulphur and arsenic oxidation represent the cost side in the NITROX PROCESS®, whereas the gold units represent the revenue side. There are many ores and concentrates with a more favourable Au to (S + As) ratio than the Dickenson material used as the basis for the present cost estimates. Cost comparisons must be carried out on the basis of air units required, and other factors, such as % gold extraction, and not only on concentrate tonnage.

CONCLUSIONS

By efficiently consuming oxygen from air at atmospheric pressure in stainless steel equipment in the oxidation of (arseno)pyrite, a "free milling" residue can be obtained for gold extraction in a small, conventional cyanide circuit. This is achieved in the NITROX PROCESS® through the use of oxidation intermediates, i.e. nitric acid and gaseous NO₂. Direct operating costs are most influenced by the cost of limestone, one of the major process consumables. This implies that lowest operating costs are achieved in a location where low cost limestone is available, i.e. near a large limestone quarry, or near a port capable of receiving large tonnage shipments of limestone.

References


Summary

The majority of base metal hydrometallurgical processing occurs in sulphate systems. Chapter one lists some of the reasons for this bias, three of the more important ones being the low vapour pressure of sulphuric acid, the possibility of discarding sulphate units as gypsum or jarosites and the fact that many base metal deposits occur as sulphides. Sulphides are readily converted to sulphates, which will readily form gypsum. The low vapour pressure of sulphuric acid allows open equipment, which is especially important in electrolytic tankhouse operation.

Whenever sulphate systems cannot be adopted to specific metallurgical requirements, other systems have been accepted. For instance, in hydrometallurgy the cyanide and ammoniacal systems have become well established over the last 90 and 40 years respectively, due to their specific capabilities for gold and nickel. This thesis reviews the alternative acid systems, i.e. the chloride and nitrate systems, with which the author has worked extensively.

Chloride systems offer specific advantages, to do with high base metal solubilities, selective complexing allowing solvent extraction and ion exchange operations, the ability to produce chlorine electrolytically and to use chlorine for redox control in the system, the ability to produce hydrochloric acid by pyrohydrolysis (or Cl₂ combustion with hydrogen) for pH control in the system, the ability to generate high redox conditions largely independent from acidity, and vice versa. The proton activity of HCl increases with increasing chloride concentration, allowing very concentrated solutions to be produced in small equipment, compared to sulphate systems.

The nitrate salts of base metals are also very soluble, allowing concentrated solutions to be produced. The nitrate system, however, is oxidizing in nature at low pH and does not offer the freedom to manipulate redox potential and acidity that the chloride system offers. Nitrates also don't complex significantly, offering more limited opportunity for metal separations. The nitrate system is extremely efficient in transferring oxygen from air into highly oxidizing process solutions, which is the basis for its use on refractory auriferous sulphides, such as arsenopyrite.
Both nitrate and chloride systems are characterized by high vapour pressures of the acids and their derivates, requiring total enclosure of process solutions. Electrowinning of chloride solutions requires elaborate systems preventing chlorine leakage into the tankhouse atmosphere. There is no system for metal electroylisis from nitrate solutions.

Extensive process development has been carried out in the sulphate, chloride and nitrate systems for the processing of chalcopyrite to elemental copper but none of the attempts has resulted in an operating facility, to date. Improved pyrometallurgical facilities offer economies of scale and an acceptable commercial product, i.e. cathode copper. Attempts are continuing to process chalcopyrite concentrates in the chloride system utilizing techniques developed in the chloralkali industry.

The regeneration of hydrochloric acid from base metal chlorides offers interesting process possibilities and the technique is described in detail for the pyrohydrolysis of partially dried nickel chloride crystals.

A final chapter is devoted to opportunities in chloride and nitrate hydrometallurgy, as envisaged by the author.
Zowel de nitraat als de chloor systemen worden gekenmerkt door hoge dampdrukken waartoe men genoodzakt is de loging in een gesloten systeem uit te voeren. In het elektrolyse proces moeten danige maatregelen worden getroffen om de ontsnapping van gassen tegen te gaan. Tot heden toe is zulk een proces voor nitraaten onmogelijk gebieden.

Ondanks uitgebreid onderzoek is men er nog niet in geslaagd om in een loogproces chalcopyriet ekonomisch direct in koper metaal om te zetten. Het smelten van koperkoncentraties is in de loop der jaren verbeterd en is ekonomisch gezien een stuk aantrekkelijker. De koperkathode is het standaard commercieel produkt. Nochtans werden pogingen voortgezet om een chalcopyriet koncentraat te raffineren in het chloride systeem. Hierbij worden technieken toegepast die zijn ontwikkeld in de chloor industrie.

De terugwinning van zoutzuur uit non-ferro chloride verbindingen biedt interessante mogelijkheden. De techniek daartoe wordt uitgebreid behandeld in de tekst. Deze bestaat uit de pyrohydrolyse van nikkelchloride.

Tenslotte is er een hoofdstuk gewijd aan de mogelijkheden die de chloor en nitraat systemen nog bieden aan de metallurgische industrie.

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CURRICULUM VITAE.

The author was born August 24th, 1933, at Rotterdam, where he received his elementary and highschool training, the latter at the Johannes Calvijn Lyceum. A HBS-B diploma was obtained in 1951, followed by enrolment at the Delft Technische H.geschool to study chemical engineering. The diploma for "Scheikundig Ingenieur" was granted in 1958, after thesis work on the cold water extraction of sugar from beets on a pilot plant scale.

In 1958, the University of Toronto offered the author a National Research Council scholarship to continue his studies in the field of extractive metallurgy. This resulted in the granting of a Masters of Applied Science degree in 1959 on the subject of magnesium production by the Pidgeon process.

Except for the period 1978 - 1985, which was spent directing technical services to the ductile iron foundry industry worldwide, the author was involved in research, development and engineering activities in the field of extractive metallurgy. After several years with the International Nickel Co. of Canada, Ltd. at Copper Cliff, Ont. and the New Jersey Zinc Company of Palmerton, Penna., the author worked 15 years for Falconbridge Nickel Mines in various capacities, including Manager-Process Metallurgy. The main effort during these years was directed at establishing successful, low cost chloride hydrometallurgy at Falconbridge's Norwegian metals refinery. Other efforts included R&D on roasting and smelting of metal sulphides. While with Falconbridge, the author was instrumental in establishing the Hydrometallurgy Section of the Metallurgical Society, CIM. In 1978, the author joined Quebec Iron and Titanium as Director of Technical Services, where he was responsible for sponsoring the covered ladle (tundish-cover) technique for the magnesium treatment of molten iron for nodularization, now in use in approx. 300 foundries.

In 1985 the author returned to the field of extractive metallurgy as General Manager of Hydrochem Developments Ltd., a small privately funded R&D company located near Toronto, Ont. Hydrochem was promoting the use of nitric acid, regenerated in situ with air at atmospheric pressure, to oxidize gold bearing sulphides as an alternative to fluid bed roasting. During this time, the author was also involved in developing a mechanically agitated, staged flotation column.