# MAKING USE OF CHLORIDE CHEMISTRY FOR IMPROVED METALS EXTRACTION PROCESSES

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## ABSTRACT

It has long been appreciated that chloride chemistry has a number of advantages over the more traditional sulphate route for both extracting and separating metals. Modern materials of construction, coupled with the development of a more cost-effective and efficient hydrochloric acid regeneration technology mean that chloride-based processes are now more competitive and attractive. Such processing routes are able to recover more of the contained metal values in a feed, including iron in a benign and/or marketable form, and particularly the so-called rare and rare-earth elements which are increasing in demand in our electronic age. These factors, therefore, add appreciably both to the overall economics of a project, but also offer a much more sustainable approach to our dwindling natural resources. Additionally, chloride-based flowsheets can be much more environmentally-friendly, offering practical alternatives to two of the biggest headaches faced by the industry, namely cyanide usage and the generation of red muds.

This paper presents a brief theoretical background, focusing on the latest developments of ferrous iron oxidation and the low-temperature, selective hydrochloric acid regeneration process, which is the key unit operation for any chloride flowsheet, and discusses in general the advantages of the chloride approach. Several recently-developed flowsheets, which have been tested at the miniplant level, are presented for gold, base metals, titaniferous magnetites and lead-silver ores wherein the advantages of considering a chloride approach are highlighted.

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## INTRODUCTION

The hydrometallurgical extraction of base metals is mostly rooted in the chemistry of sulphuric acid and accompanying sulphate salts, partly because so many ores are sulphide-based, and partly because of the easy availability and relatively low cost of sulphuric acid. Sulphate systems are less aggressive than the corresponding chloride-based systems, thereby allowing for cheaper and more readily-available materials of construction. Furthermore, calcium sulphate, in its various forms, is insoluble which therefore allows lime to be used as a universal reagent in a sulphate circuit, since a non-toxic solid residue can be disposed of more easily when compared to a liquid effluent.

Chloride-based systems, whilst far from being unknown, have not attained anything like the same level of acceptance, despite the several advantages that chlorides have in metals processing schemes. The big drawbacks that chlorides have faced in the past, namely the availability at reasonable cost of suitable materials of construction, and the necessity to recycle the lixiviant (usually hydrochloric acid) in an efficient and cost-effective manner, are no longer valid. Modern plastics and alloys are much more readily-available, and at relatively low-cost, and an effective, efficient methodology for recovering and recycling the acid now exists.

This paper presents some of the background as to the advantages of chloride systems, and shows how this can beneficially be incorporated into modern flowsheets.

## SOME FUNDAMETAL ASPECTS OF CHLORIDE CHEMISTRY

Consideration and understanding of some of the fundamental aspects of chloride chemistry, and in particular of concentrated systems (brines), demonstrates why its use has a number of advantages over the corresponding sulphate system. Of special interest is the activity of the hydrogen ion (acid activity) and the solubility/complexation of metal ions in chloride environments.

### Activity of Hydrogen Ion and Water

Chemical "activity" is a well-known, but generally little understood, aspect of chloride systems. At its simplest level, activity can be considered as the "effective (rather than true) concentration" of a species in a solution. Activity coefficients (defined as that coefficient by which actual concentration is multiplied to get activity) in chloride salts are generally significantly greater than the values for the corresponding sulphate salt. For most transition metal sulphates, the mean activity coefficient ($\gamma_{\pm}$) decreases sharply as the molality, m (defined as kg solute per kg solvent, and not to be confused with molarity, M, defined as the number of moles of solute per litre of solution), increases from the ideal value of unity in very dilute solutions, to as low as 0.05. In contrast, the value of $\gamma_{\pm}$ for the corresponding chloride salt typically passes through a minimum of about 0.5, at a concentration of about 0.5m, and then rises to above 10 in highly concentrated chloride solutions. Acidity function and potentiometric measurements have established that the activity of HCl rises even more sharply above 3m HCl or in the presence of high concentrations of chloride ions, the mean activity coefficient ($\gamma_{\pm}$) increasing from about 1 in 2m HCl to about 6 in 8m HCl (Muir, 2002, Senanayake and Muir, 2003). Increasing the temperature decreases the activity of HCl, presumably because the structure of water is broken down at elevated temperatures making water more basic. However, this increase in activity is still very considerable compared to the corresponding sulphate system.

The increase in the activity of HCl has long been recognized when salts such as NaCl, $CaCl_2$ or $MgCl_2$ are added to dilute solutions of HCl. Peters (1976) estimated that the activity of 2m HCl in 3m $MgCl_2$ or 3m $CaCl_2$ is the same as the activity of 7m HCl, with the increase in the reactivity of HCl being a function of the $Cl^-$ concentration. Majima and Awakura (1981) reported that the activity of 1m HCl is 3 times higher in 1M NaCl and 20 times higher in 3M NaCl than in the absence of added salt. Similarly, the activity of 2M HCl rises to 50 in 3M NaCl or 1.5M $CaCl_2$, as shown in Figure 1. At the same time, the addition of salts also ties up the available free water by forming strongly solvated ions. Thus, the increase in the activity of the HCl is related to the change in the activity of free water.

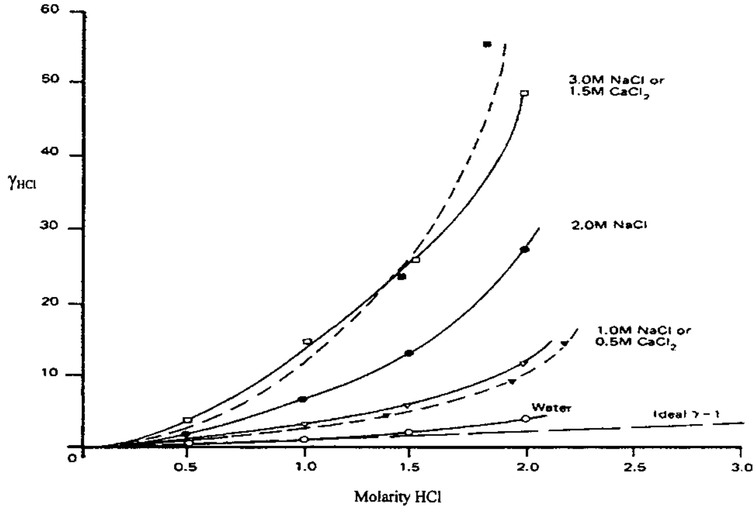

Figure 1 - HCl Activity as a function of concentration in chloride salts (Majima & Awakura, 1981)

Changes in the activity of free water in concentrated electrolyte solutions may be determined readily by vapour pressure measurements. The activity of pure water ($a_w$) is unity by definition, and it decreases with an increase in concentration of the electrolyte as a result of ion-water interactions, as noted above for HCl. The activity of water is found to decrease with the addition of HCl and other chloride salts, as shown in Table 1 (Muir, 1983, 2002).

Table 1. Change in the activity of water at different chloride salt or acid additions to an ionic strength of 10 (Muir, 1983).

| Salt or Acid Added (Ionic Strength) | Activity of Water Measured |
|---|---|
| HCl (10) | 0.40 |
| NaCl (10) | 0.60 |
| $MgCl_2$ (10) | 0.75 |

The effect of the addition of $MgCl_2$ to HCl is shown in Figure 2, where the concentration of $MgCl_2$ is plotted against the activity of $H^+$ (or, more correctly, of $H_3O^+$). It is evident that the activity of the $H^+$ ion increases with an increase in the concentration of $MgCl_2$, and that an increase in the HCl concentration has further contributed to the increase in the $H^+$ ion activity (Jansz, 1983). Figure 2 also shows that at higher temperatures at a given HCl and $MgCl_2$ concentration, the activity of the $H^+$ ion decreases, but this decrease is nowhere near as great as is the effect of decrease in overall chloride concentration.

Table 2 shows how increasing the overall chloride content facilitated increased metal extraction from a scandium laterite, all tests being carried out for 4 hours at 600 kg/tonne acid addition at 95°C. It is clearly evident that firstly, in this example, chloride is more effective than sulphate, and secondly that extraction increased as the overall chloride concentration increased. Others have observed similar phenomena, especially with magnesium chloride (Lakshmanan, Sridhar, & Roy, 2011).

The point about this brief (and somewhat theoretical) preamble discussion of chemical activity is to demonstrate that in high-concentration chloride media, the net effect is that even small amounts of acid can act as though they were highly concentrated. This, therefore, means that the driving force in leaching reactions is very high, leading to potentially both increased levels of extraction and to more rapid kinetics, as shown in Table 2.

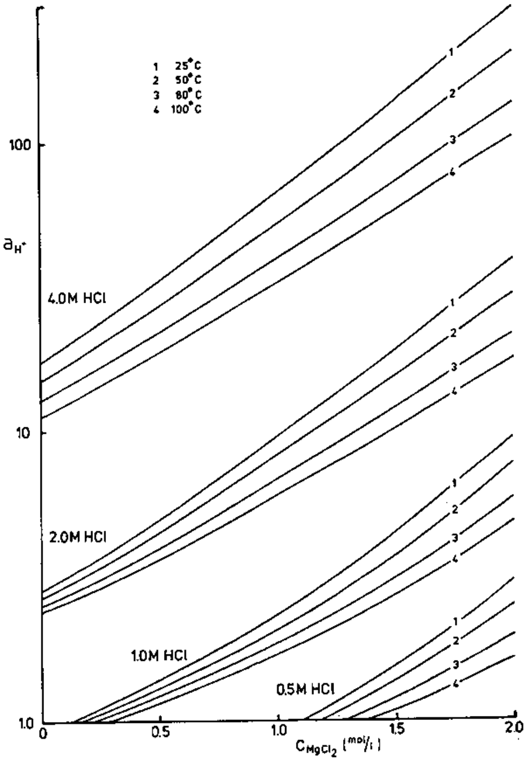

Figure 2 - Effect of $MgCl_2$ concentration on the activity of $H^+$ in HCl solutions (Jansz, 1983)

Table 2 – Metal extraction as a function of acid and total chloride concentration

| Acid | $MgCl_2$ | Extraction, % | | | |
|---|---|---|---|---|---|
| | g/L | Ni | Co | Fe | Sc |
| $H_2SO_4$ | 0 | 4.7 | 2.8 | 26.6 | 18.7 |
| HCl | 0 | 25.5 | 43.9 | 26.6 | 18.9 |
| HCl | 175 | 72.6 | 86.9 | 75.3 | 63.6 |
| HCl | 360 | 80.0 | 93.4 | 86.6 | 75.7 |

## Complexation and Solubility

Figure 3 shows the potential-log [$Cl^-$] predominance area diagram of various metal chlorides. The obvious thing to notice is the variety and range of the various different metal anionic chloride species that exist (Senanayake & Muir, 2003). It is also apparent that nickel, unusually, does not form any chloro-complexes, a fact which is made use of in effecting a separation scheme from cobalt, for example. As far as iron is concerned, the diagram indicates that at a concentration of 10M $Cl^-$ and 0.73V, iron will be present as ferric chloride, whereas ferrous chloride is the most predominant from 1.0M $Cl^-$ and higher and between –0.4V and 0.73V. Furthermore, it can be seen that the oxidation of iron to the ferric state is also favourable under these conditions, which, as will be discussed later, is a significant factor in high concentration chloride flowsheets.

This ability to form many and varied complexes is tied in very closely with the fact that the solubility of most metal chlorides, on a metal ion basis, is very much higher than for the corresponding sulphate salt. The solubility of some selected salts is shown in Table 3, where the data have been re-calculated as g metal per 100 g of water (Wikipedia, 2013). It is clearly seen that, with the exception of aluminium, the chloride salts are very much more soluble than their sulphate counterparts. This is especially the case for zinc, which also happens to be the salt with the largest predominance area in Figure 3.

Table 3 – Solubilities of selected metal salts (calculated as g metal/100g water)

| Metal | 20°C | | 100°C | |
|---|---|---|---|---|
| | Chloride | Sulphate | Chloride | Sulphate |
| Aluminium | 9.3 | 5.7 | 9.9 | 14.0 |
| Copper (II)1 | 34.5 | 8.1 | 56.7 | 29.0 |
| Cobalt (II) | 24.0 | 13.7 | 48.1 | 14.8 |
| Magnesium | 13.9 | 6.8 | 18.7 | 10.2 |
| Nickel (II) 6H20 | 30.3 | 9.9 | 39.7 | 17.1 |
| Zinc | 189.5 | 21.8 | 294.6 | 24.5 |

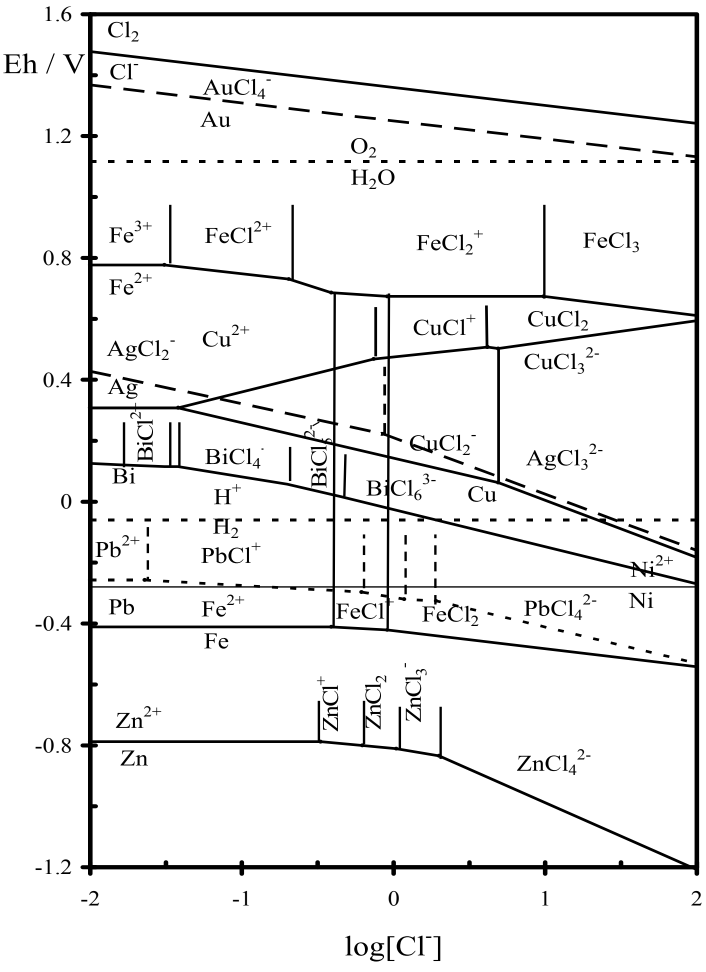

Figure 3 - Eh-log[Cl$^-$] diagram at 25°C (Senanayake & Muir, 2003)

## IRON OXIDATION IN CONCENTRATED CHLORIDE MEDIA

The control and removal of iron from hydrometallurgical process solutions is often the main purification step in any flowsheet. This usually involves the oxidation of ferrous iron to ferric in order to effect precipitation as hydroxide, goethite or hematite. Conventional wisdom has it that ferrous iron oxidation in aqueous solutions, even chloride-based ones, is kinetically slow, virtually impossible to achieve effectively with air, and with the rate being dependent upon both ferrous iron concentration and mass transfer of oxygen gas. Whilst in general this is true for dilute solutions, relatively recent work carried out at SGS Lakefield has shown that mass transfer is by far the most important factor, and that if gas bubble size can be made small enough then a reasonable rate of oxidation can be attained under atmospheric conditions (Dry, Verbaan, Bourricaudy, & Moran, 2011). Similar results were obtained in work carried out by McGill University (Becze, Hock, & Demopoulos, 2011). Both studies, although requiring very high impeller power inputs, which would be impractical in a commercial operation, at least demonstrate that oxidation can be achieved without recourse to the autoclave operating at 150°C as employed by SMS Siemag (Mach, 2009, Vogl, Mach, Bartel, & Weissenbaeck, 2009), and PORI (Burtch, 1975, 1976).

First inspection would suggest that to achieve oxidation of ferrous iron in a chloride medium, there would need to be sufficient hydrochloric acid present to close the chloride balance. In reality, though, this is not the case, since the reaction proceeds according to equation 1 below, where it can be seen that HCl is neither liberated nor consumed, and that one third of the iron forms hematite:

$$12FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 8FeCl_3 \qquad (1)$$

and in both of the studies mentioned above, this was the reaction path followed. The SGS Lakefield study, in particular, employed very high concentration chloride systems, to the extent that they were more like molten salt hydrates rather than true aqueous solutions.

In dealing with such molten salt hydrate systems, where there is little or no free water present, then the role of water also has an impact. Work carried out in Australia during the 1930s showed that by progressively eliminating water from the system, ferrous chloride oxidation rates could be increased by up to over 4000 times (Pound, 1939a, 1939b). In this work, water was replaced by alcohols, with progressively higher density (longer chain) alcohols. Organic chemistry designation of an alcohol is R-OH, where R represents the carbon chain of the alcohol (H-, $CH_3$-, $C_2H_5$-, $C_3H_8$-, $C_4H_{10}$-, etc.), such that in theory, the simplest alcohol is H-OH, otherwise known as water. It was found that as the carbon chain length increased (i.e. as the alcohol became less and less like water), then the oxidation rate of ferrous iron increased. The molten salt hydrate nature of concentrated chloride brines is equivalent to there being no free water, as with the work with alcohols, and thus, enhanced oxidation rates can be attained.

As for the oxidation reaction being kinetically slow and not possible with air, this can be shown to be otherwise through a very simple test, one also demonstrating the importance of mass transfer. Such a test was carried out using an off-the-shelf home food blender. One litre of ferrous chloride solution analysing 172 g/L Fe (i.e. 3M, highly concentrated, and no free HCl), was placed in the blender at room temperature, and operated at maximum speed for ten minutes. No gas of any sort was sparged into the mixture, oxidation being effected purely by air drawn in through the vortex. The solution rapidly became very hot (the actual temperature was not measured) and a dark reddish brown slurry formed (Figure 4). There was no ferrous left in the solution at the conclusion of the test.

This demonstrates that oxidation of ferrous chloride solutions with air is not only possible, but also that it can be achieved rapidly under appropriate conditions, and further confirms the highly exothermic nature of the reaction. The nature of the blender is such that it generates extremely fine bubbles, much like an emulsion, thereby facilitating mass transfer of the oxygen from the gas phase into the liquid, and presenting a very large bubble surface area for this to happen. However, clearly as with the above work by SGS Lakefield and McGill, it is impractical to scale-up a blender to industrial operation, simply because of the massive power input that would be needed.

Figure 4 - Blender demonstration test: starting solution and final slurry (10 minutes)

A further, and very important observation during this work, was that the mixture, particularly at the bubble surface, was highly reactive and corrosive. The impeller (stainless steel) at the end of the ten-minute blender test was severely corroded (Figure 5, left), which meant that, effectively, a blender could be used once only.

Additional stirred tank reactor tests were carried out using 6-blade, titanium grade 2 radial impellers. Similar impellers had been used industrially in high-concentration chloride circuits without any corrosion problems in both the commercial Magnola Magnesium Leach Plant (three years operation leaching serpentine with 33% HCl) and for 25 years at the CCR Gold Refinery (leaching silver refinery anode slimes with 52% hydrogen peroxide and 31.45% HCl). However, surprisingly, these impellers also corroded rapidly during the oxidation reaction, indicating that the conditions in the vessels were highly reactive, especially at the impeller blade tips where essentially all the action takes place. Subsequent to this, titanium impellers specially-coated with a Teflon compound were used, but these also suffered the same fate (Figure 5, right), although they did last for three tests. However, oxidation rates were nowhere close to those achieved in the blender test. Further testing on other feed solutions has shown that, under certain conditions, in these concentrated chloride solutions it is possible to partially oxidize, for example, even calcium chloride to hypochlorite with air, which, ordinarily, would not be expected. This clearly demonstrates a very reactive system, one not encountered when dealing with more dilute solutions, nor in the sulphate system.

Figure 5 – Impellers at end of oxidation tests (blender, left and coated titanium, right)

It can be seen from Figure 5 (right) that corrosion occurs primarily on the leading edges. Oxygen gas had been sparged into the solution underneath of the impeller blades, as per standard practice, in order to achieve maximum shear and the smallest possible bubble size. It is reasonable to assume, therefore, that the surface of the bubbles is the area of greatest reactivity, which places great emphasis on finding materials that would withstand such conditions. Work over several years has shown that the reaction pathway of equation 1 is not straightforward and is somewhat complicated, involving cycling exotherms and endotherms (equated to oxidation followed by hydrolysis), together with the formation of intermediates such as FeOCl and akaganéite, the discussion of which is significantly beyond the scope of this paper.

Given the corrosion and kinetic obstacles in attempting to achieve satisfactory oxidation without recourse to an autoclave, a different approach was required. This has resulted in the design of a proprietary novel reactor, one specifically with no moving parts, and which has opened up new possibilities in this respect. Following on from the above observations, the next logical step was to investigate the behaviour of real industrial process solutions, of which steel plant waste pickle liquors are ideal, at a higher temperature (i.e. with less free water present), and also to use air rather than oxygen gas. Figure 6 shows the oxidation of ferrous iron using air during a static, miniplant-scale test using steel plant pickle liquor (75 g/L $Fe^{2+}$).

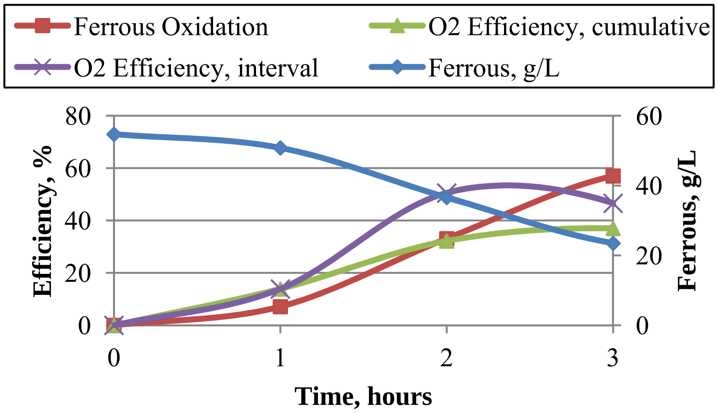

Figure 6. Oxidation of ferrous chloride in ferric chloride at initial 135°C

The initial temperature was 135°C, and rose during the test to 165°C. The feed solution also contained 25 g/L ferric iron, since there will always be some ferric present during continuous operation. The presence of ferric iron also allows the temperature of the system to be raised, since pure ferrous chloride is limited to 145°C before solidifying, whereas mixtures can attain higher temperatures. It can be seen that between 1 and 3 hours, wherein the system can be regarded as having been operating steadily, the oxidation rate was linear, and the overall oxygen usage efficiency was just under 40%, which is an extremely high number when using air. In terms of operation in conjunction with ferric iron hydrolysis, and under continuous operation, it is not necessary to push the oxidation to its limits, since the presence of some ferrous iron is beneficial. As noted above, the fundamental reasons for this are somewhat complicated and are beyond the scope of this paper. The results of Figure 6 essentially confirm the results of the blender test, and demonstrate that air can be effectively used for ferrous iron oxidation.

Combined with the overall heat balance situation (oxidation is exothermic, hydrolysis endothermic), this throws up the possibility of using a single reactor to effect both oxidation and hydrolysis. From a heat balance perspective, this is certainly attractive, but such is far from being the only consideration. Optimal performance of oxidation requires that it operate at around 150±10°C, which is below the hydrolysis temperature. Further, oxidation can be effectively operated without producing any

HCl as shown in equation (1), but, importantly, generating hematite which can, and does, act as seed during hydrolysis.

## IRON HYDROLYSIS AND HYDROCHLORIC ACID RECOVERY

The fundamental process on which the chloride circuit revolves is the hydrolysis of ferric chloride (and, to a lesser extent, other metal chlorides) to form the metal oxide and super-azeotropic hydrochloric acid ($\geq$30%). This process has variously been referred to as “hydrolytic distillation” (the more appropriate description) and “hydrothermal acid regeneration.” A number of papers have been published on various aspects of the process, demonstrating that it is technically viable as well as being economically attractive (Harris, White, Dry, & Evans, 2009, Harris &White, 2011a, 2011b, Harris & and White, 2013). A brief summary of these data confirms that high-strength acid can be generated, that good quality hematite can be produced, being both crystalline and of high-purity, with very low liquor retention (<10%), and that there is a split in behaviour of other metals. Data generated to date indicate that metals with a valency of 3 and higher hydrolyse along with the iron (aluminium, vanadium, for example), whereas divalent and monovalent metals remain in the liquid phase (Harris & White, 2013). Interestingly, the metals which hydrolyse along with the iron tend to be amphoteric, and are amenable to subsequent selective leaching from the hematite in an alkaline medium. This, therefore, opens up opportunities for their recovery, particularly with respect to aluminium (alumina), since it offers a pathway to generate alumina without the production of red mud.

Secondary hydrolysis of the divalent metals remaining in the liquid phase has shown that these can also be recovered, with the order of recovery (especially for base metals) seeming to follow the conventional pH precipitation order. However, it should be pointed out that at this time, these are indications only from preliminary work, and that this is being studied in ongoing work.

## APPLICATIONS OF CHLORIDE PROCESSING

Making use of enhanced chemical activity, complexation and solubility, coupled with employing aspects of iron oxidation and hydrolysis, allows the chloride-based process to be applied in a number of different situations. To date, miniplant campaigns have been carried out for the treatment of gold ores and concentrates, titaniferous magnetite ores, lead-silver concentrates, nickel laterites and electric arc furnace dust. The latter is the subject of a separate paper at this conference, and is therefore not included here. As noted above, the possibility of producing alumina without recourse to red mud is also very real, but whilst there have been indications that such can be achieved, no concerted effort has been directed into this at the present time.

### Cyanide-Free Gold Recovery

The results of the miniplant campaign for this process have been published previously (Harris & White, 2011b). There is increasing pressure on the gold industry to reduce, recycle or completely eliminate processing schemes based on cyanide, with its use already having been banned in several jurisdictions. Final refining of gold (and platinum-group metals in general) has always been carried out in chloride, and this has simply now been expanded to recover gold from ores and concentrates, thus circumventing the need for using cyanide. The main aspects of the process can be summarised as follows:

1. Single or two-stage leaching, depending on the nature of the feed. With predominantly sulphide-based feeds, a two-stage leach is preferred, with the first stage being reducing and eliminating much of the iron and reactive sulphide. A second, oxidising leach then dissolves the gold and other value metals that might be present.
2. Recovery of gold via ion exchange. It is possible to selectively recover gold of four nines or greater purity directly via this route, thus avoiding the need for off-site refining.

3. In some feeds, there are other value metals present, such as gallium and tellurium, and these can also be recovered via ion exchange processes. Often, their recovery can more than offset the complete operating costs of the circuit.
4. Oxidation of iron from the reducing leach, followed by hydrolysis of the solutions from both leach circuits, resulting in a hematite product and hydrochloric acid for recycle to the leach.

As noted above, a miniplant campaign has been carried out on this approach, yielding gold recoveries of >99% from a feed of 1.2 g/t. Process modeling and preliminary costing show economics favourable when compared to conventional processing. If a concentrate were to be treated instead, however, then the economics are extremely favourable.

### Nickel Laterite Processing

As with gold, details of the nickel laterite flowsheet have been published previously (Harris & White, 2011a, 2013). The chloride flowsheet offers a very competitive option to HPAL (Dry & Harris, 2012), which whilst it remains the conventional choice, has still not really gained much acceptance within the industry. The main aspects of the chloride process can be summarised as follows:

1. Leaching of all profiles of the laterite in recycled (30-36%) hydrochloric acid. The high chloride concentration tends to dehydrate the leach solids, which are predominantly silica, allowing for vacuum filtration to be carried out, rather than CCD as with HPAL, and thus, significantly more concentrated solutions are obtained. This results in capex savings.
2. Hydrolysis of the iron, which from a laterite is predominantly ferric, and therefore no oxidation step is required. The aluminium reports with the iron in the hematite solids as an oxide phase, which preliminary work has indicated can be washed out with caustic solution if desired. Laterites contain appreciable aluminium (and magnesium) values, which in a sustainable environment can be recovered for value.
3. Secondary hydrolysis to recover a mixed nickel-cobalt basic chloride salt. This can be calcined as-is to form an intermediate mixed oxide for sale and further processing, or re-dissolved in order to effect nickel-cobalt separation, which is relatively straightforward in a chloride medium.
4. Tertiary hydrolysis to recover magnesium hydroxy-chloride, which can be calcined to magnesia.

The process is relatively simple, has been tested at the miniplant scale, and has been extensively modelled. The objective of modeling was to test out the feasibility of the various unit operations prior to embarking on an ambitious and costly pilot plant campaign, and to develop the variable costs associated with the process in order to determine whether or not it is competitive with other technologies being proposed for nickel laterite processing (Dry & Harris, 2012).

### Titaniferous Magnetite

Various titaniferous magnetite ores have been tested from different areas of the world. All of these ores have significant vanadium values, which the conventional smelting route, as practiced by QIT, for example, is not able to recover. With some of these ores, it is possible to selectively leach out the vanadium prior to any titanium leaching, whereas with others, both elements dissolve at the same time. The salient features of the process comprise:

1. Single or two-stage leach with recycled hydrochloric acid, depending on the nature of the ore being treated.
2. For a single-stage leach, hydrolysis of titanium to form $TiO_2$. The purity of this during a miniplant run was 98.7%, as shown in Figure 7 (left), which can be upgraded to 99.97% (pigment quality) by a second leach and hydrolysis step, if so desired (Figure 7, right). The former purity is sufficient as a feed to the existing pigment process used by paint manufacturers, however. XRD spectra of these products have shown them to be rutile rather than anatase.

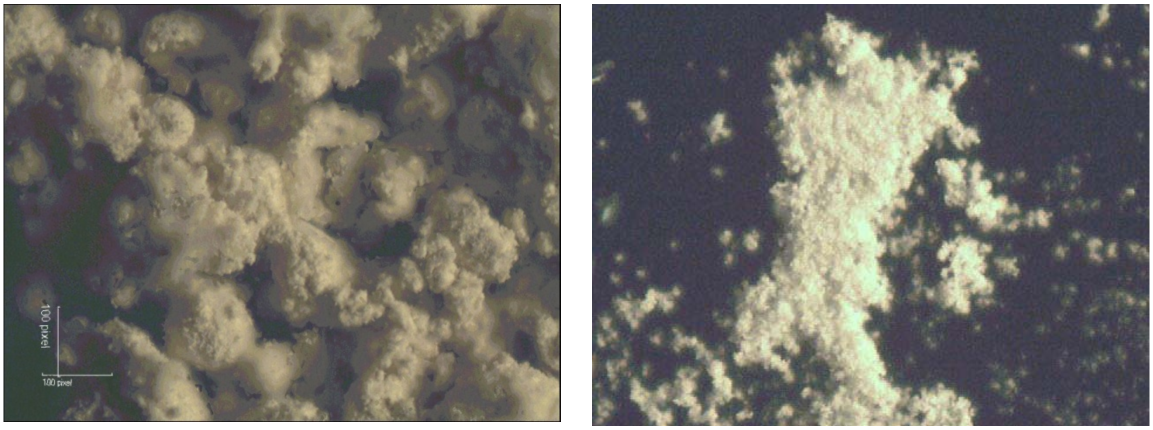

Figure 7 – Micrographs (100X) of impure (98.7%) and purified (99.97%) $TiO_2$

3. Where vanadium is selectively extracted in the leaching stage, it can be recovered as ammonium metavanadate (AMV) via solvent extraction. The AMV is then calcined to form $V_2O_5$ as a final product.
4. Where vanadium and titanium dissolve together, the titanium is first hydrolysed prior to vanadium solvent extraction.

Process modeling and preliminary economic assessments of this process have shown it to be very robust, and more attractive than the current smelting process. A major advantage of the process over smelting, in addition to its ability to recover vanadium, is that there are no constraints on the magnesium content of the feed. The smelting process is unable to handle magnesium levels much above 2%, since it causes problems with the fluidity of the slag in the furnace.

## Lead-Silver Ores and Concentrates

The process for these feeds is very similar to that presented elsewhere in this conference for the treatment of electric arc furnace dust (EAFD). The major difference is that the lead and silver contents are very much higher than for the EAFD, whereas the zinc is very much less, but some of the fundamental unit operations are the same. The main points of the process are:

1. A single or two-stage leach, depending on the nature of the feed, as for the other processes described here, except for the laterite. Ores with a high level of reactive sulphides are best treated with a two-stage leach, whereas concentrates are more likely to require just a single stage. Due to the high chloride matrix, both lead and silver extraction has been over 90% in the materials tested to date.
2. Crystallisation of lead chloride. This is a well-known operation for lead in chloride media, due to lead having a very steep solubility versus temperature curve. Figure 8 shows the progression of crystallization under very gentle agitation from a typical leach liquor. The washed crystals were extremely coarse and well grown, and analysis showed only traces of impurities.
3. The crystals obtained above were slurried in very dilute acid with metallic iron powder to effect the cementation of lead. In practice, depending upon the location, it is likely that DRI (Direct Reduced Iron) made on site from the hematite product of hydrolysis would be used as being the most sensible approach to obtaining the metallic iron needed. Figure 9 shows the lead granules obtained using this method.

Figure 8 - Crystallisation of lead chloride at 5, 10 and 20 minutes as solution cooled to 40°C

Figure 9 - Metallic lead granules from cementation of lead chloride crystals

4. Cementation of silver with recycled copper. There is always some copper present in these types of ores, so it acts as a readily-available reagent. Alternatively, ion exchange may be used, but cementation is a preferred option, particularly when high silver levels (several tens of oz/t) are present. Additionally, it generates metal directly, which can be melted and cast into good delivery silver bars directly.
5. Cementation recovery of copper, followed by residual lead.
6. Iron oxidation and hydrolysis to recover hematite and recycle the acid to the leaching stage. Any impurity build-up in the circuit, such as magnesium or manganese, or the alkali metals, is dealt with by a bleed from this circuit.

The chloride route is particularly attractive for silver ores where there is a high copper content. This copper is readily recoverable in a chloride process, whereas in conventional cyanidation, it is a major problem. Furthermore, since there is less need to effect a clean separation of a lead concentrate, overall metals recoveries are higher using this route compared to conventional approaches. As with the processes discussed above, modeling and preliminary economic assessment have shown the chloride-based approach to be very attractive.

## DISCUSSION

This paper has reviewed some of the major points pertaining to chloride-based metals extraction and recovery. Its primary purpose has been to present the possibilities of working in chloride systems, and in particular, high-concentration chloride systems, with a view to opening up the possibilities that such systems have in achieving the goals of sustainable development, of maximizing the useful recovery of all of the values in the rock that is currently mined, or at the very least, of generating benign residues for disposal. In this respect, it is true to say that the metals extraction industry does not currently in any sense make the most of its resources, resources that are not really renewable, although some recycling does take place. The industry is happy to dig up a tonne of ore to recover 1 gram of gold, or 10 kg of nickel, and return the balance back into the environment, laced with cyanide or acid. Such a situation cannot continue indefinitely.

It has been demonstrated that chloride systems have the potential for greater recovery of metals due to the enhanced activity of hydrochloric acid, and that due to complex ion formation, there is a greater choice of methods available for metals separation. Additionally, the significantly greater solubility of metal chlorides over the corresponding sulphate salt allows for smaller process equipment, and hence potential savings in capital outlay. And further, because of the aggressive nature of chloride extraction circuits, there is the possibility of recovering minor metals such as gallium, the rare earths, tellurium and other so-called rare metals, because all of these dissolve in chloride media. Iron is converted to hematite, which in many cases will have value on its own, but at the very least, is a far more environmentally-friendly option than current practices such as ferrihydrites, red muds and jarosites.

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