THE APPLICATION OF HYDROLYTIC STRIPPING
TO THE IRON PROBLEM IN HYDROMETALLURGY

A.J. MONHEMIUS and G. THORSEN
Dept. of Metallurgy Dept. of Chem. Engng.,
& Materials Science, Norwegian Institute
Royal School of Mines, of Technology,
Imperial College, 7034 Trondheim-NTH,
London SW7 2BP, U.K. Norway.

ABSTRACT

The problems encountered in the production of environmentally safe iron residues by current aqueous phase hydrolysis methods are discussed. The technique called hydrolytic stripping is described. This involves reacting an iron-loaded carboxylic acid solution with water at 150-200°C, whereupon the following type of reaction occurs:

$$2R_{2}Fe + 3H_{2}O \rightarrow Fe_{2}O_{3} \downarrow + 6RH$$

Iron is thus precipitated directly as hematite and the carboxylic acid is regenerated and can be recycled to extraction. The advantages of this technique compared with conventional iron precipitation processes are outlined. An alternative technique, called precipitation stripping, is also described. In this, the iron-loaded carboxylic acid is heated with dilute mineral acid solutions at 100°C at atmospheric pressure, with the result that iron precipitates from the mixed system, normally as a hydrated oxide. The application of solvent extraction and hydrolytic stripping to iron removal in the electrolytic zinc process is outlined.

INTRODUCTION.

"The problem of iron in hydrometallurgical processes, both in solution and in residues, has not yet been resolved to the satisfaction of either metallurgists or environmentalists."

This statement, which was made five years ago (1), is still an accurate assessment of the current situation with respect to the iron problem in hydrometallurgy. There are various facets to the overall problem, but one of the most pressing is the removal of iron from acidic leach liquors which has yet to be resolved in a fully satisfactory manner.

Over the past fifteen years, great progress has been made in the application of hydrolysis methods to the precipitation of iron from such liquors. The most important development was the introduction of the Jarosite process, whereby iron can be precipitated from acidic sulphate liquors as crystalline, easily filterable, basic sulphates known as jarosites MFe$_3$(SO$_4$)$_2$(OH)$_6$. This process has been adopted in particular by a large number of electrolytic zinc plants and this has led to a very significant increase in the overall recovery of zinc that can be achieved by the electrolytic route. More recently, the Goethite and Hematite processes have been developed, both designed to do much the same as the Jarosite process.
All three processes can achieve their primary objective, namely the removal of iron from acidic leach liquors, in a technically successful manner. However, the outstanding problem, which is growing more acute in certain parts of the world, is the disposal of the iron residues generated by these processes in an environmentally acceptable manner. The problems involved are illustrated by the data given in Table 1, where it may be seen that the iron products are contaminated by significant quantities of zinc and sulphur. The former arises principally from zinc calcine, which is added during the precipitation of iron to neutralise the acid produced by the hydrolysis reactions, while the latter is due either to the incorporation of sulphate in the crystal lattice of the iron product or to the co-precipitation of basic sulphates. Furthermore, the iron precipitates are prone to further contamination by small but significant amounts of other heavy metals which may be present in the leach liquors due to secondary effects such as adsorption, occlusion or co-precipitation.

**TABLE 1. Compositions and quantities of iron residues (2)**

<table>
<thead>
<tr>
<th>Process</th>
<th>Jarosite</th>
<th>Goethite</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. residue/wt.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn concentrate</td>
<td>0.4</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>Fe wt. %</td>
<td>25-28</td>
<td>40-45</td>
<td>58-60</td>
</tr>
<tr>
<td>Zn wt. %</td>
<td>4-6</td>
<td>5-8</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Total S wt. %</td>
<td>10-12</td>
<td>2.5-5</td>
<td>3</td>
</tr>
</tbody>
</table>

This contamination of the iron residues makes them unacceptable for further uses such as iron-making and the only remedy is to dispose of the residues by dumping. However, weathering of the dumps leads to leaching of the contaminating elements and this effect can create serious problems of containment and treatment of the run-off effluents from the dumps.

At the present time, these difficulties are most evident in the electrolytic zinc industry, but similar problems arise in other hydrometallurgical processes, particularly those designed to treat sulphide concentrates by acid leaching.

The obvious solution to this situation would be to devise a method for precipitating iron from solution as a clean, uncontaminated solid, preferably an oxide, which could be utilised as feed to an iron-making process, thereby obviating the need for dumping. However, judging by the results of the considerable amount of research and development effort expended over the past decade or so, this goal does not appear to be achievable if precipitation of iron is carried out from an aqueous phase. Even if the iron solution is highly purified prior to precipitation, contamination of the precipitate with the anion present in solution is almost inevitable.

In spite of the fact that ferric iron can be readily removed from aqueous solutions by solvent extraction, by organic acids for example, or amines in the case of chloride solutions, very few applications of this process for iron extraction are in commercial use. One of the reasons for this is that solvent extraction as currently practised does not solve the fundamental iron problem - it merely transfers iron from one aqueous solution to another. The iron will finally report in an aqueous strip liquor from which it still has to be precipitated for ultimate disposal. However, the new technique of hydrolytic stripping (3), by which iron oxides can be precipitated directly from organic phases, offers an alternative approach to the iron problem.
which shows promise of overcoming the difficulties associated with aqueous phase precipitation outlined above.

Hydrolastic stripping, which has been shown to be applicable in particular to organic phases containing alkyl carboxylic acids, involves heating an iron-loaded carboxylic acid solution with water to temperatures in the region of 150–200°C, whereupon the following type of reaction occurs:

$$2\text{R}_3\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{RH}$$

(1)

where a bar over a species indicates that it is in the organic phase and R represents the alkyl carboxylic radicle. Thus by this simple procedure, iron is precipitated directly from the organic phase as an oxide and the carboxylic acid is regenerated in the acid form for recycle to extraction. At the elevated temperatures required for the process, thermal stability is a primary requisite of the organic acid utilised to carry the iron. In addition to alkyl carboxylic acids, alkyl phosphoric and alkyl sulphonic acids have been examined, but neither of these has shown the necessary thermal stability. In all the experimental work reported below, Versatic acids, commercially available, tertiary alkyl carboxylic acids, produced by Shell, have been used.

**EXPERIMENTAL**

Solutions of 33% by volume Versatic 10 in Escaid 110 were used. Iron was loaded into the organic phase by first dissolving solid CaO into the Versatic acid solution by heating and stirring and then vigorously shaking the calcium-loaded organic solution with aqueous ferric chloride solution. After iron loading, the organic solutions were washed with acidified water to remove residual calcium and then filtered through phase-separation paper to remove entrained water.

Kinetic studies on the rates of hydrolastic stripping at elevated temperatures were carried out in a stainless-steel autoclave of 300 ml internal volume, equipped with an efficient stirrer and a sampling system. The required volume of iron-loaded organic phase (usually 120 to 200 ml) was heated to the reaction temperature in the sealed autoclave, usually under a nitrogen atmosphere. After temperature stabilisation, a sample of the organic phase was taken and then the required volume of water (usually 10 ml) was injected into the autoclave from a reservoir. Samples of the organic phase were then taken periodically, via the sampling system, immediately filtered, and stored for later analysis by atomic absorption.

Experiments on precipitation stripping at the boiling point were carried out in a stirred glass reaction vessel of 250 ml volume, heated by an electric mantle. The required volume of iron-loaded organic phase (usually 100 ml) was put in the reaction vessel and heated with stirring to 100°C. The required volume of aqueous phase (usually 100 ml), containing the appropriate concentration of acid, was heated to the boiling point and then added to the hot organic phase in the reaction vessel to start the reaction. The rate of reaction was followed by periodically withdrawing samples of the mixed phases from the vessel by pipette. These were allowed to separate, any solids were filtered off, and then the iron contents of each phase were determined.

The acid values of the organic phases before and after stripping were determined by potentiometric titration. Residual iron was first removed from the organic phase by mineral acid stripping followed by water washing.
Weighed amounts of organic phase were then dissolved in ethanol and titrated with standard aqueous sodium hydroxide solutions.

RESULTS

1) Hydrolytic Stripping.

The effect of temperature on the rate of precipitation of ferric iron from solutions of Versatic 10 reacted with water is shown in Figure 1. It may be seen that the rate of precipitation is strongly influenced by temperature. At 150°C only approximately 15% of the iron had been precipitated after 2 hours, whereas at 185°C virtually total precipitation had occurred within 20 minutes. At temperatures below 200°C the iron oxide product was usually hematite and the overall reaction may be represented by Equation (1). The particle size range of the precipitates generally increased with temperature - the d50 (particle size at 50% cumulative weight) rising from 20μm at 170°C to 40μm at 215°C. No major difficulties were experienced with filtration of the organic/oxide slurries and simple acetone washing reduced levels of adsorbed organic to less than 1% by weight of the solid products.

At reaction temperatures of 200°C and below, there was no observable change in the acid value of the organic phase after hydrolytic stripping and it was concluded that Versatic acid was stable under the reaction conditions at least up to 200°C.

The rate data shown in Figure 1 strongly suggest that the precipitation of hematite in this system occurs by a nucleation and growth mechanism. Further evidence of this is provided by the effect of "seeding" shown in Figure 2. These data were obtained by adding to the system iron oxide precipitated in a previous experiment. The presence of the solid particles in the system at the beginning of the reaction provided growth sites and reduced the nucleation period, with the result that the time required for total precipitation was substantially reduced. This procedure also increased the mean particle diameter of the oxide product.

2) Precipitation Stripping.

Although hydrolytic stripping, using water as the stripping agent, has a number of advantages as outlined in the following discussion, pressurised equipment is necessary to contain the water vapour pressures at the elevated temperatures required for the process. It is however possible to carry out similar reactions at temperatures close to the boiling point at atmospheric pressure. In order to do this it is necessary to change the stripping agent from pure water to a dilute mineral acid solution. The presence of acid in the aqueous phase is required to initiate stripping of iron from the organic phase. Thereafter the reaction is self-sustaining due to the production of hydrogen ions during the hydrolysis and precipitation of iron. Experimental evidence suggests that, under these conditions, the overall reaction occurs in two stages:

\[
\text{Stage 1 - Stripping } \quad \text{R}_3\text{Fe} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{RH} \quad (2)
\]

\[
\text{Stage 2 - Precipitation } \quad \text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH}^+ + 3\text{H}^+ \quad (3)
\]

The hydrogen ions formed in Stage 2 are then available to continue the Stage 1 reaction. Thus the metal is precipitated from the aqueous phase, and stripping is a separate, albeit interrelated, process. For this reason
FIG 1.
Hydrolytic stripping: effect of temperature on rate of precipitation. Organic phase: 120 ml 33% Versatic 10 containing 10.5 g/l Fe$^{3+}$. Aqueous phase: 10 ml H$_2$O.

FIG 2.
Hydrolytic stripping: effect of recycled solids on rate of precipitation. Temperature: 170°C. Organic phase: 200 ml 33% Versatic 10 containing 21.5 g/l Fe$^{3+}$. Aqueous phase: 10 ml H$_2$O.
this type of reaction at the normal boiling point has been named "precipitation stripping" to distinguish it from hydrolytic stripping, where pure water and elevated temperatures are used.

As can be seen from equations (2) and (3), unlike conventional aqueous hydrolytic precipitation there is no necessity to add a neutralising agent during the reaction. The system is self-buffering, with the basic organic acid radicle consuming the hydrogen ions produced by the hydrolysis of iron.

Sulphuric acid can be used to initiate the reaction. Figure 3 illustrates results obtained when solutions of Versatic 10 containing about 25 g/l Fe³⁺ were reacted at 100°C with equal volumes of dilute sulphuric acid, containing from 5 to 40 g/l H₂SO₄. The results show the concentrations of iron in the organic and aqueous phases as a function of reaction time, together with the percentage of iron precipitated as a solid product and the changes in pH of the aqueous phases.

It may be seen that with an aqueous phase containing 5 g/l H₂SO₄, no reaction occurred and all the iron remained in the organic phase. This was because the pH of the aqueous phase was about 5 and was too high to cause stripping. However at 10 g/l H₂SO₄ the aqueous phase was sufficiently acidic for stripping and subsequent precipitation to occur and, after 6 hours, over 95% of the iron had been removed from the organic phase and precipitated from solution. At an initial acidity of 20 g/l H₂SO₄ the stripping rate was considerably faster, with over 95% of the iron removed from the organic phase in 2 hours. However, the percentage of iron precipitated was reduced due to the lower pH of the aqueous phase and the consequent higher solubility of iron in this phase. This effect was accentuated with an initial acidity of 40 g/l H₂SO₄.

The form in which iron is precipitated depends on the composition of the aqueous phase and the concentration of iron in the organic phase. For sulphuric acid stripping, the iron product is usually goethite, FeOOH, except when the initial sulphate/iron ratio in the system is high, i.e. when the sulphuric acid concentration of the aqueous phase is high or the iron concentration in the organic phase is low. Under these conditions, basic sulphates such as glockeite, Fe₄S₀₄(OH)₁₀, or jarosite, H₃OFe₃(SO₄)₂(OH)₆, may be formed. If hydrochloric acid is used in place of sulphuric acid, then the iron product is normally hematite, Fe₂O₃.

As in the case of hydrolytic stripping, the rate of precipitation stripping can be considerably increased by "seeding" with solids recycled from previous runs. A comparison of runs (c) and (e), shown in Figure 3, illustrates this effect. Furthermore, this procedure promotes particle growth and greatly improves the solid/liquid separation characteristics of the precipitates.

DISCUSSION.

The unique characteristic of hydrolytic stripping is that iron is precipitated directly from loaded carboxylic acid solutions by reaction with pure water. Because of the strong affinity of carboxylic acids for iron, the organic phase can be purified to any desired degree by standard solvent extraction techniques prior to stripping. Therefore there need be no inorganic ions in the system, except iron and those derived from water itself, with the result that the product of the process is pure iron oxide, uncontaminated
Precipitation stripping: Rate of change in organic and aqueous iron concentrations, aqueous pH and percent precipitation.

Temperature: 100°C. Organic phase: 100 ml 33% Versatic 10 containing 25 g/l Fe₃⁺. Aqueous phase: 100 ml containing H₂SO₄ at (a) 5 g/l, (b) 10 g/l, (c) 20 g/l, (d) 40 g/l and (e) 20 g/l, plus 3.5 g recycled FeOOH.
by inorganic anions or cations. This is the key difference and major advantage of hydrolytic stripping compared with conventional aqueous phase hydrolytic precipitation. The iron oxides from hydrolytic stripping should therefore be suitable for further use, particularly in iron-making processes. It is likely, of course, that the oxide will be contaminated by some adsorbed organic phase, but this will merely act as "free" reducing agent during iron-making.

A secondary advantage of the process is that it reduces the number of unit operations required to produce a solid product via solvent extraction, since the conventional stripping stages are eliminated. Pressurised equipment will be necessary because of the elevated temperature required. However, as illustrated in Figure 1, reaction rates can be made to be very rapid and therefore throughputs in the pressurised equipment will be high - a simple pipeline reactor may suffice.

Although hydrolytic stripping offers considerable potential advantages over current processes used for iron removal from process liquors, the major economic problem is likely to be the cost of loading iron into the carboxylic acid in the first place. Because extraction occurs by a cation exchange mechanism, the protons produced during the reaction have to be neutralised in order to bring about full metal loading in the organic phase. For a low-value product like iron, direct neutralisation with an alkali will often not be economically viable and an alternative method has to be sought. In the case of iron removal from zinc process liquors, the alkaline property of zinc calcine, ZnO, can be used to overcome this problem, as discussed in a recent paper by Thorsen and Grislingas (4). Briefly, the technique is to react the carboxylic acid solution directly with the zinc calcine to produce an organic solution containing zinc carboxylate:

\[ 2RH + ZnO \rightarrow R_2Zn + H_2O \]  

(4)

This step is termed organic leaching. The zinc carboxylate solution is then contacted in a conventional solvent extraction system with the main iron-bearing aqueous zinc leach liquor, where an exchange extraction mechanism occurs, with iron entering the organic phase and being replaced in the aqueous phase by zinc:

\[ 3 \overline{R_2Zn} + 2Fe^{2+} \rightarrow 2\overline{R_3Fe} + 3Zn^{2+} \]  

(5)

Thus the combination of organic leaching and exchange extraction enables iron to be removed from the main leach liquor into the organic phase without any extraneous alkali requirement. The overall organic cycle can then be completed by utilising hydrolytic stripping for iron removal. A conceptual flowsheet of the integrated process is shown in Figure 4.

The main practical difference between hydrolytic stripping and the alternative technique discussed in this paper, namely precipitation stripping, is that in the latter method pressurised equipment is not necessary. However, this apparent advantage is offset by the fact that it is necessary for the aqueous phase to contain mineral acid. This of course introduces a source of inorganic anions into the system and therefore anion contamination of the iron product must be expected. Nevertheless the iron product from precipitation stripping is still likely to be purer than those produced by current aqueous phase hydrolytic processes, for the following reasons.
Firstly, traces of contaminating cations can be eliminated from the organic phase prior to precipitation and, secondly, no neutralising agent has to be added during precipitation because of the self-buffering property of the precipitation stripping system.

CONCLUSION

The techniques outlined in this paper are clearly not a panacea for all aspects of the iron problem in hydrometallurgy. Nevertheless, it is believed that the basic concept of direct hydrolytic reaction with iron contained in an organic phase, where it is chemically isolated from the usual sources of contamination, is one which may help to overcome some of the problems encountered when dealing with aqueous solutions containing this ubiquitous element.

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REFERENCES