

DEVELOPMENT OF A NOVEL HIGH-CHLORIDE CIRCUIT FOR THE STARFIELD RESOURCES' FERGUSON LAKE PROJECT

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Abstract

Starfield Resources is developing a novel circuit for the recovery of nickel, copper, cobalt, iron oxide, sulphuric acid and precious metals from the Ferguson Lake deposit in Nunavut, Canada. In this deposit, pentlandite is too finely disseminated in pyrrhotite for the production of a smelter-grade nickel concentrate at an acceptable nickel recovery, so established technology is not applicable and a novel chloride-based circuit is under development. The enabling aspect of this circuit is the hydrolysis of ferric chloride to hematite, releasing gaseous hydrochloric acid that is recycled. Conventional steps are used for separating and recovering the valuable metals from the chloride solution generated. This paper briefly outlines the circuit and presents the results of experimental work on the enabling steps, *viz.* the oxidation and hydrolysis of iron chloride to hematite and gaseous hydrochloric acid.

Introduction

The Ferguson Lake bulk sulphide ore body in Nunavut, Canada, owned by Starfield Resources Inc., contains significant amounts of base and precious metals but its mineralogy is such that it is not amenable to conventional processing. Pentlandite, for example, is too finely disseminated in pyrrhotite for even modern techniques such as fine grinding and improved flotation reagents to be effective [1] and extracting the value requires processing the entire bulk sulphide, including the pyrrhotite. To give the project a total green footprint, in terms of both carbon emissions and acid rock drainage, Starfield imposed the following requirements:

- No reactive tailings to generate acid rock drainage.
- No gaseous emissions other than normal atmospheric constituents.
- No liquid effluents.
- No regular consumption of fossil fuel.
- High recoveries of all the valuable metals.

The circuit under development has been designed to meet these requirements [2; 3]. A recent techno-economic evaluation of the circuit gave a pre-tax Internal Rate of Return of 13.4% [3], ignoring contributions to revenue from the sale of hematite, precious metals in the final leach residue and surplus electricity generated from heat released in the conversion of H₂S to sulphuric acid. Further development work, commissioned by Starfield Resources Inc., is in progress at the Minerals Services group of SGS Canada Inc., in Lakefield, Ontario, Canada. Arithmetek Inc. is incorporating the data into detailed mass/energy balances over the circuit to generate the information needed for engineering design and costing calculations. This paper focuses on the oxidation and hydrolysis sections of the circuit.

Circuit

The circuit is illustrated in Figure 1. The solid arrows denote solid or slurry flows, the dashed lines liquid flows and the dotted lines gaseous flows. The two leaching sections have been described elsewhere [4] and the recovery section uses established technology. These sections are therefore not discussed in this paper. The oxidation section is an extension of conventional practice and the hydrolysis section is novel.

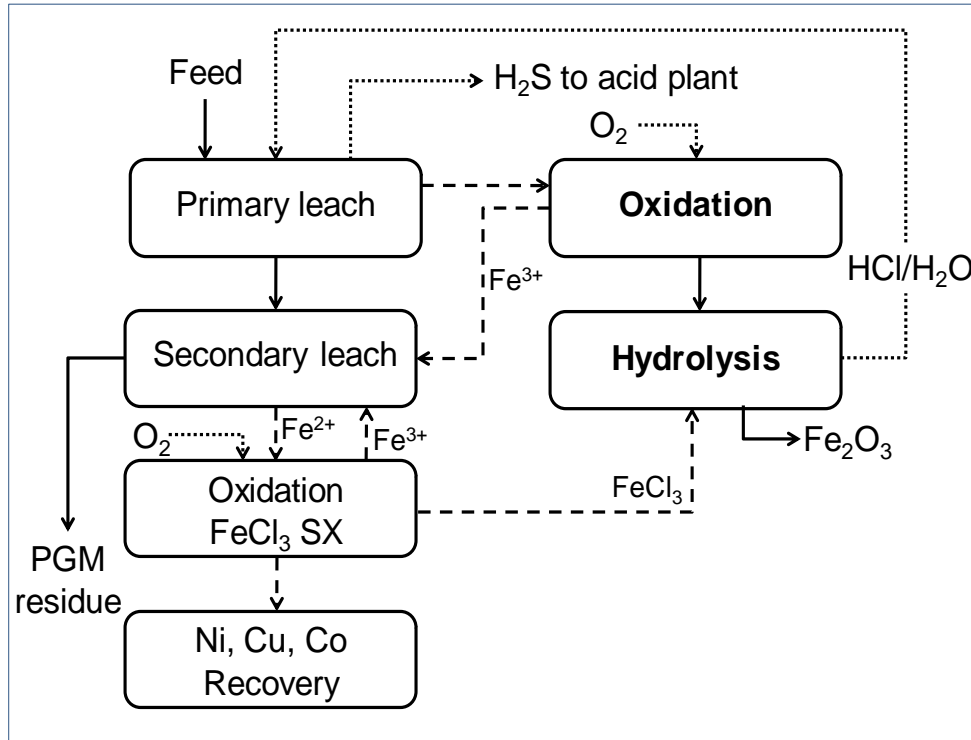


Figure 1. Simplified circuit outline.

The overall concept of the circuit is as follows:

- The primary leach contacts the bulk sulphide with recycled strong hydrochloric acid in a background solution of high chloride concentration, converting the pyrrhotite to aqueous ferrous chloride, gaseous hydrogen sulphide and some elemental sulphur.
- The ferrous chloride in the high-chloride solution from the primary and secondary leaches is oxidized with oxygen, at atmospheric pressure, to ferric chloride.
- The secondary leach contacts the residue from the primary leach with ferric chloride from either of the oxidation stages, dissolving base metals and converting the associated sulphide sulphur to elemental sulphur.
- The hydrolysis step converts the ferric chloride from the oxidation steps to hematite and gaseous hydrochloric acid. The hematite is a stable residue or a saleable by-product and the acid is recycled to the primary leach.
- A conventional wet-gas acid plant converts the hydrogen sulphide and elemental sulphur from the primary and secondary leach steps to concentrated sulphuric acid, releasing enough energy to drive the overall circuit.
- Extraction, separation and recovery of the base metals from the solution *ex* the oxidation step after the secondary leach uses established solvent extraction and electrolysis technology.

Oxidation

Equipment

Figure 2 shows the set-up used for the experimental work on oxidation. The feed reservoir and the boiler were heated using electric mantles and the oxidation reactor was jacketed and heated with hot oil. Synthetic feed solution was held at about 80°C in the feed reservoir. From there it was pumped to the boiler at a controlled rate. The function of the boiler was to evaporate excess water from the feed solution to make the overflow into the reactor contain the required concentrations of the various salts (ferric, ferrous, nickel, cobalt, copper and magnesium chlorides). The boiler was necessary to allow the feed solution to be sufficiently dilute to enable pumping without blockages due to crystallization, at the small flows used. At a commercial scale this particular problem will not arise because the flows will be sufficient to keep the liquid hot enough to avoid crystallization.

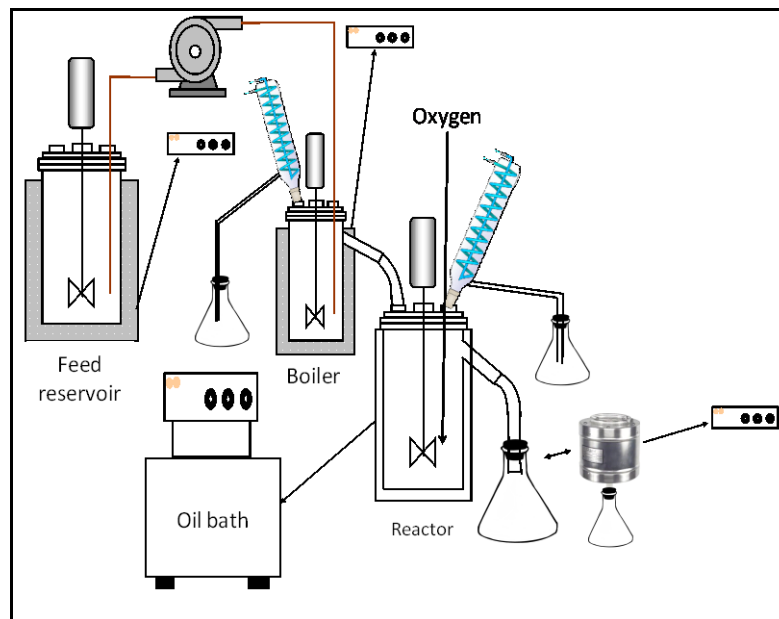


Figure 2 – Experimental set-up

Operation

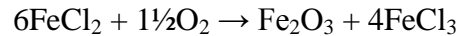
The hot concentrated solution (representing leach liquor) overflowed from the boiler into the reactor, where it reacted with injected oxygen. The overflow from the reactor was captured into batches of pre-weighed acidified (pH 2) water. After collection, each batch was weighed and filtered, the filter cake was washed, the solids and filtrate were weighed and analyzed and the results were used to compute the mass and composition of that batch of reactor effluent.

The temperatures in the boiler and oxidation reactor, the flow of oxygen through the oxidation reactor, the composition of the feed solution and the impeller type and rotation speed were varied in a set of short (8 hour) tests. The parameters varied in an extended test (78 hours) were the agitation intensity, the feed rate into the system and the refluxing or not of condensate from the gas phase back into the reactor.

Condensate from the boiler was removed from the system. Initially, condensate from the reactor was returned to the reactor. Later, this condensate was also removed.

Theory

The chemical reaction involved in the oxidation of ferrous chloride to ferric chloride is as follows:



The oxidant is gaseous oxygen that is injected into a solution of ferrous/ferric chloride. The rate at which the ferrous chloride is oxidized depends on two internal rates, *viz.*

- The chemical reaction between the ferrous iron and dissolved oxygen.
- The transfer of oxygen from the gas into the solution.

The slower of these two rates controls the overall rate of oxidation. Reactions between dissolved ions and dissolved oxygen are often much faster than the rate at which oxygen can be dissolved into the solution, thus the overall rate is often controlled by the transfer of oxygen into the solution. That, in turn, is strongly influenced by the intensity of agitation, which determines the number and size of oxygen bubbles that can be produced in the reactor (*i.e.* the gas-liquid interfacial area). It is also influenced by the pressure of oxygen in the bubbles, greater pressure leading to faster dissolving of oxygen. In larger reactors, the depth of liquid gives increased pressures in the deeper zones of the reactor, which assists the dissolution of oxygen. In the small vessels necessarily used in laboratory-scale work, this effect is negligible at atmospheric pressure above the fluid phase. The basic material balance governing any given species in a chemical reactor, and applied to ferrous iron in this work, is:

$$\text{Accumulation} = \text{In} - \text{Out} - \text{Reaction}$$

A transient numerical model was set up using the above equation and fitted to the data from the extended run. The Reaction term, *i.e.* the rate of oxidation of ferrous iron, used in the transient model was fitted using the following empirical equation:

$$\frac{d[\text{Fe}^{2+}]}{dt} = \frac{A[\text{Fe}^{2+}]}{1 + (B + Cn)[\text{Fe}^{2+}]}$$

In this equation $[\text{Fe}^{2+}]$ is the amount of ferrous iron in the reactor, n is the stirrer speed and A, B and C are fitted constants. The partial pressure of oxygen in the gas phase (oxygen bubbles) is lumped into the value of the constant A. Two sets of values for the constants A, B and C were found using a search engine, minimizing the sum of the squared differences between the model predictions and the measured data, one for when the water vapor condensed from the oxygen leaving the oxidation reactor was refluxed back to the reactor and one for when the condensate was removed. The reason for using two sets of these constants is that the fraction of water vapor in the oxygen leaving the reactor could not be determined explicitly when the condensate was returned to the reactor and therefore the partial pressure of the oxygen in the gas phase could not be calculated explicitly.

The In term for each time increment was calculated from the amount of feed solution entering the boiler over that time increment and the Out term was the amount leaving the reactor over the time increment. The accumulation term captured the change in the composition of the material in the reactor over the time increment, and approached zero as the system steadied out.

Results

Table 1 lists the operating conditions tested during the extended run. The density of the feed entering the boiler was 1.4 kg/L and it contained 191 g/L of Fe^{2+} and 19 g/L of Fe^{3+} . The solvent was water. The measured data and the values predicted by the transient model are shown in Figure 3. The left-hand graph shows the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the reactor discharge and the right-hand graph shows the level of ferrous iron in the discharge. While there is some scatter in the data, the model tracks the data reasonably well.

Table 1. Oxidation conditions

Period hours	Fe^{2+} into boiler g/h	Impeller speed RPM	Reactor condensate
0 to 12	50	1000	Refluxed
12 to 24	43	750	Refluxed
24 to 34	43	1250	Refluxed
34 to 44	60	1250	Refluxed
44 to 53	72	1250	Refluxed
53 to 59	78	1250	Refluxed
59 to 60	78	1250	Removed
60 to 66	88	1250	Removed
66 to 72	82	1250	Removed
72 to 78	75	1250	Removed

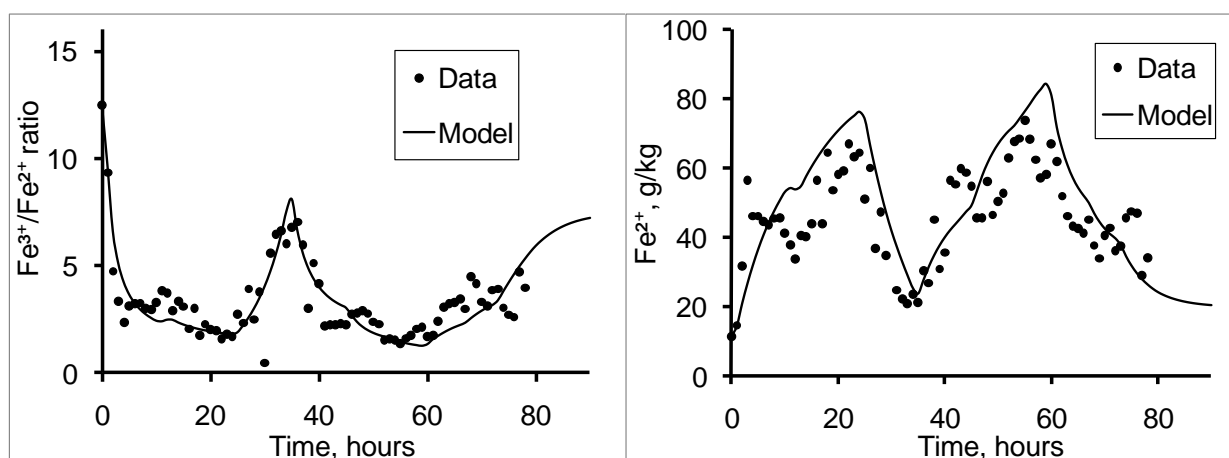


Figure 3. Oxidation data (reactor discharge)

The rates of oxidation fitted *via* the model are shown in Figure 4, along with the corresponding stirrer speeds and amounts of ferrous iron in the reactor. Even though the level of ferrous iron changed during the different periods of the test, the oxidation rates were found to be constant at each stirrer speed, and to correlate with the stirrer speed. This implies that the rate of oxidation of ferrous iron does not depend on the concentration of ferrous iron in the reactor, at least over the range seen in this work. A plausible explanation for this is that the rate of oxidation of ferrous iron depends on the rate at which oxygen can be dissolved into the solution, which would depend on the intensity of agitation and the partial pressure of oxygen in the gas phase.

The values found for the constants A, B and C in the equation used to represent the rate of oxidation of the ferrous chloride are listed in Table 2. These are purely empirical values, but

they do make the transient model fit the data. Two sets of values were found, one for while condensate was returned to the oxidation reactor and one for when it was removed.

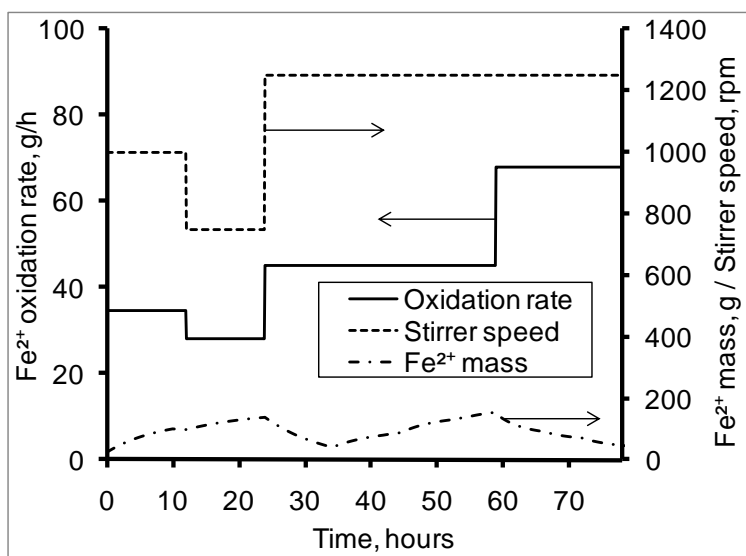


Figure 4. Oxidation rates and stirrer speeds

Table 2. Constants in the rate expression

Condensate	A	B	C
Refluxed	5.93E+05	3.28E+04	-1.58E+01
Removed	1.35E+06	3.96E+04	-1.58E+01

Removing the water condensed from the oxygen leaving the reactor instead of returning it to the reactor (about 60 hours into the run) increased the rate of oxidation of ferrous iron by just over fifty percent. This is consistent with the rate of oxidation depending on the rate at which oxygen is dissolved into the solution, which depends on the agitation and on the partial pressure of oxygen in the gas phase. Returning the condensate resulted in a circulating load of water in the system, with the water being evaporated, condensed, returned and re-evaporated. The resulting greater proportion of water vapor in the gas phase would have lowered the partial pressure of oxygen and thus also the rate at which oxygen was dissolved into the solution.

Discussion

Figure 5 shows plots of the rate of oxidation of ferrous iron against the concentration of ferrous iron in the reactor, extrapolated to very low levels of Fe^{2+} using the constants fitted to the rate expression from the measured data, for the condensate from the oxygen leaving the system being returned to the reactor (refluxed) and for the condensate being removed. The horizontal axes on these two plots are logarithmic to stretch out the lower-concentration range relative to the higher-concentration range. Two things are immediately apparent from these graphs - the oxidation rate appears to be independent of the concentration of Fe^{2+} in the reactor, down to very low levels of Fe^{2+} and removing the condensate increased the rate of oxidation from 45 to 68 g/h, an increase of just over 50 percent, *i.e.* a decrease in the required residence time in the oxidation reactor, and therefore the required reactor volume, by a third.

Although this is an extrapolation not yet experimentally proven, if the rate of oxidation is independent of the concentration of ferrous iron down to very low levels of ferrous iron, it

should be possible to achieve a very high overall extent of oxidation in a single reaction stage, merely by allowing sufficient residence time. A single-reactor design would eliminate the extra agitators, *etc.* associated with a multiple-reactor train.

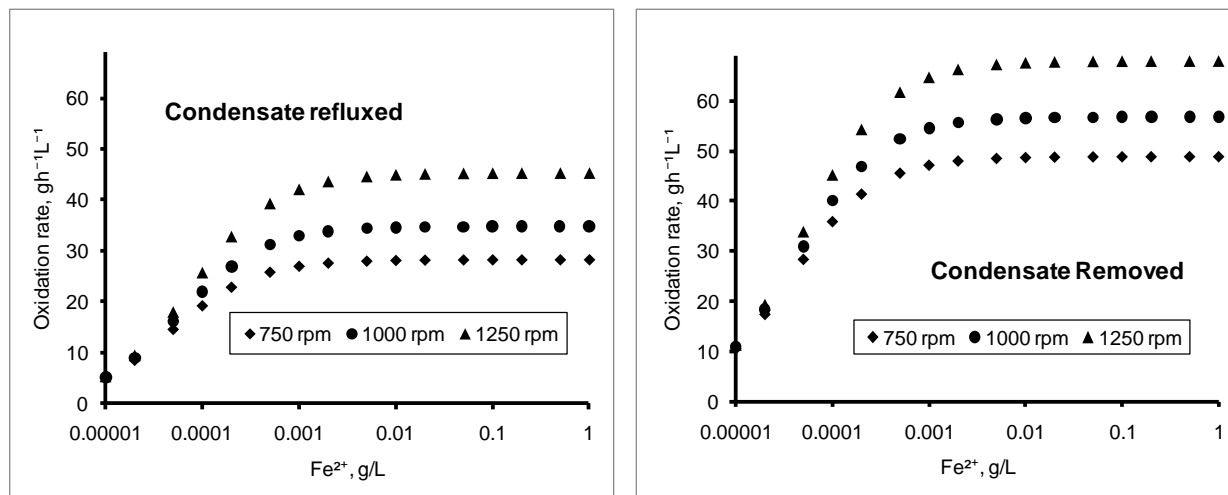


Figure 5. Oxidation rates versus Fe²⁺ concentration

Hydrolysis

Equipment

Figure 6 illustrates the apparatus used for the hydrolysis tests. All the vessels were heated by electric mantles (not shown in the diagram). The feed was made up and stored at 80°C in the feed reservoir. (As in the oxidation work, the feed concentration needed to be low enough to avoid crystallization in the feed line.) The warm feed was pumped from the feed reservoir to the boiler and heated to just below the temperature at which the hydrolysis reaction begins. The steam evolved was condensed and collected. The hot evaporated feed overflowed from the boiler into the reactor, where it was heated further to the hydrolysis temperature. The steam and hydrochloric acid evolved were condensed and collected. The remaining liquid and the solids formed overflowed from the reactor and were collected, measured and assayed in the same way as was done in the oxidation work. Each batch of condensate collected from the boiler or the reactor was weighed and its density and HCl content were measured.

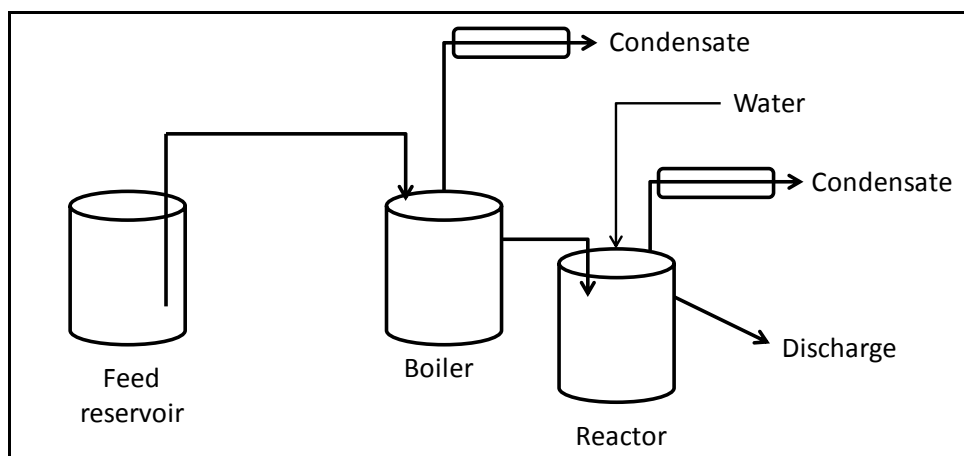


Figure 6. Hydrolysis set-up

Results

The overall hydrolysis reaction is $2\text{FeCl}_3 + 6\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{HCl}$. Preliminary tests showed that the appropriate temperature for the hydrolysis reaction is about 180°C and that the hydrolysis reaction begins at close to 140°C .

A series of short (8 hour) tests was done to set up preliminary operating conditions for the system, after which an extended test (80 hours) was conducted. The objectives of the extended test were to demonstrate stable operation of the hydrolysis reactor, show that hematite and strong hydrochloric acid are the reaction products and to measure the extent of hydrolysis that can be achieved. The feed was a synthetic solution mimicking the composition of the most oxidized solution actually produced in the oxidation work. Table 3 shows the overall mass and individual elemental balances measured over the extended hydrolysis test.

Table 3. Material balances (grams)

Mass, grams	Total mass	Element								
		Fe ³⁺	Fe ²⁺	Cu	Co	Ni	Mg	Cl ⁻	H	O
Starting inventory	2527	464	92	25	2	22	18	990	99	814
Total input	26023	2703	622	169	14	146	120	6668	1743	13837
Total discharged	25255	2303	445	121	9	99	77	6715	1845	14579
Final inventory	2509	337	120	34	3	29	23	1055	92	801
Balance (Out/In)	97%	83%	79%	80%	70%	76%	73%	101%	105%	105%

The left-hand graph in Figure 7 shows the measured composition of the fluid phase leaving the hydrolysis reactor. The symbol M^{2+} is an abbreviation for the total mass of nickel, copper, cobalt and magnesium per kilogram of fluid phase. The right-hand graph shows the extent of hydrolysis of the ferric chloride, calculated from the amounts of ferric iron in the solids and the fluid in the reactor discharge. The values for nickel, magnesium and cobalt had steadied out by about 30 hours, but between about 60 and 75 hours these values fluctuated, possibly due to temperature fluctuations that occurred about then.

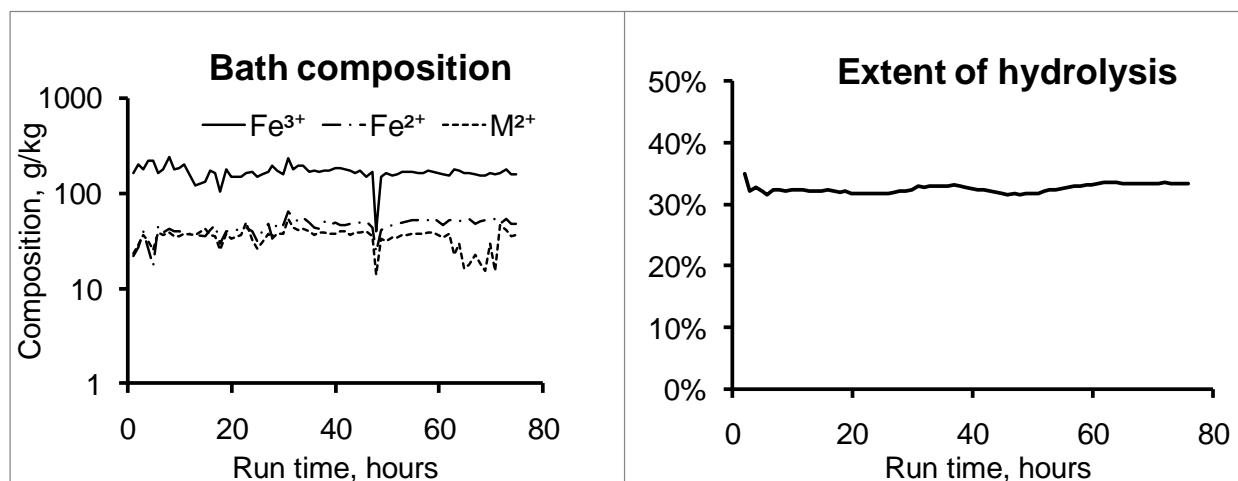


Figure 7. Hydrolysis results

Figure 8 shows the rates and extents of hydrolysis achieved through the extended test, plotted against the rate at which ferric iron was fed into the system.

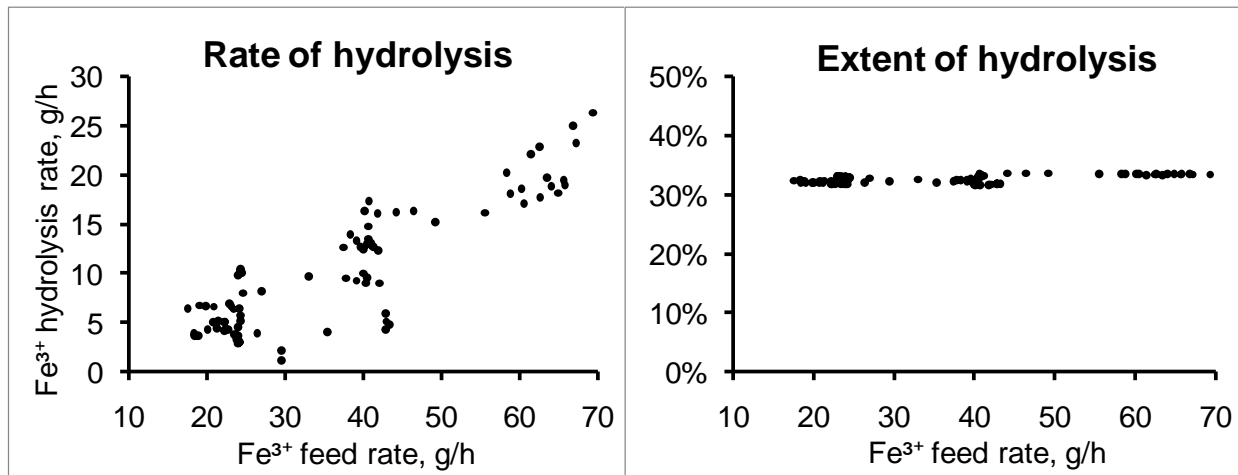


Figure 8. Hydrolysis kinetics

The rates of hydrolysis do exhibit some scatter, but the trend in the left-hand graph is clearly towards higher rates of hydrolysis as the feed rate increased. The right-hand graph shows only a little scatter and also shows quite clearly that the extent of the hydrolysis reaction was not dependant on the feed rate into the system, *i.e.* the residence time in the hydrolysis reactor was long enough, throughout, for the Fe^{3+} concentration in the reactor to equilibrate with the gas phase. Interestingly, the extent of hydrolysis does not seem to depend particularly strongly on the exact temperature, at least between 180°C and 185°C . Nor does the extent of hydrolysis seem to depend on the ratio of water to feed used, within the range tested. The extent of hydrolysis being just over 30 percent is beneficial – had the reaction gone to high conversion, the amount of hematite formed could have made the slurry in the reactor lose its fluidity. At the lower per-pass conversion, the overflow can be filtered and the filtrate returned to the reactor.

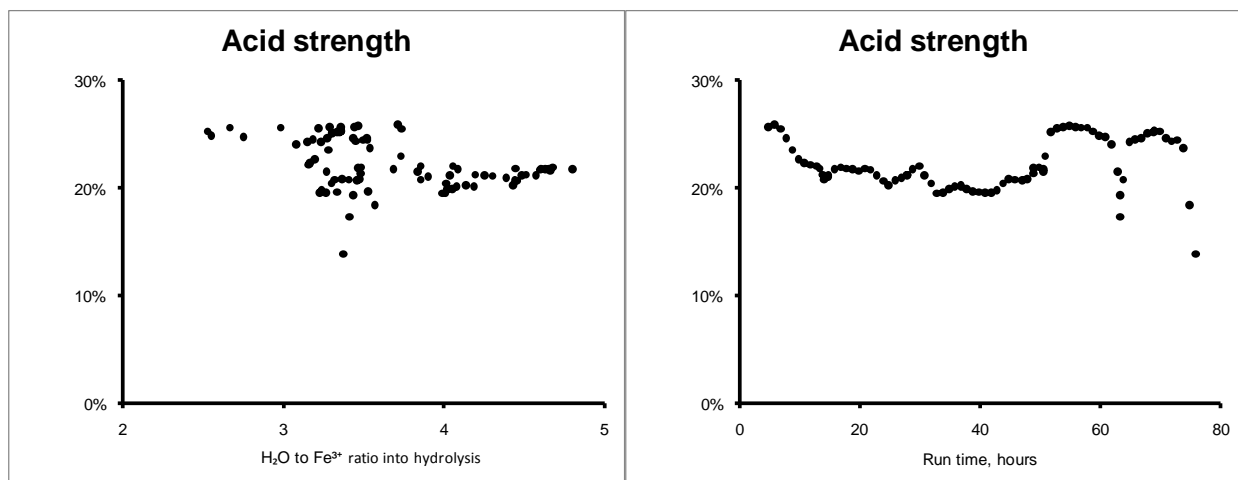


Figure 9. Acid strength

Figure 9 shows the strength of the hydrochloric acid in the condensate from the hydrolysis reactor, plotted against the mass ratio of water to ferric iron entering the reactor, and against run time. The values are somewhat scattered, but it does seem that, below about 3.5 grams of water

per gram of ferric iron into the reactor, the condensate contained up to about 25 percent HCl and above that ratio of water to ferric iron the condensate contained about 20 percent HCl.

The solids recovered from the hydrolysis reactor discharge contained 68.9 percent iron, which corresponds to 98.5 percent Fe₂O₃. Mineralogical analysis showed the solids to be hematite. The average chloride assay of the solids was 0.9 percent and the lowest value was 0.5 percent.

Conclusions

The technical conclusions to be drawn from the data generated are as these:

- Oxidation of ferrous chloride with oxygen at atmospheric pressure is technically feasible, at the scale tested.
- From the parameters obtained by fitting the rate expression used to the data, it appears that the rate of oxidation appears to be independent of the concentration of ferrous iron, down to very low levels. (This has yet to be confirmed experimentally.)
- Hydrolysis of ferric chloride to hematite and strong hydrochloric acid is technically feasible, at the scale tested.
- The rate of the hydrolysis reaction appears to be fast enough for the conversion of ferric chloride to hematite and hydrochloric acid to be controlled by chemical equilibrium.

The work on synthetic feed has shown that the oxidation and hydrolysis sections of the Ferguson Lake circuit can be operated reliably in continuous mode, and has generated realistic operating conditions and good process data for both sections.

The next phase of this work, which is currently underway at SGS Canada Inc., is to generate feed from Ferguson Lake ore, repeat the oxidation and hydrolysis work using that “real” feed and use the data generated to revise the overall mass/energy balance and the projected capital and operating costs.

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