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# *Hydrolysis of Ferric Chloride in Solution*

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# DISCLAIMER

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# HYDROLYSIS OF FERRIC CHLORIDE IN SOLUTION

by

Guy Lussiez and Leo Beckstead

## ABSTRACT

The Detox™ process uses concentrated ferric chloride and small amounts of catalysts to oxidize organic compounds. It is under consideration for oxidizing transuranic organic wastes. Although the solution is reused extensively, at some point it will reach the acceptable limit of radioactivity or maximum solubility of the radioisotopes. This solution could be cemented, but the volume would be increased substantially because of the poor compatibility of chlorides and cement.

A process has been developed that recovers the chloride ions as HCl and either minimizes the volume of radioactive waste or permits recycling of the radioactive chlorides. The process involves a two-step hydrolysis at atmospheric pressure, or preferably under a slight vacuum, and relatively low temperature, about 200°C. During the first step of the process, hydrolysis occurs according to the reaction below:

$$FeCl_{3\ \mathrm{liquid}} + H_2O \longrightarrow FeOCl_{\mathrm{solid}} + 2\ HCl_{\mathrm{gas}}\ .$$

During the second step, the hot, solid, iron oxychloride is sprayed with water or placed in contact with steam, and hydrolysis proceeds to the iron oxide according to the following reaction:

$$2\ FeOCl_{\mathrm{solid}} + H_2O \longrightarrow Fe_2O_{3\ \mathrm{solid}} + 2\ HCl_{\mathrm{gas}}\ .$$

The iron oxide, which contains radioisotopes, can then be disposed of by cementation or encapsulation. Alternately, these chlorides can be washed off of the solids and can then either be recycled or disposed of in some other way. This process may find applications in treating industrial solutions of ferric chloride or ferrous chloride (like pickling liquor) after oxidation, or possibly other chloride solutions such as nickel chloride generated during solvent extraction refining in nickel plants.

## INTRODUCTION

The Detox™ process uses catalyzed oxidation to destroy organic wastes. A solution of six normal ferric chloride, one normal hydrochloric acid, and trace quantities of platinum and ruthenium catalysts is used under pressure at temperatures of 150°C to 200°C. Organic matter is oxidized to carbon dioxide and water. Hydrochloric acid is formed when the organic compound is chlorinated. Ferric chloride is reduced to ferrous chloride but reoxidized simultaneously with oxygen. Los Alamos National Laboratory (LANL), is considering using this process for volume reduction of a variety of transuranic-contaminated organic wastes. The resulting solution will be contaminated with radioisotopes, especially plutonium. High-concentration chloride solutions are very corrosive, and solid chlorides absorb water readily. Encapsulation or cementation are not reliable alternatives for treating spent Detox solution. A process must be developed that will permit safe storage of the plutonium or allow for recycling of plutonium chloride to the processing facility.

Ferric chloride hydrolyzes easily to iron (III) oxide and hydrochloric acid.[1] However, hydrolysis does not reach completion unless the acid formed is removed. During preliminary testing, it was shown that upon being heated at atmospheric pressure, a solution of 6 n ferric chloride and 1 n hydrochloric acid—subsequently referred to as ferric chloride solution—first lost water, then the free acid as hydrochloric gas, then more water. Finally bound water and hydrochloric gas from hydrolysis were released at an accelerated rate above 170°C. Around 190°C, HCl release rate was especially rapid, and the boiling solution had a composition close to $FeCl_3$, 2.5 $H_2O$ or $FeCl_3$, 2 $H_2O$, based on the amount of water released. Both compounds are reported in the literature.

In the process under investigation the Detox solution was heated to a temperature between 170°C and 190°C, for which hydrolysis proceeds rapidly. Hydrolysis of one mole of $FeCl_3$, 2.5 $H_2O$ (or 2 $H_2O$) requires 1.5 moles of water and produces 3 moles of hydrochloric gas. The theoretical reaction is

$$FeCl_3, 2.5\ H_2O_{liquid} \longrightarrow 3\ HCl_{gas} + 0.5\ Fe2O3_{solid} + H_2O_{gas} \ .$$

According to this reaction, 1-mole steam would be released for each 3 moles of HCl gas. However, at every temperature the ratio was found to be higher, meaning that dehydration of the melt occurs according to the reaction as follows:

$$2\ FeCl_3, 2.5\ H_2O_{liquid} \longrightarrow 3\ HCl_{gas} + 0.5\ Fe_2O_{3solid} + n\ H_2O_{gas} + FeCl_3, (3.5-n)\ H_2O_{\ s\ or\ l} \ .$$

In this reaction $n<1$, and $3.5\ n < 2.5$. With time, enough water is lost, and the melt solidifies. If all the steam is condensed and returned to the reactor, the melt is diluted, and the boiling temperature decreases as well as the hydrolysis rate. The reaction above becomes

$$2\ FeCl_3, 2.5\ H_2O_{liquid} \longrightarrow 3\ HCl_{gas} + 0.5\ Fe_2O_{3solid} + FeCl_3, 3.5\ H_2O_{liquid} \ .$$

Hydrochloric gas goes through an appropriately designed condenser. The principle of the process considered was to turn the condenser on and off to return part of the water to the shrinking pool of solution and keep it at a constant composition (2 to 2.5 moles of water) and boiling temperature (170°C to 190°C). Hydrochloric gas released can then be scrubbed in a conventional scrubber. As will become apparent in this report, this approach was partially successful.

## CONCLUSIONS

Ferric chloride is an oxidant used in many processes. For example, it has been used for oxidation of gold-bearing pyrite and other sulfide ores and solubilization of precious metals. In the Detox process, it is used with small amounts of catalyst and at high temperature to oxidize organic compounds to carbon dioxide and water. The ferrous chloride produced is continuously reoxidized with air to ferric chloride, which is reused. This process is under consideration for treatment of transuranic, organic wastes. The radioactive metals in this case are solubilized. In all processes, the concentrated ferric chloride solution must be further processed before disposal. It is only a reagent and not the final product. It is highly corrosive and cannot be discarded as is. In the case of radioactive wastes, the solution is reused until a safe limit for radioactivity or metal solubility is reached. This solution must then be treated for safe disposal. Because chloride solutions cannot be cemented unless substantially diluted, it is best to eliminate the chloride ions. Hydrolysis at high temperature, above 600°C, is practiced industrially on pickle liquor, the result of etching steel with hydrochloric acid before galvanizing. Hydrolysis produces iron oxide, $Fe_2O_3$, and hydrochloric gas, which is scrubbed and converted into hydrochloric acid that is recycled. Because the solution is sprayed in the hot zone, the process is inherently dusty. Also, chlorides of some radioactive metals could have a significant vapor pressure at this temperature and volatilize. A better process would hydrolyze the solution at lower temperature and in solution.

The process developed for treating spent Detox solution requires two steps. During the first step, the solution is heated to boiling at atmospheric pressure, or under slight vacuum. The solution progressively loses dilution water and then hydration water. As the number of moles of hydration in the various ferric chloride compounds ($FeCl_3$, n $H_2O$) decreases, the boiling temperature increases. Hydrolysis to hydrochloric acid becomes significant above 160°C. It has been demonstrated that the main reaction is

$$FeCl_{3\,\text{liquid}} + H_2O \longrightarrow FeOCl_{\text{solid}} + 2\,HCl_{\text{gas}} \quad .$$

When heating is rapid, this is by far the dominant reaction, and hydrolysis stops when all ferric chloride is converted to the oxychloride, at about 190°C to 200°C. However, when heating was extended over a few days, a second reaction occurred

$$2\,FeOCl_{\text{solid}} + H_2O \longrightarrow Fe_2O_{3\text{solid}} + 2\,HCl_{\text{gas}} \quad .$$

However, this reaction never went to completion. Experiments concluded using the oxychloride with water at near boiling showed that this reaction stops around pH 1.5. A second step was required where a small amount of water was sprayed continuously onto the oxychloride at about 200°C, also at atmospheric pressure, and under vacuum. Under these conditions, the hydrochloric gas was released. Hydrolysis to $Fe_2O_3$ was then almost complete, with less than 1% chloride left in the solids, and completion could certainly be reached with better water distribution. The second reaction also occurred with steam, to even greater completion, producing solids that contained about 0.3% of the chloride.

Two heating systems were tested. Indirect heating, for example through use of a heating mantle, was slow. A tantalum-lined reactor was not affected either by the chloride solution or the thermal shock of water sprayed on hot surfaces. Microwave heating was much faster, and hydrolysis came closer to completion. Metals cannot be used, and the Pyrex vessel used often cracked. Ceramics would have to be tested, although good results were obtained by exposing the solids to steam in a quartz crucible. Solids temperature was also difficult to control with microwave heating because a thermocouple cannot be inserted in the field. The unit used had only on-off control, with the percentage of time at full power being varied. Hot spots, up to bright red, developed in the solids.

Ferric oxychloride formed a hard, bright-red cement. The ferric oxide formed was black and crumbly. Most of it was identified as hematite, $Fe_2O_3$, by X-ray diffraction. However, some was ferromagnetic. This fraction was magnetically separated and analyzed by X-ray diffraction also. It was a mixture of hematite and magnetite, $Fe_3O_4$. If, as probable, the chlorides of transuranic metals are left untouched, they could be easily washed off the oxide, which is easy to filter.

During all of the tests, the gas was scrubbed by two water scrubbers in series. This arrangement was a very simple design. The design was very effective, as the first scrubber collected virtually all of the hydrochloric gas as acid. A little ferric chloride was also entrained in the gas and collected in the first scrubber but was less than 0.1% of the ferric chloride in the chloride solution.

The process developed may have industrial applications. When a fluid-bed furnace is used for hydrolysis, the fluidizing air has to be heated. Some fines, which represent a loss of energy, are generated, carried out with the gas and redissolved and rehydrolyzed. It may be possible to hydrolyze other chlorides in the same fashion. The nickel industry has been looking for ways to hydrolyze the pure chloride from the refining process. Fluid-bed production has not been very satisfying. A lot of fines are produced, which are difficult to separate from the gas, and there is risk of exposure of the workers to this toxic metal.

## RECOMMENDATIONS

The scale of the experiments, typically one to two liters of solution, was small. The flow rate of water added during step two was about 100 ml per hour. No water sprays were found that could produce such a low flow. A higher flow could be used, but it would increase the volume of water, which could be secondary waste, collecting on the scrubber. In some tests a rotating disc was used to disperse the water. A more uniform water distribution may have resulted in a faster reaction. An alternative would be to optimize steam hydrolysis.

Microwave heating is much faster than indirect heating and is more energy-efficient. This approach needs optimization. A proportional power output is needed to prevent the pressure variations produced when the full power comes on and off. Temperature control through appropriate means, for example infrared detection, would prevent formation of hot spots. The microwave heater must have a beam wide enough for uniform heating of the solution and solids. Materials resistant to thermal shock, for example, silicon nitride, should be tested. Steam hydrolysis, however, may decrease materials requirements.

We recommend optimizing the engineering design including different construction material, improved microwave heating, and a better water-distribution scheme. When these factors are optimized, the process can be tested on transuranic waste including the disposal or recycling of radioisotopes.

## EXPERIMENTAL RESULTS

Hydrolysis of a standard Detox solution was effected using two types of heating. Although the distinction is not, *a priori*, important, it will be seen that the type of heating used affects the outcome of the test and will affect the engineering design.

## 1. Tests with Resistor Heating

Many tests were run using indirect heating of the vessel containing the Detox solution. Full-length or bottom-heating mantles, or a heating bath were used. In one case, a glass immersion heater was tested.

### 1.1. Description of the Apparatus

A schematic diagram of the apparatus is shown in Figure 1. A Pyrex reaction kettle containing the Detox solution was indirectly heated as mentioned above (except for one attempt with an immersion heater). A small gas flow (about 100 ml/min) was introduced into the vessel and exited with other gases generated through a water-cooled condenser that returned water vapor to the vessel but let most of the hydrochloric gas pass through. The condenser was designed as a straight tube distillation column, or Allihn condenser. The Graham type condenser, with a spiraling tube, tended to scrub hydrochloric gas. Alternatively, the condenser could be bypassed to remove both the water vapor and the hydrochloric gas from the vessel. Either way, the gases then passed through two scrubbers in series. Each was a filtration flask equipped with a small glass tube, which bubbled the gas through a few inches of water. This design effectively scrubbed hydrochloric gas. A vacuum pump aspirated the scrubbed gas and maintained the vessel at a few inches of negative pressure. This pressure was maintained at a constant rate by using a water column at the inlet of the pump. A Teflon-coated thermocouple measured the solution temperature and could be used for temperature control. Another thermocouple was sometimes placed between the vessel wall and the heat source to control the heat input. Slow stirring of the solution with a Teflon paddle was tested on a limited basis. A few tests were run in a tantalum-lined vessel.

### 1.2. Principle of the Operation

Hydrolysis was expected to proceed according to the following reaction:

$$2\,FeCl_{3\,\mathrm{solution}} + 3\,H_2O \longrightarrow Fe_2O_{3\mathrm{solid}} + 6\,HCl_{\mathrm{gas}} \quad . \qquad (1)$$

From a literature survey,[ii] it was found that at 250°C hydrolysis of ferric chloride hydrates, $FeCl_3$, n $H_2O$, proceeded to the oxychloride when n<1. The reaction involved is shown below:

$$FeCl_{3\,\mathrm{solution}} + H_2O \longrightarrow FeOCl_{\mathrm{solid}} + 2\,HCl_{\mathrm{gas}} \quad . \qquad (2)$$

However, according to this survey, hydrolysis of $FeCl_3$, 6 $H_2O$ proceeded according to reaction 2 if water and HCl were quickly released, and according to reaction 1 when

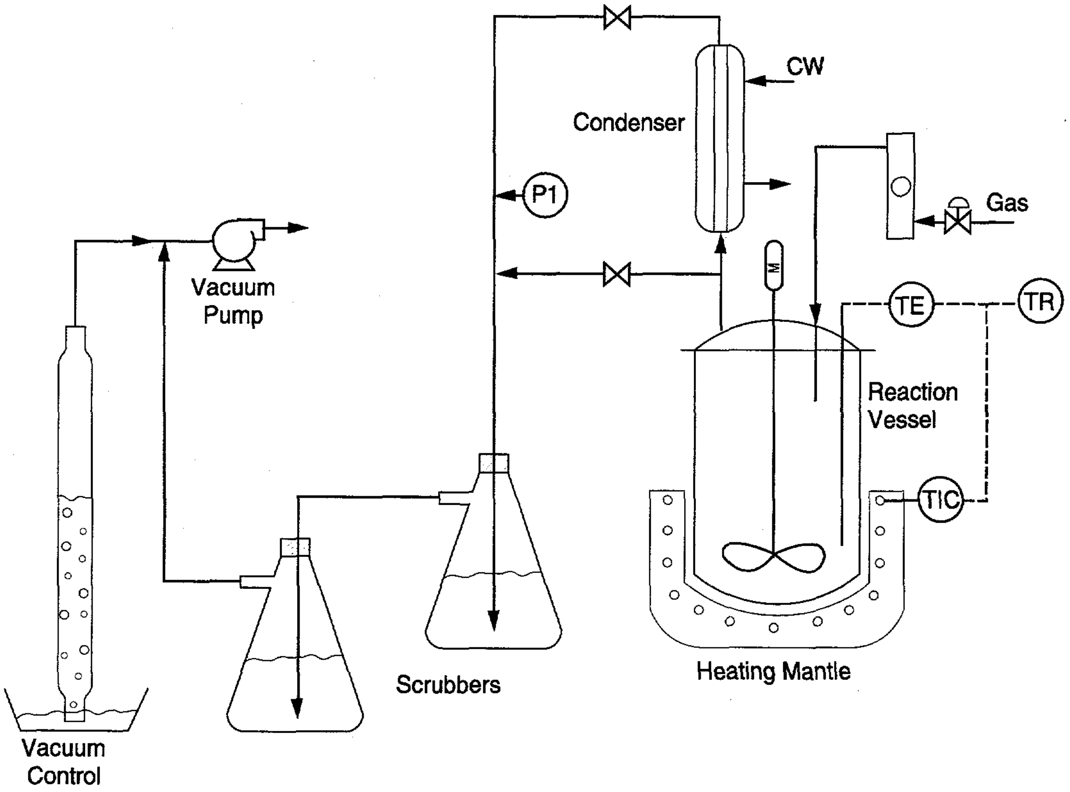


Figure 1. Experimental apparatus.

water was available for reaction. Our own experiment conducted using the hexahydrate, shown in Figure 2, indicates that hydrochloric gas evolution starts at about 160°C and is especially rapid at about 190°C. The test was terminated after 11 hours of operation. Based on the amount of hydrochloric acid produced and water evaporated, over 60% of ferric chloride was hydrolyzed, and the composition of the melt was approximately $FeCl_3$, 2.5 $H_2O$. It was believed that if enough water were returned to keep this composition constant, the boiling temperature would remain constant, and hydrochloric gas would keep evolving.

The reaction was monitored by weighing the scrubbers on a regular basis, titrating the hydrochloric acid in the scrubbers, calculating the water condensed in the scrubbers, and determining the number of moles of water remaining in the vessel per mole of ferric chloride. The gas could be routed through a condenser, and some of the water was returned (as needed) to the melt to keep a constant composition. In addition, a thermocouple in the melt was used to ensure that the boiling point did not change.

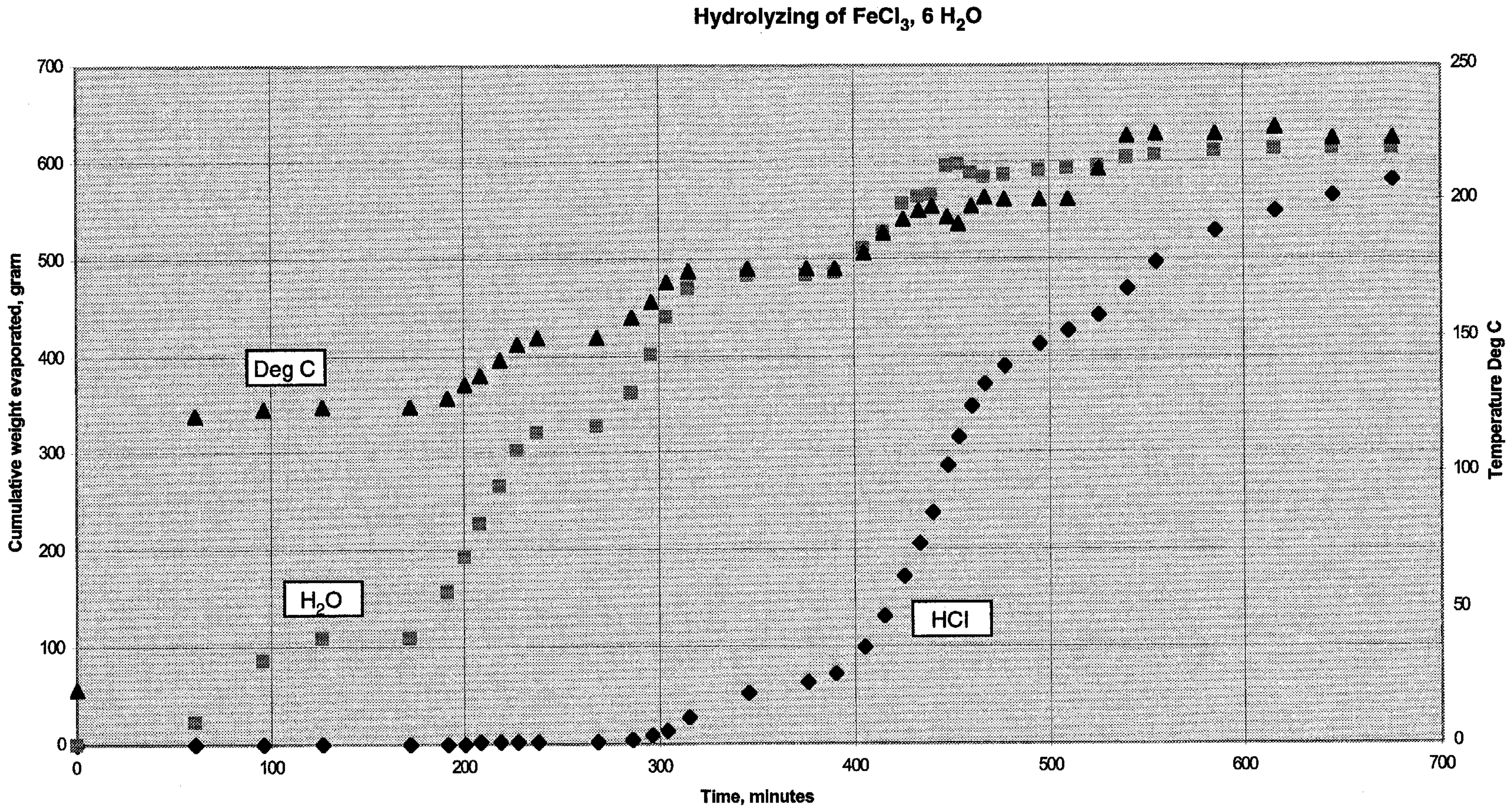


Figure 2. Hydrolyzing of FeCl$_3$, 6 H$_2$O.

Note: During heating from one temperature plateau to the next, the heating mantle delivers full wattage, and more energy is available for hydrolysis or dehydration than at equilibrium temperature.

## 1.3. Results and Design Modifications

Some qualitative observations resulted in important design changes. These are reported first. Quantitative results for the best tests are then analyzed.

### 1.3.1. Solids build-up and design changes

Many tests were run to try to achieve 100% hydrolysis. An abstract of the most successful tests and results is given in Appendix 1. However, even tests that extended over many days with careful control of the water of hydration left in the vessel rarely achieved 90% based on the hydrochloric acid collected and assuming Reaction 1 was occurring.

Qualitatively, it was observed that solids accumulated on the wall of the vessel near the air/liquid interface. As the solution volume decreased through loss of water and hydrolysis, the thickness of the solids increased. This can be explained in part by the fact that the thermocouple used for temperature control was inside the solution. When a set point was selected for temperature control, the heating mantle delivered the full wattage until this temperature was reached. Mixing relied on convection currents and agitation during boiling, but the solution viscosity increased as dehydration and production of solids through hydrolysis occurred. A higher temperature existed at the vessel wall, and either anhydrous ferric chloride or a low hydrate that was solid at this temperature was formed. As the solids layer thickened, it insulated the liquid pool, and more heat was required to maintain the temperature.

To solve this problem, a number of approaches were tested. A slow-moving Teflon paddle was installed that scraped the vessel wall. (A faster impeller was effective only at the beginning when the mix was relatively fluid). The build-up decreased, but the mixture became too thick to maintain after about 70% hydrolysis. It was observed that solids did not accumulate where condensation occurred and ran down the vessel wall. The full-length heating mantle was replaced by a bottom-heating mantle. This change resulted in some improvement. Control of the heat input was then tested by placing the thermocouple for temperature control between the heating mantle and the vessel's outside wall or by using a heating bath at a fixed temperature. Again, there was some improvement. However, a temperature gradient still existed, and as solids were building up, the temperature by the outside wall had to be increased, or HCl release slowed down considerably. After all these design changes were made, the tests that gave the highest rate of hydrolysis, in the range of 90%, were run slowly, over the course of many days.

All calculations of completion of hydrolysis, or control of the hydration of the pool of solution, was based on Reaction 1. This is an imperfect assumption as will be demonstrated below.

### 1.3.2. Solids composition and hydrolyzing path

Even when calculations showed that the remaining ferric chloride was sufficiently hydrated to stay liquid, the heated mixture ended up being solid. The solids retrieved upon cooling were very hard and had to be chiseled out of the glass vessel. To confirm calculations, the solids were slurried in water to dissolve and analyze any ferric chloride remaining. However, they would break down very slowly even after weeks of immersion and regular agitation and mechanical breaking of the chunks. All $FeCl_3$, n $H_2O$ compounds are highly soluble in water. The color of the test solids was blood-red before slurrying, somewhat too bright for chlorides and iron oxide. After slurrying, they were light brown and extremely difficult to filter.

Samples of solids, including some that had been slurried in water, filtered, and dried, were examined by X-ray diffraction. Results are given in Appendix 2. The most striking sample came from a test (4-11-96) that had reached only 68% hydrolysis. During this test the solution and then the solids had been heated rapidly and to much higher temperature than usual. (The Teflon coating on the thermocouple was melted.) The unwashed sample showed only well-crystallized iron oxychloride, FeOCl. After the same solids were slurried, filtered, washed and dried, they showed only poorly crystallized hematite, the alpha or low-temperature form of $Fe_2O_3$). Other samples that were more hydrolyzed and heated to lower temperature showed mostly hematite, but with some iron oxychloride, except when hydrolysis was very high. The results indicate that hydrolysis proceeds at least in part according to Reaction 2.

$$2\,FeCl_{3\ \mathrm{solution}} + 3\,H_2O \longrightarrow Fe_2O_{3\mathrm{solid}} + 6\,HCl_{\mathrm{gas}}\ . \qquad (1)$$

$$FeCl_{3\ \mathrm{solution}} + H_2O \longrightarrow FeOCl_{\mathrm{solid}} + 2\,HCl_{\mathrm{gas}}\ . \qquad (2)$$

The iron oxychloride is insoluble in water and acts as a cement to the iron oxide particles. It is reported in the literature as being bright red. It is believed that when it is slurried with water for weeks, a slow hydrolysis process takes place according to Reaction 3 below:

$$2FeOCl_{\mathrm{solid}} + H_2O \longrightarrow Fe_2O_{3\mathrm{solid}} + 2\,HCl_{\mathrm{liquid}}\ . \qquad (3)$$

To verify this assumption, samples of partially hydrolyzed solids were repulped in hot water as explained below.

### 1.3.3. Repulping of hydrolyzed solids

The solids used for repulping were partially hydrolyzed. Hydrochloric acid released during hydrolysis was equal to or higher than 60% of the maximum amount. At 67%, if Reaction 2 is the only route at the temperatures investigated, all ferric chloride has been hydrolyzed to the oxychloride. Because chunks of solids typically require weeks to be completely repulped in cold water, the solids were crushed or ground and repulped in hot water. As dissolution and hydrolysis took place during repulping, the pH decreased. Sodium hydroxide was continuously added to maintain the pH above about 2 and below about 4 to prevent iron precipitation, if any. Toward the end of the test, the pH was increased to about 7 or higher. When iron was present, even a small amount of precipitate was very visible as a fluffy, black agglomerate. These tests extended over a 2-day period. Details on some of these tests can be found in Appendix 3.

The main results indicate the following:

- There was little ferric chloride in the solids. This was expected because they were not hygroscopic, nor did they break down easily in water.

- Hydrochloric acid was released. When left overnight, the pH decreased but not much below 1.5. Reaction 3 probably slows down considerably or stops around this pH. When neutralization was done with sodium hydroxide to maintain the pH in the range of 2 to 3, reaction 3 proceeded slowly. Hydrochloric acid could not exist as free acid in the starting solids because they had been heated to over 200°C, and sometimes above 300°C.
- Based on the weight of the solids, upon completion of repulp-hydrolysis, they are hydrated, with 1 to 1.5 moles of water per mole of $Fe_2O_3$. This is fairly typical of naturally-formed goethite and limonite in laterite deposits.

A small amount of solids was repulped in a large volume of near-boiling water to keep the pH relatively high and to allow hydrolysis to reach completion. The reaction took a few hours. Titration to pH 4 and then pH 7 showed that less than 2% of the chloride ions were present as ferric chloride. The rest was hydrochloric acid. These solids were taken from a hydrolysis test that was 63% complete and showed oxychloride by X-ray diffraction.

Finally, samples from various tests were repulped in boiling water for 10 minutes by an analytical laboratory. The solution was assayed for soluble chloride and soluble iron. The intent was not to hydrolyze all available FeOCl, but to show that soluble iron was not stoichiometric with chloride in solution. Results are shown in Table 1, below. It is obvious that the majority of soluble chloride after repulping is not ferric chloride and must be hydrochloric acid. Because these samples had been heated to temperatures above 200°C, free hydrochloric acid could not exist in the solids and was generated by hydrolysis. Some repulped solids were analyzed by X-ray diffraction and found to be hematite, $Fe_2O_3$, even when the starting solids showed only FeOCl.

**Table 1. Analyses of Hydrolysis Solids**

| Test # | Cl, % (1) calculated | soluble Cl, %(2) | soluble Fe, % (2) | Fe $Cl_3$ % (3) | hydrolyzed FeOCl, % (4) | Total Cl, fusion, % | Total FeOCl, % (5) | Total Fe % | $Fe_2O_3$ % (6) | X-ray major | diffraction minor (7) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H1-4-U | 13.5 | 12.5 | 1.03 | 2.99 | 31.9 | 14.0 | 36.4 | 58.4 | 52.1 | $Fe_2O_3$ | FeOCl |
| H1-16-U | 36 | 14.4 | 1.96 | 5.69 | 32.3 | 28.0 | 73.5 | 48.6 | 6.7 | | |
| H2-22-U | 27.2 | 16.3 | 2.25 | 6.54 | 36.4 | 28.0 | 71.8 | 49.9 | 8.6 | FeOCl | $Fe_2O_3$ |
| H4-2-U | 25.8 | 9.45 | 0.42 | 1.23 | 26.2 | 9.87 | 27.5 | 59.9 | 63.5 | | |
| H4-11-U | 36.9 | 22.0 | 1.28 | 3.72 | 59.2 | 27.1 | 74.6 | 52.1 | 13.6 | FeOCl | |
| H4-18-U | 36.2 | 23.5 | 2.74 | 7.96 | 55.3 | 28.1 | 69.2 | 42.0 | -2.9 | | |
| H4-30-U | 11.2 | 3.22 | 0.71 | 2.05 | 5.7 | 3.74 | 7.3 | 64.4 | 83.7 | $Fe_2O_3$ | |
| H5-14-U | 15.0 | 6.46 | 1.31 | 3.81 | 12.0 | 20.3 | 53.9 | 56.7 | 35.5 | | |
| H6-7-U | 5.7 | 0.45 | 0.022 | 0.06 | 1.2 | 0.78 | 2.2 | 67.1 | 94.2 | $Fe_2O_3$ | $Fe_3O_4$ |
| H6-14-U | 6.7 | 1.46 | 0.58 | 1.68 | 1.1 | 2.27 | 3.6 | 65.6 | 88.8 | | |
| H6-27-U | 4.2 | 0.81 | 0.143 | 0.42 | 1.6 | 1.61 | 4.0 | 67.7 | 93.2 | $Fe_2O_3$ | |
| H7-22-U | | 0.24 | 0.053 | 0.15 | 0.4 | 0.33 | 0.7 | 68.4 | 97.1 | $Fe_2O_3$ | $Fe_3O_4$ |

(1) From HCl released during hydrolysis test. (2) After 10 min at boiling. (3) Calculated from soluble Fe. (4) calculated from soluble Cl minus Cl in $FeCl_3$. (5) Calculated from total Cl minus Cl in $FeCl_3$. (6) From total Fe minus Fe in FeOCl and $FeCl_3$. (7) $Fe_3O_4$ was visible only after magnetic separation.

Test H6-7-U in Table 1 was run with microwave heating and a rotating disc to disperse the water added. H6-14-U and H6-27-U were run in a tantalum autoclave, also with a rotating disc. H7-22-U used solids from test H-4-11-U (mostly FeOCl) and reacted them with steam in a microwave-heated quartz crucible. The final solids in these tests had low total chloride. Test 4-30-U is the only test that was run with a heating mantle and produced relatively low total chloride solids. This was a 5-day test.

Table 1 indicates that the main hydrolysis route is reaction 3. This has consequences for reaction control, which was effected assuming that Reaction 1 was taking place. During each test, the hydrochloric acid and water that collected in the scrubber were determined by titration and weighing, and the number of moles of water associated with the remaining ferric chloride was calculated. The goal was to maintain the solution composition at $FeCl_3$, 2-2.5 $H_2O$. For the hydrolysis path of Reaction 1, one mole of ferric chloride is hydrolyzed for each 3 moles of hydrochloric acid collected. If Reaction 2 is the main path, 1.5 moles of ferric chloride are hydrolyzed for each 3 moles of hydrochloric acid. Both reactions, however, use the same 1.5 moles of water for each 3 moles of hydrochloric gas generated. The calculated amount of water remaining in the bath is correct, but the amount of nonhydrolyzed ferric chloride is much less. In fact, if Reaction 2 were the only one occurring, all the ferric chloride would be converted to iron oxychloride although calculations based on Reaction 1 would indicate only 67% conversion to $Fe_2O_3$. In many initial tests conducted at high heating rates, the hydrochloric gas release rate almost stopped around this value. Attempts to control the reaction based only on the boiling point of the pool of solution were partially successful. The thermocouple became embedded in the solids, through which there was a temperature gradient.

As previously mentioned, tests run at high heat input released less hydrochloric gas before release stopped than tests run over many days at low heat input. It is believed that Reaction 2 takes place in each case, but that with time, heat, and the remaining water, Reaction 3 (hydrolysis of the oxychloride) proceeded. Reaction 3 was slow because the remaining water was in a pool of solution at the center of a "bowl" of impervious solids. Remaining solids were always hard and very difficult to slurry, with minor hygroscopicity even after fine grinding. This would not be the case if these solids were a mixture of iron oxide and a ferric chloride. Based on these results, tests were run in attempt to enhance Reaction 3 by adding water when the solids were mostly dehydrated and at high temperature, above 190°C.

### 1.3.4. Tests with water addition at high temperature

In most tests a bowl of solids formed at the bottom of the reaction vessel. While the solids were not affected by contact with the pool of remaining solution, they were dissolved where a water drip occurred. For example, solids accumulated during the first part of the test when the condenser was bypassed to eliminate most of the water. When the condenser was turned on, at high temperature, the solids were removed relatively quickly at the point where water from the condenser dripped. It was believed that hydrolysis of the iron oxychloride occurred, leaving loose iron oxide that was pushed aside. Any addition of water to enhance Reaction 3 would have to be evenly distributed. Given the size of the condenser and the scrubbers, a water addition rate in the range of 200 ml/hour was appropriate. Also, this process is intended for treatment of radioactive waste, and generation of secondary waste (scrubber solution) should be minimized. However, the smallest commercial spray nozzle, to our knowledge, had a low rate of about 2000 ml/hour. A Teflon disc, 4 inches in diameter (the vessel diameter was 5 in.) and perforated with 20 one-eighth-inch holes, was fabricated. This disc was rotated at different speeds and elevations in the vapor space. As water was added, it was distributed onto the solids by the rotating disc. This is obviously not as even a distribution as with a spray, but over 90% and up to 98% hydrolysis was obtained with this approach.

From a design point of view, some of the cold water dispersed by the disc hit the vessel wall, which may be at 250°C or even higher. When the reactor was made of Pyrex, the vessel frequently cracked near the end of the test. One test was done in a tantalum-lined autoclave, a Parr design, to which the usual Pyrex lid and associated condenser and scrubbers had been attached. (Pressure in the autoclave was maintained at a few inches of vacuum as for other tests). It was heated by a furnace. This test was deliberately run over an extended time span, close to 48 hours, to come close to equilibrium at every temperature plateau. The results are informative and are detailed below. Because of the thermal mass of the autoclave and its contents and a relatively sluggish temperature control, the temperature significantly overshot or undershot at each control point. The control thermocouple read the autoclave's outside bottom temperature. At high temperatures, it was as much as 5°C to 10°C over or under the control point, for up to 10 minutes. Heat input varied accordingly, producing scatter of the data points, which were taken every 15 minutes. However, the temperatures and results are consistent.

**Overview of results of test run in a tantalum autoclave.** Figure 3 shows water and hydrochloric acid collected with time, as well as the solution temperature. It does not show water collected after we started adding water to the autoclave. At the rate of about 100 g of water per hour, the data points would have been out of scale. The scatter of the data points for the solution temperature at high control temperature is obvious and is explained in the preceding paragraph. Low temperature points every 8 to 10 hours indicate start-up at the beginning of new days. They have been eliminated from subsequent data evaluation.

Hydrochloric acid collected amounted to about 97% hydrolysis. The final solids weight was 100.6% of the theoretical weight calculated from complete hydrolysis of ferric chloride to ferric oxide, corresponding to 98.5% $Fe_2O_3$ and 1.5% FeOCl. Analyses showed total chloride to be 1.6%, with only 0.14% of the iron being water-soluble. Based on analyses, the FeOCl remaining was 4%.

A tantalum coupon in the autoclave did not show any weight loss. (The coupon gained 0.025%, or 1 mg, probably because of a slight film of solids).

**Moles of water in the ferric chloride solution versus boiling temperature.** The composition of the solution in the vessel was calculated based on the water collected in the scrubber. Figure 4 shows the relationship between the number of water molecules left in solution per mole of ferric chloride versus temperature. Gray squares are calculated assuming Reaction 1 occurs, while black diamonds are calculated assuming Reaction 2 to the oxychloride occurs. There is actually little difference; the black diamonds are covered most of the way by the gray squares, except toward the end. Note that it takes a temperature of 175°C and a total of about 7 hours at boiling before all the free acid is released. This acid is added as a 1.5 N solution to the anhydrous ferric chloride when preparing the

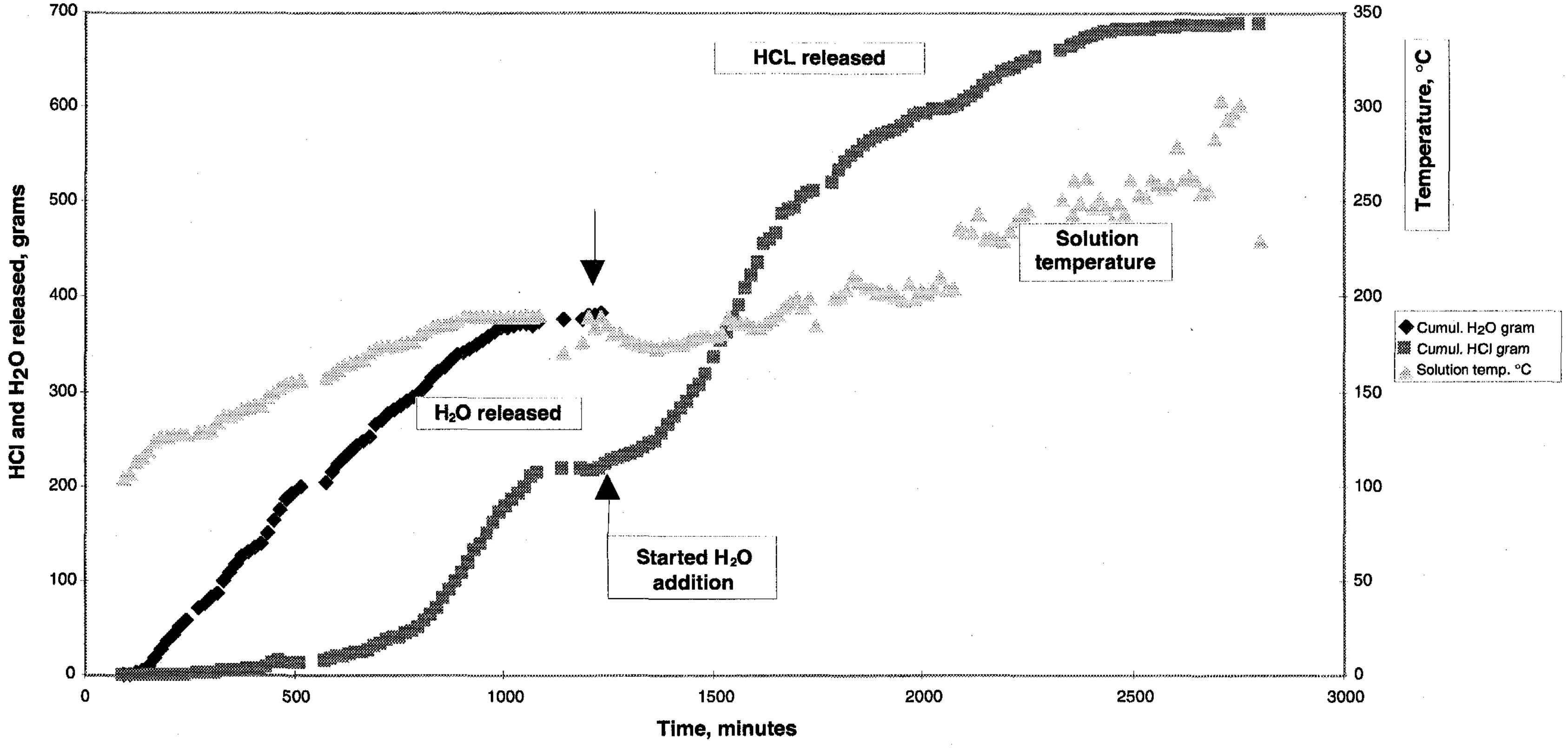


Figure 3. Hydrolysis of Detox solution in tantalum autoclave.

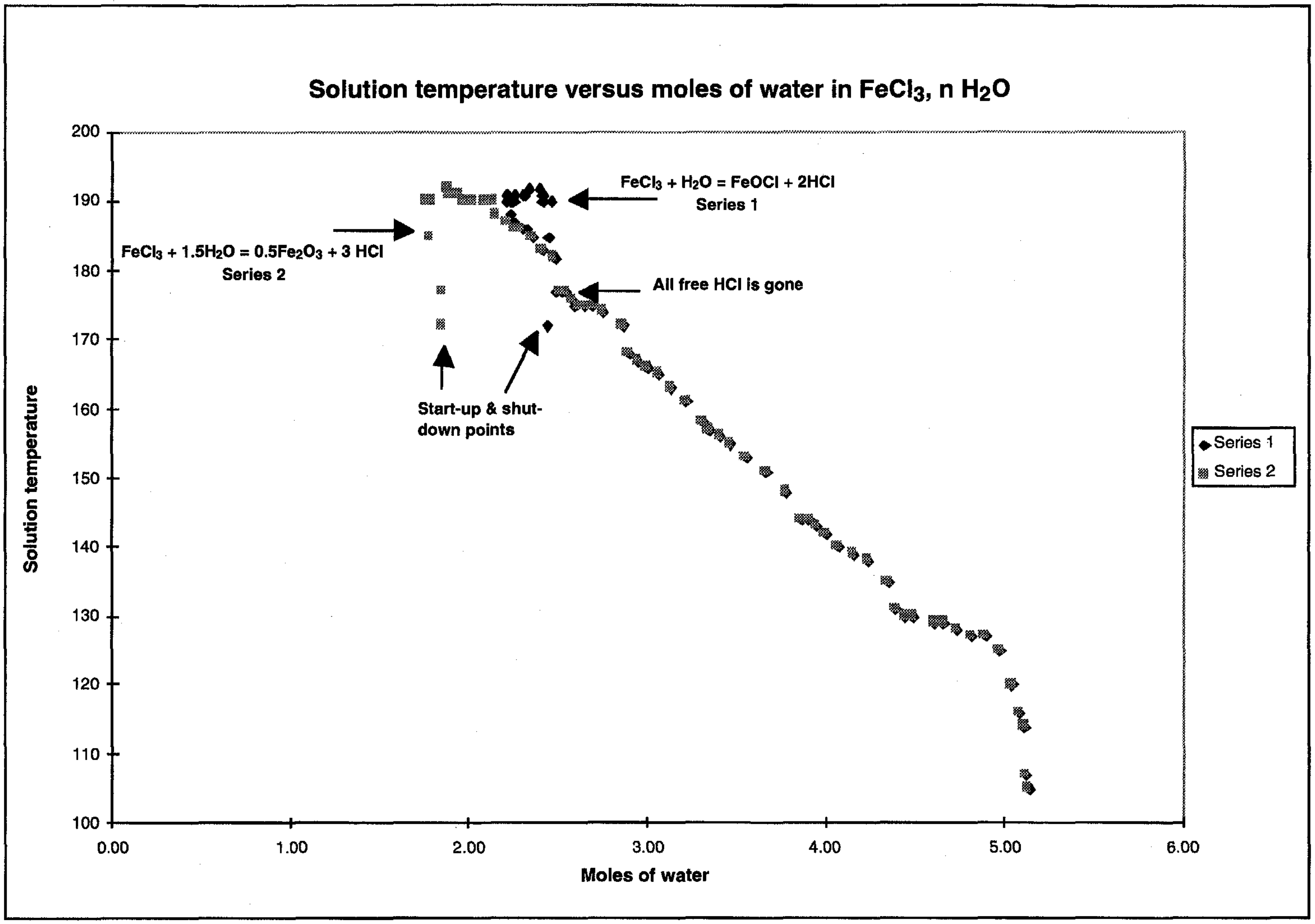


Figure 4. Solution temperature versus moles of water in $FeCl_3$, n $H_2O$.

Detox solution. Although some acid was released at the boiling point of the Detox solution, about 125°C, it was very slow. Compounds of the form $FeCl_3$, HCl, n $H_2O$, with n=2, 4 or 6 are reported in the literature,[1] although their domain of stability is not given.

**Evolution of hydrochloric release at various temperatures.** Figure 5 shows the hydrochloric gas released and captured in the scrubber at various times for various control temperatures. The control temperature and the corresponding solution (or solids) temperature are indicated under each graph. The solution temperature is a good indication of the reaction temperature as long as the thermocouple is in a liquid. Toward the end of the test the pool of liquid was shrinking, and the thermocouple was likely to be in the solids. At the wall, the temperature must be close to the outside wall (control) temperature since this is a metal wall. There is a temperature gradient across the solids.

At a solution temperature of 140°C, the HCl release rate was low, around 0.05 g/min. As temperature increased, the rate increased up to about 0.6 g/min at 190°C. Typically, at constant temperature, hydrochloric gas generation decreased with time. The heat output of the furnace was constant at a constant control temperature. Although short-term variations occurred as a result of erratic temperature control, the heat output was relatively constant over the length of the test. This heat was available for hydrolysis, an endothermic reaction, and hydrochloric gas release should have been constant. The decrease observed could be because of changes in solution composition or generation of solids acting as insulation. After more than 4 hours at 190°C, water was added at the rate of about 100 g/hr, using the disc to disperse it. The temperature decreased to 180°C. Hydrochloric gas release did not increase immediately, but did increase slowly over a period of 3 hours from about 0.1 g/min to 0.6 g/min, and stabilized at this value for the next 2 hours. Higher temperatures increased the rate, which then decreased with time until the next temperature increase. At the last temperature tested, 260°C, in the autoclave, hydrochloric gas generation was essentially zero.

**Evolution of water release rate at various temperatures.** The water release rate is shown on Figure 5 for various control temperatures, up to the point when water was added. The rate decreased with time for each temperature tested. Like the hydrochloric release, the rate decrease can be the result of a change in the composition of the solution that, in turn, leads to a higher boiling point or to solids building up and insulating the liquid. However, it was shown that little HCl was released up to a temperature of 170°C. Previous experiments in glass vessels indicate that up to this point solids build-up was small. The decrease in the rate of dehydration is a result of the change in solution composition. It is possible that given enough time, the rate would have been zero because of the formation of a stable melt. However, it is unlikely. In a separate experiment, a sample of ferric chloride hexahydrate was placed in an oven at 110°C. It was still losing weight after 39 days. The weight at this point was less than theoretical for anhydrous ferric chloride, which means that hydrolysis had been taking place.

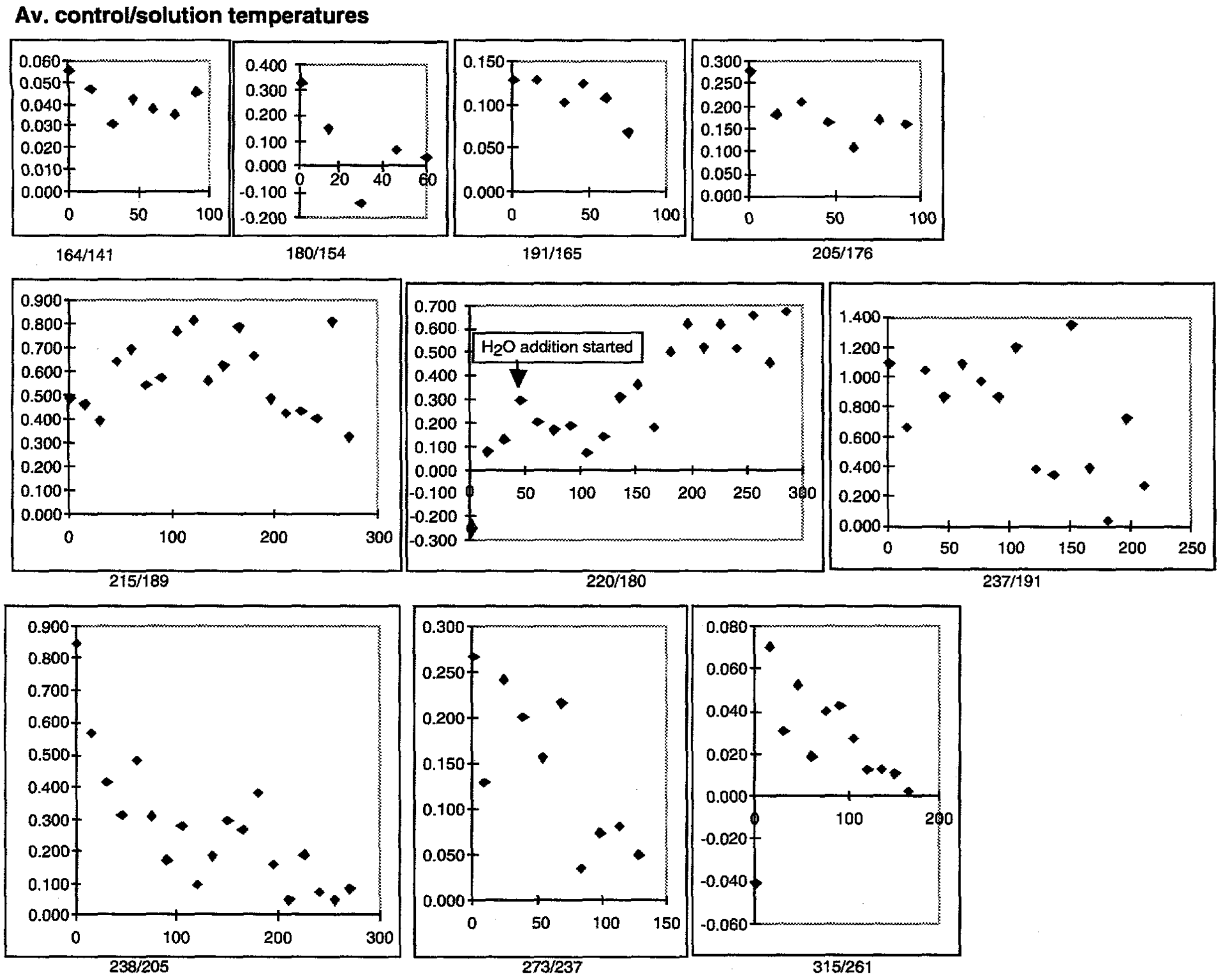


Figure 5. Evolution of HCl release rate at various control temperatures (g/minute vs. time in minutes).

**Other information.** The first scrubber was in service until hydrochloric acid concentration was 22 percent by weight. The acid was then replaced with fresh water. The only reason not to continue with the same scrubber solution was that titration became inaccurate at this high concentration. The second scrubber, in series with the first one, was in use during the whole test, and its pH was 2.5 at the end of the test. Scrubber efficiency at high acid concentration depends on solution temperature, which, if no cooling is used except for heat losses, depends mostly on the amount of water released by the process as steam.

A small amount of ferric chloride was carried over with the gas and was also scrubbed. The iron concentration reached a peak of 0.45 g/l, or less than 0.1% of the ferric chloride in the feed solution.

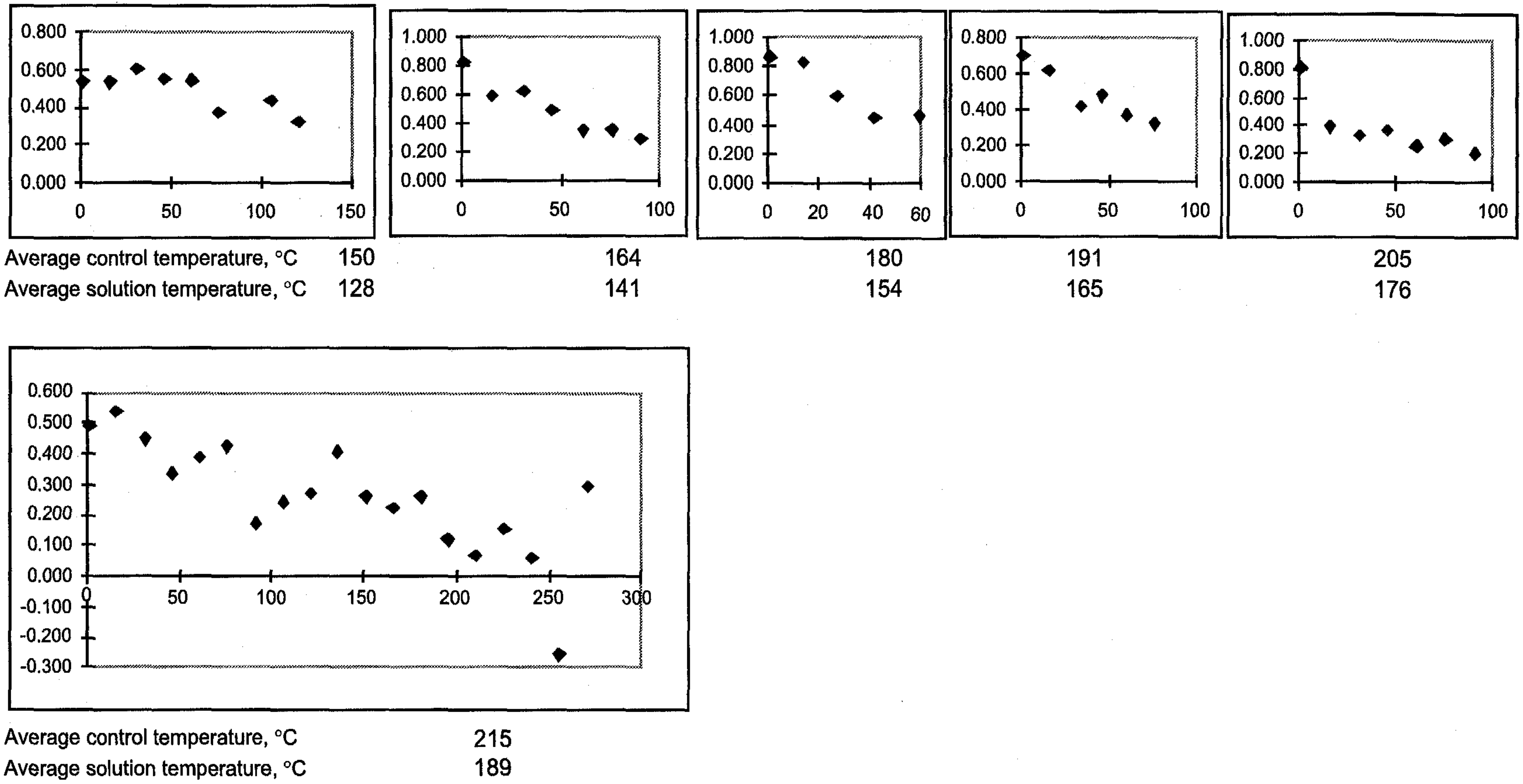


Figure 6. Evolution of water release at different control temperatures (g/minute vs. time in minutes).

## 2. Tests with Microwave Heating

Indirect heating with a mantle has some drawbacks. Since there is a temperature gradient across the wall, solids build up by the wall. As this layer of solids grows, it insulates the remaining solution, and the mantle temperature has to be increased. The reaction stops prematurely. The best results were obtained at low heat input (and lower temperature gradient) by spraying the solids with water toward the end of the test. Typically, at least 16 hours were needed to reach about 95% hydrolysis. Microwave heating on the other hand, provided heating directly in the solution. With proper test design, sufficient heating is fairly uniform in the vessel volume.

### 2.1. Description of the apparatus

The experimental setup was similar to that used for indirect heating. However, no thermocouple or thermometer was used in microwave heating, and temperatures were unknown. Control of the reaction was based on the amount of hydrochloric acid and water released and on calculations used to determine the status of hydrolysis. When a heating mantle was used, it compensated for higher heat losses at higher temperatures. The power input varied according to the control temperature, the conductivity of the glass and solids layer, and endothermicity of the reaction. With microwave heating, the power input was fixed for a given power setting. Power was adjusted from 10% to 100% in 10 increments. Power control was on/off; for example, at 10% setting the microwave was on at full power but only 10% of the time. The microwave furnace produced 1100 watts at full power although not all was available as microwave energy because of conversion efficiency, and not all microwave energy was dissipated in the vessel.

### 2.2. Principle of the operation

The operation principle was the same as for indirect heating. It was assumed that the reaction proceeded according to Reaction 1.

$$2\ \mathrm{FeCl_{3\ solution}} + 3\ \mathrm{H_2O} \longrightarrow \mathrm{Fe_2O_{3solid}} + 6\ \mathrm{HCl_{gas}} \quad . \qquad (1)$$

Amounts of hydrochloric acid and water collected in the scrubber were used to calculate the ferric chloride that hydrolyzed and the composition of what was left. The condenser was turned on and off to keep 2 to 2.5 moles of water for each mole of ferric chloride left.

### 2.3. Results

Microwave heating was much faster than indirect heating, up to the point when everything in the reactor was solid. This phase was reached in a few hours. Hydrolysis then could proceed only if water was added. Solids build-up was more uniform than with indirect heating. For both types of heating, there was no build-up where water condensed and dripped back into the reactor.

When the mixture reached the solid state, local spots became more conductive and glowed dark red to bright red. When this happened, brown fumes were released for a short time. The fumes apparently hydrolyzed in the vapor space, and small amounts of black solids collected in the glass outlet, where some moisture condensed. One reaction probably occurring is

$$3\ \mathrm{FeOCl}_{\mathrm{solid}} \longrightarrow \mathrm{Fe_2O_{3solid}} + \mathrm{FeCl_{3\ gas}}\ . \tag{4}$$

Reaction 4 is reported in the literature.[ii] It takes place during the heating of FeOCl. No temperature is given, except that it occurs above 250°C. From visual observation on one occasion when using the heating mantle, it appeared that fuming occurred at about 300°C. The reaction in the gas phase could produce $Fe_2O_3$ or FeOCl, depending on the temperature. FeOCl is not a conductor. Experiments were run on solids in which only FeOCl was detected by X-ray diffraction. These solids were exposed to various levels of microwave power for 30 minutes, the power was turned off, and the temperature was measured immediately. The temperature of the solids at most power settings did not exceed 160°C. However, when a hot spot developed, the temperature shot up to above 400°C. After the solids cooled, black crumbly solids, often crystalline-looking, were observed where the hot spot had developed, while the rest of the solids were the hard, red mass typical of incomplete hydrolysis.

During most of the tests conducted using microwave heating, these hot spots produced localized high temperature on the glass vessel. When water was sprayed into the reactor to continue hydrolysis, some cooler water invariably contacted the hot spots and caused the Pyrex vessel to crack. Teflon did not fare better, as it decomposes at this temperature.

When water was sprayed on the solids, hydrolysis continued relatively quickly to near completion. The final solids were black and crumbly and easy to wash and filter. They were identified as hematite, $Fe_2O_3$, by X-ray diffraction. Their weight is very close to the theoretical weight for $Fe_2O_3$. Upon repulping, samples from some tests had a relatively large ferromagnetic fraction that attached to the magnetic stirrer. This fraction was found to be a mixture of hematite (major) and magnetite, $Fe_3O_4$.

The solids from the best microwave test had virtually no soluble iron, meaning that all ferric chloride had been hydrolyzed. Only 2.2% FeOCl was left.

## 2.4. Microwave Heating of Hydrolyzed Solids with Steam

Hydrolysis of ferric oxychloride was effected by spraying water on heated solids. We wondered if hydrolysis could be completed by contacting these heated solids with steam. Solids from an incomplete hydrolyzing test, during which 63% of the hydrochloric acid was released, were ground to minus 100 mesh and placed in a quartz crucible. The crucible was placed on a stand in the usual 2-liter Pyrex vessel. As the solids were microwave-heated, water was dripped to the bottom of the vessel and converted to steam, also as a result of microwave heating. Hydrochloric acid was generated, captured in the scrubber, and titrated. The test was repeated 3 times, with improvements in the apparatus each time. The last test was completed in a little over one hour.

In each case, some hot spots developed, from dull to bright red. The weight of the final solids and the amount of hydrochloric acid released were virtually identical in each test and close to the calculated value for complete hydrolysis. The solids were black and crumbly. Repulping in boiling water followed by titration showed less than 0.1% hydrochloric acid or equivalent ($FeCl_3$). Substantial amounts of repulped solids were attached to the magnetic stirrer.

Chunks of solids, incompletely hydrolyzed, were submitted to the same treatment. The hydrochloric acid was released in a little over one hour. Note that in all these tests, a small amount of ferric chloride was present (see section 1.3.3). At sufficiently high temperature, about 300°C, when a heating mantle and a thermocouple were used, this ferric chloride was released as a brown fume for a short time. This fume hydrolyzes where condensed moisture is present.

Analyses showed that the final solids contained 0.33% total chloride and 0.033% water-soluble chloride. Essentially all ferric chloride was hydrolyzed, and only 0.7% of the oxychloride was left. X-ray diffraction showed only hematite, $Fe_2O_3$. However, a magnetic fraction after separation was found to be a mixture of hematite and magnetite, $Fe_3O_4$.

Using steam instead of spraying water did not result in cracking of the Pyrex reactor. When the above procedure was used, the Pyrex vessel was only at steam temperature (about 100°C) when cold water was dripped in. However, more work is required to determine the kinetics with steam for the bowl of solids that accumulates at the bottom of the vessel. This test could not be run for lack of a steam generator.

## 2.5. Advantages and Disadvantages of Microwave versus Indirect Heating

The advantages of microwave heating are 1) speed of reaction and 2) formation of crumbly solids that are easy to filter. Plutonium chloride probably will not hydrolyze during ferric chloride hydrolysis because the vapor pressure is very low in the temperature range investigated. It may be necessary to wash it off the product solids for recycling to the plutonium circuit, or other treatment. In comparison, most solids from indirect heating were hard to grind and extremely difficult to filter after repulping. It would take days to filter the plutonium-loaded solution and wash the filter cake. However, one 5-day test in an indirectly heated tantalum-lined vessel produced solids that were mostly black and crumbly. Optimization of the water-spraying system or somewhat higher temperature may produce a final product similar to microwaving.

Microwave heating produced some hot spots in the reaction mass. According to the temperature color scale, these may be at 650°C to 750°C (dark red) or even 850°C to 950°C (bright red). Microwave heating will also most likely vary with the power per unit of volume. This may be an advantage or a disadvantage. Hot spots could produce local hydrolysis or vaporization of some chlorides, including plutonium chloride. Hydrolysis may produce a stable and inert mixture of iron and plutonium oxides that would be easy to discard. Vaporization would send plutonium chloride into the scrubber. The hydrochloric acid and plutonium chloride mixture would be recycled to the hydrochloric circuit. Some power control of the microwave unit, to control solids temperature, may be possible using an infrared detector. More expensive microwave units may have a better spatial distribution of the energy. This particular unit had a turning table designed to even out micrwave distribution in the food. This table could not be used under the test conditions described.

## REFERENCES

i. J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry,* Volume XIV, Longmans & Green, London, UK (1935, reprinted 1942).

ii. Harald Shafer, "Preparation of Iron Oxychloride," *Zeitschrift fur Anorganische Chemie,* **Vol. 260,** pp. 279-294 (1949).

## Appendix 1. Abstract of Conditions and Results of Hydrolyzing of Detox Solution

All tests were run using one liter of Detox solution in a 2-liter vessel, except for tests in a 4-liter tantalum-lined autoclave. All vessels were sealed and maintained under a few inches of negative pressure. A condenser and a condenser bypass allowed either return or removal of the water. In any case, the gas went through two water scrubbers. Calculated hydrolysis is based on the assumption that only $Fe_2O_3$ is formed, not FeOCl. However, FeOCl has been detected in one test and is likely to form at the beginning in all tests.

| Operating Conditions | | | | | | | Comments/Results |
|---|---|---|---|---|---|---|---|
| Test # | Vessel | Heating | Agitation | $H_2O$ return/addition | Temp. control | Others | |
| 12/1/95 | glass | mantle | no | none | inside thermocouple | $FeCl_3$,<br>6 $H_2O$ | 61% completion based on HCl. Temperature up to 220 in steps. Final weight 80% of $FeCl_3$. |
| 1/4/96 | glass | mantle | yes | Water addition at various times | inside thermocouple | $FeCl_3$,<br>6 $H_2O$ | 88% complete. A 4-day test. Temperature up to 220°C. Condenser on/off for water control. Final weight 57% of $FeCl_3$. Final solids lost 15% weight when repulped in water. |
| 1/16/96 | glass | mantle | yes | none | inside thermocouple | Detox solution from now | 67% completion. Temperature to 220°C with condenser on/off for water control around 190°C. Final weight 62% of $FeCl_3$. Repulp of a solid sample over weeks gives a final weight 73% of starting weight. |
| 2/22/96 | glass | bottom mantle | yes | none | inside thermocouple & meter | | 67.6% completion. Final weight is 62% of $FeCl_3$. A condenser bypass had been installed for water control. |
| 4/2/96 | glass | bath + graphite | yes | addition before start-up every day | outside thermocouple | | 76% complete. Final weight 61% of $FeCl_3$. Repulped sample is 64% of starting weight. |
| 4/11/96 | glass | bath + graphite, then mantle | no | none | outside thermocouple | heat tracing of glass reactor | 63% complete. Heavy white fuming at 270°C. Brown fumes at higher temperatures. Teflon thermowell melted. XRD shows well crystallized FeOCl on unwashed solids; poorly crystallized $Fe_2O_3$ on washed solids. Final weight 65% of $FeCl_3$. This is theoretical weight if FeOCl is formed instead of $Fe_2O_3$. |

| Operating Conditions | | | | | | | Comments/Results |
|---|---|---|---|---|---|---|---|
| Test # | Vessel | Heating | Agita-tion | $H_2O$ return/addition | Temp. control | Others | |
| 4/18/96 | glass | heating mantle | no | none | outside thermocouple | heat tracing of glass reactor | Silicone tubing was not resistant to acid fumes. Numerous leaks. Hydrolysis 63% complete. Final weight 67% of $FeCl_3$. Temperature inside is erratic toward the end. |
| 4/30/96 | glass | bottom mantle w. copper lining | no | condenser at center, water added before start-up on a new day toward the end. | Outside thermocouple | heat tracing of glass reactor | A 5-day test ***(Leo's note: how many hours?)***. There are some interesting results. Upon addition of water to cold solids and heating, the boiling temperature increases very slowly to what is expected based on the moles of water in $FeCl_3$, n $H_2O$. But solids are very slow to dissolve. It is not complete after 21 hours. Good agreement between final solids and calculated weight. Hydrolysis is 91%. Final weight 51.6% of $FeCl_3$ (at completion it would be 49.3%). Solids are red as for other tests, and extremely hard. XRD shows poorly crystallized $Fe_2O_3$. |
| 5/8/96 | glass | central glass heater | no | condenser at center, no water added. | none | heat tracing of glass reactor | The thermocouple did not read in solution because of magnetic interference from the heater. Wall stays clean from condensation and dripping. Build-up on heater increases in diameter as level goes down and solution splashes on hot surface. Heater breaks at 14% hydrolysis. |
| 5/14/96 | glass | microwave | no | water added during the run the last day | none | | Can't have a thermocouple in the microwave. Test ran smoothly, except addition of water finally stresses the glass, which breaks. Hydrolysis is 88% complete. Final weight 52.6% of $FeCl_3$. Unwashed solids show only hematite ($Fe_2O_3$) but color is black. |
| 5/30/96 | glass + Teflon liner | microwave | no | water added during the run the last day | none | | Temperature must have been too high toward the end because Teflon decomposed into light, gray powder and a yellow, sulfur-like powder that floats on water. The Teflon liner has become brittle. Spots on the wall are thin. Hydrolysis 78% complete. |
| 6/4/96 | glass + Teflon liner; then glass. | microwave | no | water added at various points during the run | none | | Teflon started to decompose slightly at end of run. Bright red spot in solids, possibly as a result of high microwave concentration. Upon cooling, this spot shows some black crumbly powder and black crystals surrounded by red solids. Hydrolysis is 76%. After transfer to the glass vessel, which will eventually crack from water addition, the solids at 83% hydrolysis are all black. Final solids 56.7% of $FeCl_3$. Microwave seems to produce crumbly black powder, and indirect heating red solids forming a very hard agglomerate. The agglomerate crumbles in water only after weeks of immersion and daily dispersion of the top soft layer with a tool. |

| Operating Conditions | | | | | | | Comments/Results |
|---|---|---|---|---|---|---|---|
| Test # | Vessel | Heating | Agitation | $H_2O$ return/addition | Temp. control | Others | |
| 6-7-96 | glass | microwave | no | water added continuously with a peristaltic pump toward the end | none | | Glass was used, but only the bottom 2.5" are in the microwave. That keeps the water condensing on the wall cooler and permits better observation. There is a Teflon disc attached to an agitator to disperse condensate return and water addition. This works well until the water is temporarily stopped. The glass is heated from the solids and cracks when addition is resumed. A spray covering the solids and wall and run without interruption should prevent breakage and increase hydrolysis. A proportional power microwave unit would also help. Power could be reduced toward the end. The on/off power produces surges of pressure. Hydrolysis is 95.7% complete. Final solids weight is 50.2% (theoretical is 49.3% at completion). Solids repulping gives 99 to 99.5% completion. Solids are black and crumbly. |
| 6/14/96 | Ta-lined autoclave | outside furnace | no | water added continuously with a peristaltic pump, starting at 40% hydrolysis | two thermocouples, one for control and one for the recorder. | | The thermocouples are either Teflon lined or in a Teflon thermowell. The top of this arrangement is the same glass cover as for the other tests. The rotating disc has been improved. Twenty 9/64: holes are distributed on its surface. Temperature control is extremely erratic toward the end because of the inertia of the autoclave and the furnace, and spot cooling from the water. Temperature goes as high as 260°C. Water distribution is not perfect: there are no solids in the center, but increasing thickness toward the wall. Solids are crumbly, but not as much as with microwave heating. Hydrolysis is 95% complete. Two-day test. |
| 6/27/96 | Ta-lined autoclave | outside furnace | no | water added as above | Outside thermocouple at bottom. | rotating disc to disperse water. | A 48-hour test to obtain as much information as possible. Hydrolysis 97% complete. Final solids weight 49.5% of $FeCl_3$ (theoretical at completion 49.3%), although a little was stuck to the wall. |
| 7/9/96 | glass & quartz | microwave | no | yes, continuously | none | | A quartz crucible was placed at the center of a Pyrex vessel. It contained the FeOCl from test 4-11-96 ground to minus 100 mesh. Water was added outside the crucible and converted to steam. The powder, when exposed to steam, released HCl. This may be a way to complete hydrolysis without spraying water, which is hard on the crucible. May not work as well on chunks, however. Final weight was reproducible at 74% of starting weight. |
| 7/19/96 | " | " | " | " | " | | |
| 7/22/96 | " | " | " | " | " | | |

# Appendix 2. X-ray Diffraction Results for Hydrolysis Solids

Major and minor compounds found by X-ray diffraction on a variety of solids from hydrolysis tests are reported with the assays in Table 1 of the text. The X-ray diffraction peaks for some samples are shown below.

| Sample & compounds | Spacing in angstrom and relative intensity | | | | | | | | | | | | | | | | | | | | Other lines | | | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | d | I | d | I | d | I | d | I | d | I | d | I | d | I | d | I | d | I | d | I | d | d | d | d | d | d | d | |
| 4-11-96 unwashed solids (1) | 7.89 | 100 | 1.98 | 20 | 3.41 | 14 | 2.54 | 13 | 1.81 | 7 | 2.06 | 6 | 1.46 | 4 | 1.58 | 4 | 1.75 | 3 | 1.21 | 3 | 1.51 | 1.55 | 2.50 | 2.16 | 2.37 | 1.89 | 2.64 | Fairly crystallized |
| Rerun | 7.89 | 100 | 1.98 | 11 | 3.41 | 12 | 2.54 | 17 | 1.81 | 7 | | | 1.47 | 4 | 1.58 | 5 | | | 1.21 | 2 | | | | 2.2 | | | | |
| FeOCl, orthorombic | 7.92 | 100 | 1.98 | 20 | 3.41 | 100 | 2.54 | 50 | 1.81 | 20 | | | 1.48 | 13 | | | | | | | 1.51 | 1.55 | | 2.18 | 2.37 | 1.89 | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4-11-96 washed solids | 2.71 | 100 | 2.53 | 46 | 1.70 | 36 | 1.85 | 30 | 1.49 | 20 | 3.70 | 13 | 1.46 | 13 | 2.22 | 13 | 1.62 | 9 | 3.04 | 6 | 1.05 | 0.98 | 1.08 | 1.15 | 0.99 | 0.91 | 1.05 | Very poorly crystallized |
| $Fe_2O_3$, maghemite | | | 2.51 | 100 | | | | | 1.47 | 40 | | | | | | | 1.60 | 20 | | | | | | | | | | |
| $Fe_3O_4$, magnetite | | | 2.53 | 100 | 1.71 | 10 | | | | | | | 1.48 | 40 | | | 1.62 | 30 | | | 1.05 | | 1.09 | | 0.97 | 0.89 | | |
| $Fe_2O_3$, hematite | 2.70 | 100 | 2.52 | 70 | 1.69 | 45 | 1.84 | 40 | 1.49 | 30 | 3.68 | 30 | 1.45 | 30 | 2.21 | 20 | 1.60 | 15 | | | 1.06 | 0.98 | 1.08 | 1.15 | 0.99 | 0.91 | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4-30-96 unwashed solids (2) | 2.71 | 100 | 1.70 | 63 | 2.52 | 53 | 1.49 | 37 | 1.84 | 22 | 3.68 | 21 | 1.46 | 19 | 2.21 | 17 | 2.54 | 15 | 7.88 | 13 | 3.41 | 0.90 | 1.08 | 1.81 | 0.98 | 1.02 | 1.99 | Poorly crystallized |
| $Fe_2O_3$, hematite | 2.70 | 100 | 1.69 | 45 | 2.52 | 70 | 1.49 | 30 | 1.84 | 40 | 3.68 | 30 | 1.45 | 30 | 2.21 | 20 | | | | | | 0.91 | 1.08 | | 0.99 | | | |
| FeOCl, orthorombic | | | | | | | | | | | | | | | | | 2.54 | 50 | 7.92 | 100 | 3.41 | | | 1.81 | | | 1.98 | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4-30-96 washed solids (3) | 2.70 | 100 | 2.52 | 68 | 1.70 | 57 | 1.84 | 36 | 1.45 | 28 | 1.49 | 27 | 3.68 | 26 | 2.21 | 25 | 1.26 | 22 | 1.31 | 12 | 1.02 | 2.54 | 1.14 | 0.95 | 1.17 | 0.98 | 1.10 | |
| $Fe_2O_3$, hematite | 2.70 | 100 | 2.52 | 70 | 1.69 | 45 | 1.84 | 40 | 1.45 | 30 | 1.49 | 30 | 3.68 | 30 | 2.21 | 20 | 1.26 | 8 | 1.31 | 10 | | | 1.14 | 0.95 | 1.16 | 0.99 | 1.10 | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5-9-96 Built-up on glass (4) | 2.71 | 100 | 2.53 | 74 | 1.70 | 50 | 1.85 | 42 | 1.46 | 32 | 1.49 | 29 | 2.21 | 27 | 3.40 | 25 | 3.69 | 24 | 1.32 | 20 | 1.53 | 1.11 | 0.95 | 0.94 | 0.96 | 0.98 | 2.34 | Poorly crystallized |
| $Fe_2O_3$, hematite | 2.70 | 100 | 2.52 | 70 | 1.69 | 45 | 1.84 | 40 | 1.45 | 30 | 1.49 | 30 | 2.21 | 20 | | | 3.68 | 30 | 1.31 | 10 | | 1.10 | 0.96 | 0.95 | 0.96 | 0.99 | | |
| FeOCl, orthorombic | | | 2.54 | 50 | | | | | | | | | | | 3.41 | 100 | | | | | 1.51 | | | | | | 2.37 | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5-18-96 unwashed solids (5) | 2.70 | 100 | 2.52 | 74 | 1.70 | 63 | 3.69 | 43 | 1.85 | 41 | 2.21 | 41 | 1.46 | 40 | 1.49 | 38 | 1.31 | 33 | 1.80 | 17 | 2.03 | 1.60 | 1.37 | 1.06 | 1.11 | 1.27 | 1.08 | Poorly crystallized |
| $Fe_2O_3$, hematite | 2.70 | 100 | 2.52 | 70 | 1.69 | 45 | 3.68 | 30 | 1.84 | 40 | 2.21 | 20 | 1.45 | 30 | 1.49 | 30 | 1.31 | 10 | | | | 1.60 | | 1.06 | 1.10 | 1.26 | 1.08 | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

1. Temperature at the end of the test was in the range of 340°C. Hydrolysis to $Fe_2O_3$ was 68% complete. Color: dark red, slightly purple when unwashed, red when washed

2. *Temperature did not exceed 190°C. Hydrolysis about 65% complete. Color: red/mahogany, somewhat purple.*

3. Temperature probably did not exceed 220°C. Hydrolysis to $Fe_2O_3$ is 96% complete. Color: brick red

4. *Heating provided with an immersed glass heater instead of a mantle. It broke. These solids accumulated on the heater in the gas phase, from splashing and hydrolysis of the solution. The glass heater outside the solution is red hot. Color: black*

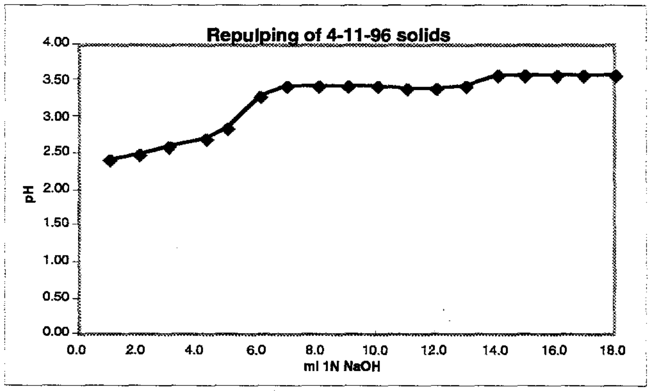
5. First test using microwave heating.

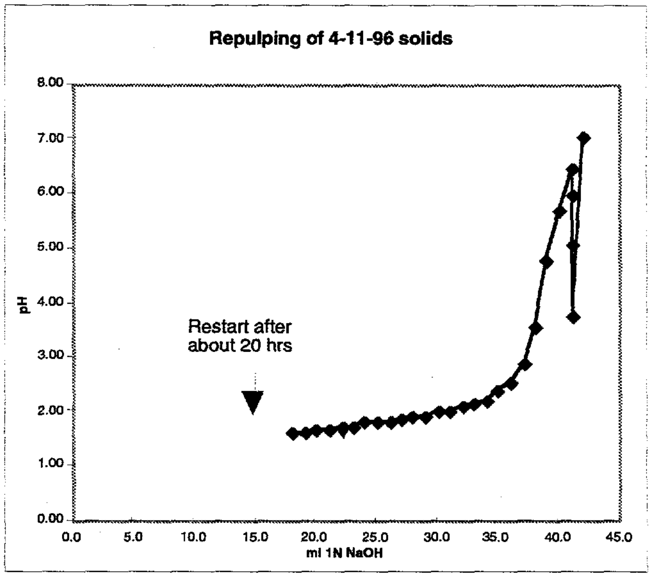
# Appendix 3. Water Repulping and Titration of Hydrolysis Solids.

## Repulping of 4-11-96 solids from hydrolysis test

Determine if repulping of FeOCl in sample 4-11-96 produces hydrolysis with time and, if so, how much. The pH of the mixture of water and solids will be continuously determined, and titration with NaOH will be used to determine HCl and $FeCl_2$. The mixture is agitated on a heating plate Starting water weight: 457 g; solids weight: 5.36 g. Solids weight after hydrolysis, filtration and drying is 4.65 g. Calculations show that the solids must be $Fe_2O_3$, 1.5 $H_2O$.

| time min | pH before | NaOH ml, 1N | pH after | HCl mg | $FeCl_3$ mg | Notes |
|---|---|---|---|---|---|---|
| 0 | 5.80 | | | | | DI water |
| 0.2 | 3.05 | | | | | Added solids |
| 15 | 2.95 | | | | | Start slow heat |
| 40 | 2.90 | | | | | 40°C |
| 65 | 2.80 | | | | | 60°C |
| 80 | 2.65 | | | | | 64°C |
| 240 | 2.45 | 1.0 | 2.42 | 36.5 | | 69°C |
| 285 | 2.42 | 2.0 | 2.50 | 73.0 | | 68°C |
| 293 | 2.50 | 3.0 | 2.60 | 109.5 | | 68°C |
| 302 | 2.60 | 4.2 | 2.70 | 153.3 | | Temp.constant |
| 308 | 2.70 | 5.0 | 2.85 | 182.5 | | |
| 311 | 2.85 | 6.0 | 3.30 | 219.0 | | |
| 313 | 3.30 | 7.0 | 3.45 | 255.5 | | |
| 315 | 3.45 | 8.0 | 3.45 | | 54 | |
| 316 | 3.45 | 9.0 | 3.45 | | 487 | |
| 318 | 3.45 | 10.0 | 3.45 | | 541 | |
| 320 | 3.45 | 11.0 | 3.40 | | 595 | |
| 322 | 3.40 | 12.0 | 3.40 | | 650 | |
| 325 | 3.40 | 13.0 | 3.45 | | 704 | |
| 326 | 3.45 | 14.0 | 3.60 | | 758 | |
| 327 | 3.60 | 15.0 | 3.60 | | 812 | |
| 327 | 3.60 | 16.0 | 3.60 | | 866 | |
| 328 | 3.60 | 17.0 | 3.60 | | 920 | |
| 329 | 3.60 | 18.0 | 3.60 | | 974 | |
| 1237 | 3.60 | 18.0 | 1.65 | | 974 | No NaOH added |
| | 1.65 | 19.0 | 1.65 | 292 | | |
| | 1.65 | 20.0 | 1.70 | 329 | | |
| | 1.70 | 21.0 | 1.70 | 365 | | |
| | 1.70 | 22.0 | 1.72 | 402 | | |
| | 1.72 | 23.0 | 1.75 | 438 | | |
| | 1.75 | 24.0 | 1.80 | 475 | | |
| 1279 | 1.80 | 25.0 | 1.80 | 511 | | |
| | 1.80 | 26.0 | 1.85 | 548 | | |
| | 1.85 | 27.0 | 1.87 | 584 | | |
| | 1.87 | 28.0 | 1.90 | 621 | | |
| | 1.90 | 29.0 | 1.95 | 657 | | |
| | 1.95 | 30.0 | 2.00 | 694 | | |
| 1290 | 2.00 | 31.0 | 2.05 | 730 | | |
| | 2.05 | 32.0 | 2.10 | 767 | | |
| | 2.10 | 33.0 | 2.17 | 803 | | |
| | 2.17 | 34.0 | 2.25 | 840 | | |
| | 2.25 | 35.0 | 2.40 | 876 | | |
| | 2.40 | 36.0 | 2.57 | 913 | | |
| | 2.57 | 37.0 | 2.87 | 949 | | |
| | 2.87 | 38.0 | 3.55 | 986 | | |
| 1309 | 3.55 | 39.0 | 4.80 | 1022 | | |
| | 4.80 | 40.0 | 5.70 | 1059 | | |
| 1318 | 5.70 | 41.0 | 6.50 | 1095 | | |
| 1342 | 6.50 | 41.0 | 6.00 | 1095 | | No NaOH added |
| 1520 | 6.00 | 41.0 | 5.10 | 1095 | | Stirrer was off |
| 1553 | 5.10 | 41.0 | 3.80 | 1095 | | No NaOH |
| 1559 | 3.80 | 42.0 | 7.05 | 1132 | | |





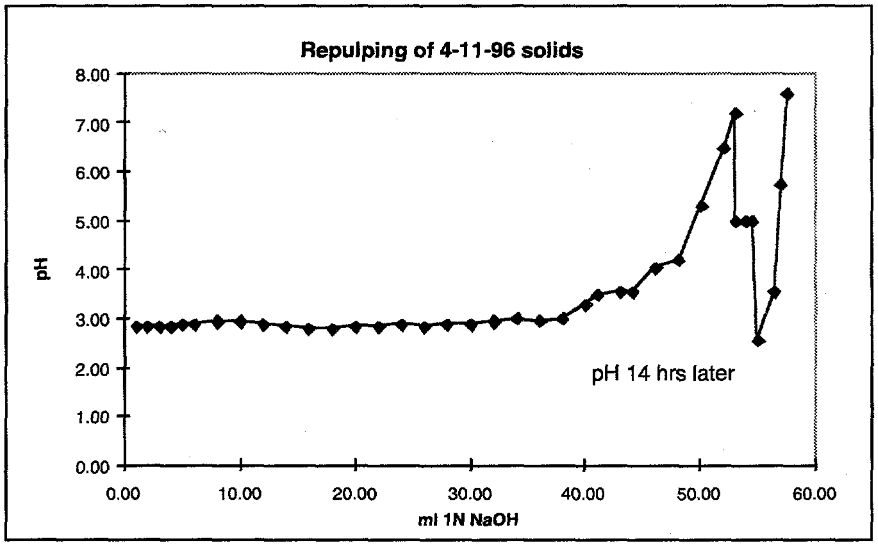
## August 15 1996. Repulp of 4-11-96 solids. Second Test

We are going to repeat pulping on these solids, but with better controled conditions. Hydrolysis will be done at relatively high temperature, about 70°C from the start. *To achieve this, water at the appropriate temperature will be poured on the solids.*

Final solids are light brown to yellowish brown, unlike the darker solids from test 4-18-96. They settle very quickly. (4-18-96 repulp solids settled quickly too).

| | | | | |
|---|---|---|---|---|
| Final solids, g | 6.00 | Solids are hard to break up. | HCl equivalent, g | 2.10 |
| Final solids, % | 83.3 | | Cl equivalent, g | 2.04 |
| | | | Cl equivalent, % | 34.0 |

| | | | | | |
|---|---|---|---|---|---|
| From hydrolysis test | | From hydrolysis test | | | |
| Initial $FeCl_3$, g | 1009.3 | Theoretical solids at completion, g | 496.8 | | |
| HCl to release, g | 680.62 | Theoretical wt/final solids wt % | 75.2 | | |
| HCl recovered, g | 462.3 | | | | |
| HCl eq. left, g | 218.3 | | 5.42 | Moles: | 0.0339 |
| Final solids wt, g | 660.4 | Difference with final wt, assumed to be $H_2O$, g | 0.58 | Moles: | 0.0324 |
| Cl in final solids, % | 32.2 | $Fe_2O_3$, n $H_2O$. n= | 0.96 | | |



## Appendix 3. Continued. Repulping of 4-18-96 solids from hydrolysis test.

Checking if repulping of FeOCl in sample 4-18-96 produces hydrolysis with time, and if so, how much. The pH of the mixture of water and solids will be continuously determined, and titration with NaOh will be used to determine HCl and $FeCl_3$. The mixture is agitated on a heating plate. Starting water weight: about 450 g; solids weight: 33.33 g.

| pH bef'r | pH after | NaOH ml (*) | HCl mg | Theor pH | Notes | time min | pH bef'r | pH after | NaOH ml (*) | HCl mg | $FeCl_3$ mg | Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6.10 | | | | | DI water | | 6.25 | 6.45 | 150 | 5475 | | to dk green |
| 6.10 | 1.90 | | | | Added solids | | 6.45 | 6.52 | 153 | 5585 | | |
| 1.90 | 1.87 | | | | room temp. | | 6.52 | 6.40 | 156 | 5694 | | 49°C |
| 1.87 | 1.90 | 1.0 | 36.5 | | | | 6.40 | 6.20 | 159 | 5804 | | |
| 1.90 | 1.90 | 2.0 | 73.0 | | | 1327 | 6.20 | 6.30 | 162 | 5913 | | |
| 1.90 | 1.90 | 3.0 | 109.5 | | | | 6.30 | 6.32 | 165 | 6023 | | |
| 1.90 | 1.95 | 4.0 | 146.0 | | | | 6.32 | 6.40 | 168 | 6132 | | |
| 1.95 | 1.95 | 5.3 | 193.5 | | | | 6.40 | 6.70 | 171 | 6242 | | 55°C |
| 1.95 | 1.97 | 7.0 | 256.5 | | | | 6.70 | 7.40 | 174 | 6351 | | |
| 1.97 | 2.00 | 9.0 | 328.5 | | | 1335 | 7.40 | 8.25 | 176 | 6424 | | |
| 2.00 | 2.05 | 13.6 | 496.4 | | | 1530 | 8.25 | 1.30 | 176 | 6424 | | 82°C, no NaOH |
| 2.05 | 2.05 | 17.0 | 620.5 | | | | 1.30 | 1.30 | 178 | 6497 | | |
| 2.05 | 2.05 | 20.0 | 730.0 | | | | 1.30 | 1.35 | 180 | 6570 | | |
| 2.05 | 2.05 | 23.2 | 847 | | | | 1.35 | 1.37 | 182 | 6643 | | |
| 2.05 | 2.07 | 29.0 | 1059 | | | | 1.37 | 1.40 | 184 | 6716 | | |
| 2.07 | 2.10 | 34.0 | 1241 | | | | 1.40 | 1.42 | 186 | 6789 | | |
| 2.10 | 2.05 | 38.0 | 1387 | | | | 1.42 | 1.45 | 188 | 6862 | | |
| 2.05 | 2.07 | 43.3 | 1580 | | | | 1.45 | 1.47 | 190 | 6935 | | |
| 2.07 | 2.12 | 47.5 | 1734 | | | | 1.47 | 1.50 | 192 | 7008 | | |
| 2.12 | 2.20 | 48.3 | 1763 | | | | 1.50 | 1.55 | 194 | 7081 | | |
| 2.20 | 2.30 | 51.3 | 1872 | | | | 1.55 | 1.55 | 196 | 7154 | | |
| 2.30 | 2.35 | 55.3 | 2018 | | | | 1.55 | 1.60 | 198 | 7227 | | |
| 2.35 | 2.40 | 60.3 | 2201 | | | | 1.60 | 1.65 | 200 | 7300 | | |
| 2.40 | 2.60 | 65.3 | 2283 | | | | 1.65 | 1.70 | 202 | 7373 | | |
| 2.60 | 2.95 | 68.9 | 2515 | | | | 1.70 | 1.75 | 204 | 7446 | | |
| 2.95 | 3.55 | 74.9 | 2734 | | solution | 1540 | 1.75 | 1.85 | 206 | 7519 | | |
| 3.55 | 3.20 | 79.0 | 2884 | | turning | | 1.85 | 1.92 | 208 | 7592 | | |
| 3.20 | 3.90 | 80.6 | 2942 | | darker | | 1.92 | 2.05 | 210 | 7665 | | |
| 3.90 | 3.75 | 80.6 | 2942 | | no NaOH | | 2.05 | 2.18 | 212 | 7738 | | |
| 3.75 | 4.80 | 85.6 | 3124 | | | | 2.18 | 2.40 | 214 | 7811 | | |
| 4.80 | 5.45 | 90.6 | 3307 | | | | 2.40 | 2.60 | 216 | 7884 | | |
| 5.45 | 4.75 | 90.6 | 3307 | | no NaOH | | 2.60 | 2.95 | 218 | 7957 | | |
| 4.75 | 3.20 | 90.6 | 3307 | | "  " | | 2.95 | 3.42 | 220 | 8030 | | |
| 3.20 | 2.00 | 90.6 | 3307 | | "  " | | 3.42 | 3.90 | 222 | 8130 | | |
| 2.00 | 2.10 | 97.9 | 3573 | | | | 3.90 | 4.30 | 224 | 8176 | | |
| 2.10 | 2.20 | 102.9 | 3756 | | | | 4.30 | 4.50 | 226 | 8249 | | |
| 2.20 | 2.37 | 109.9 | 4011 | | | | 4.50 | 4.70 | 228 | 8322 | | |
| 2.37 | 2.42 | 113.0 | 4125 | | | | 4.70 | 4.90 | 230 | 8395 | | |
| 2.42 | 2.62 | 118.0 | 4307 | | | | 4.90 | 5.02 | 232 | 8468 | | |
| 2.62 | 3.52 | 123.0 | 4490 | | | | 5.02 | 5.15 | 234 | 8541 | | |
| 3.52 | 3.75 | 126.0 | 4599 | | | | 5.15 | 5.30 | 236 | 8614 | | |
| 3.75 | 4.12 | 128.0 | 4672 | | | | 5.30 | 5.45 | 238 | 8687 | | |
| 4.12 | 4.60 | 130.0 | 4745 | | | | 5.45 | 5.60 | 240 | 8760 | | |
| 4.60 | 5.00 | 132.0 | 4818 | | start heat'g | 1548 | 5.60 | 6.10 | 242 | 8833 | | 78°C |
| 5.00 | 5.32 | 134.0 | 4891 | | | 1550 | 6.10 | 5.60 | 242 | 8833 | | no NaOH |
| 5.32 | 5.50 | 136.0 | 4964 | | | | 5.60 | 6.40 | 244 | 8906 | | |
| 5.60 | 5.80 | 138.0 | 5037 | | | | 6.40 | 7.30 | 246 | 8979 | | |
| 5.80 | 6.07 | 140.0 | 5110 | | | | 7.30 | 8.05 | 248 | 9052 | | still very black |
| 6.07 | 6.30 | 142.0 | 5183 | | | 1590 | 8.05 | 6.42 | 248 | 9052 | | no NaOH, 76°C |
| 6.30 | 6.52 | 144.0 | 5256 | | 40°C | 1800 | 6.42 | 5.75 | 248 | 9052 | | no NaOH, 67°C |
| 6.52 | 6.02 | 144.0 | 5256 | | No NaOH | 2700 | 5.75 | 5.25 | 248 | 9052 | | 68°C |
| 6.02 | 6.25 | 147.0 | 5256 | | turning black | | 5.25 | 5.70 | 249 | 9089 | | |
| | | | | | | | 5.70 | 6.15 | 250 | 9125 | | |
| | | | | | | | 6.15 | 6.52 | 251 | 9162 | | |
| | | | | | | | 6.52 | 6.95 | 252 | 9198 | | |
| | | | | | | | 6.95 | 7.25 | 253 | 9235 | | |
| | | | | | | | 7.25 | 7.70 | 254 | 9271 | | |

(*) IN

## Appendix 3. Continued Repulping of 4-18-96 Solids

Filtration is somewhat slow on a 5-µm millipore filter; it's done overnight. A few pieces of starting solids did not break down. Solids are very dark brown to almost black.

| | |
|---|---|
| Filter tare | 437.9 g |
| Final solids, g | 25.73 |
| Final solids, % | 77.2 |

Solids are hard to break up.

| | |
|---|---|
| HCl equivalent, g | 9.271 |
| Cl equivalent, g | 9.017 |
| Cl equivalent, % | 27.1 |

From hydrolysis test

| | |
|---|---|
| Initial $FeCl_3$, g | 992 |
| HCl to release, g | 669 |
| HCl recovered, g | 453.6 |
| HCl eq. left, g | 215.4 |
| Final solids wt, g | 665 |
| Cl in final solids, % | 31.503 |

From hydrolysis test

| | |
|---|---|
| Theoritical solids at completion, g | 488 |
| Theoritical wt/final solids wt % | 73.43 |