Fe-Separation and HCl regeneration technologies

for ore leaching process

New and economic route

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1. GENERAL/OVERVIEW

In the present paper a new and highly economic route for Fe-separation from HCl leaching processes in hydrometallurgical applications is described. HCl is recycled and Fe precipitated as Ferric oxide. Potential technologies for regeneration of HCl with separation of Fe are shown and compared.

In many hydrometallurgical leaching applications HCl has become the most interesting leaching agent, because it can be regenerated. And in most of ore leaching processes Fe is involved and needs to be separated. HCl leaching is made with elevated temperature and pressure to limit leaching time. Recent technologies are using oxidative leaching, but this means using expensive chemicals which usually does not allow to oxidize all Fe from cost point of view.

Usually as result a mix of Fe$^{2+}$ and Fe$^{3+}$ is obtained. Fe$^{3+}$ can be separated from other 1-, 2-, and 4- valent ions by solvent extraction, whereas the classic HCl regeneration technology by Pyrohydrolysis , which has been a proven approach for regenerating HCl from iron chloride solutions for many years, but has limitations regarding size, and operation costs and needs to work with Fe$^{2+}$.

Fe-control in HCl-based processes has represented the shortcoming of chloride leaching.

TENOVA HYDROMET process:

A low temperature, PORI-inspired approach has been developed, which is particularly attractive for hydrometallurgical applications using HCl leaching. Actual processes with hydrothermal regeneration need oxidation at high pressure which is a challenge for safety and materials.

Recently an alternate electrochemical oxidation approach has been developed that would involve the ‘in situ’ – oxidation with chlorine (Cl$_2$ (g)), which has been electrolytically generated in a Fe$^{2+}$ → Fe$^{3+}$ oxidation cell. Oxidation with Cl$_2$ (g) is much more effective than O$_2$ and can be completed under atmospheric conditions. This configuration leads to a simplification in the overall design, presumably with a lowering in the overall capital cost. With this configuration complete, fast and economic conversion of Fe$^{2+}$ to Fe$^{3+}$ can be assured.
In the next step the Fe$^{3+}$ is separated from other ions by SX technology (TENOVA proprietary technology), it shows that also interesting by-products like e.g. V can be recovered either by SX or IX.

After SX there will by Hydrolysis of Fe$^{3+}$ at elevated temperature with recovery of HCl. The hydrolysis reactors, where the HCl would be regenerated, are expected to be easier to implement on a modular basis than a conventional pyrohydrolysis reactor, as there is no large-scale gas handling and pollution prevention equipment necessary.

The hydrolysis reactors could be steam or electrically heated and tied together through a common manifold, which would collect the HCl(g) and water vapour to condenser units.

This technology has the potential to find widespread application in the minerals industry.

**TENOVA HYDROMET PROCESS STEPS**

Leaching with HCl offers
- a means of process intensification without reliance upon autoclave reactions
- regenerating HCl with producing a marketable iron by-product
- applications for
  - titaniferrous magnetite
  - nickel laterite,
  - bauxite,
  - and many more
The main difference to existing regeneration technologies is that this new process is a wet process, which means that all reactions take place in liquid phase. Total evaporation of leaching solution is not needed and the main reason for the energy saving.

The PORI Process is based upon a three step sequence:

- Concentration,
- Oxidation,
- Hydrolysis.

Originally designed for the treatment of spent liquor from steel mill pickling operations (FeCl$_2$). The process first concentrates the solution by evaporation from 20 wt% FeCl$_2$ to approximately 35 wt% FeCl$_2$, raising the boiling point of the solution in the process. Pressure oxidation at approx 150 °C then converts Fe$^{+2}$ to Fe$^{+3}$ and hematite (Fe$_2$O$_3$):

$$6 \text{FeCl}_2 + \frac{3}{2} \text{O}_2 (g) = 4 \text{FeCl}_3 + \text{Fe}_2\text{O}_3$$

In the last step of the process, hydrolysis of the ferric ion with simultaneous release of HCl (g) takes place under atmospheric conditions at a temperature of 180°C:

$$2 \text{FeCl}_3 + 3 \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6 \text{HCl} (g)$$

With this approach, higher strengths than 20% of HCl are possible.
2. HCL REGENERATION TECHNOLOGIES

Regeneration processes are per definition such recovering processes, where the total amount of chlorides in the metal chloride solution is recovered.

2.1. PYROHYDROLYSIS

The pyrohydrolysis is a process occurring in the presence of water (oxygen) vapors above 300°C with technically sufficient speed according to the following global reactions:

$$\text{Me}_x\text{Cl}_y + z\text{H}_2\text{O} \Rightarrow \text{Me}_x\text{O}_z + y\text{HCl}$$

Not all metal chlorides can be pyrohydrolyzed, only the ones having:

1) Negative Gibbs energy $\Delta G^\circ$ for decomposition which should be lower than 15 kJ/mol, some values for the most important reactions are given in fig. 1

2) Low volatility: The metal chlorides must have a low vapor pressure at the reactor temperature, otherwise they distill off without reaction as chlorides and condense anywhere in the cooler roast gas duct. Some metal chlorides can be pyrohydrolyzed in the vapor phase, when reaction thermodynamics and kinetics (means Gibbs energy of reaction and residence time in the reactor) are suitable. Vapor pressure of some chlorides as depicted in fig. 2. The chlorides of Fe$^{3+}$, Al, V, Si or Ti have high vapor pressures at common reactor temperatures, but some of them (Fe$^{3+}$, Al) can nevertheless be pyrohydrolyzed from vapor phase.

The metals which fulfill the restrictions given above are shown in fig. 3:

In fig. 4, the most important application of HCl regeneration is shown, the recovery of Waste Acid from Steel pickling. Industrially two such regeneration processes are used:
- Spray Roasting Process
- Fluidized Bed Process

Both are based on the same chemical reaction, but with different reactor design, while other process parts are practically identical. Both of them are relying on direct heat transfer and on the combustion of hydrocarbon fuels to maintain the required elevated temperature for
evaporation and reaction in a reactor. The absorption and off-gas treatment is practically the same.
The recovery rate is almost 100% of the total chloride content and the process highly optimized already. Energy consumption and investment cost are high compared to alternative processes, but above 4,000 m³/y Waste Acid the technology becomes highly economic.

Process Overview

The pyrohydrolysis process is not only used for recovery of spent pickle liquor, but also as metallurgical process for production of mixed oxides or ceramic specialties.
See fig. 5 with closed HCl cycle for the production of pure metal oxides according to the pyrohydrolysis process. The regeneration process can be applied to metal chloride solutions that come from a metal pickling line, a leaching unit for mineral ore processing or a dissolving station to solve scrap for oxide ceramic production.
The spent solution is fed into the preconcentrator (working as a recuperator), where the hot roast gas is cooled by direct heat exchange and the liquid is partially evaporated (concentrated). The concentrate from the preconcentrator is fed into the reactor, which can be a spray roaster or a fluidized bed. A combustion gas with a certain amount of excess air is let into the reactor and delivers the heat needed for evaporation and pyrohydrolysis reaction. The roast gas from the reactor contains HCl which is absorbed in an absorption column to obtain 20% HCl to be reused for pickling or leaching. All further steps are for gas cleaning and increasing efficiency of the HCl recovery.
So far, approximately 400 pyrohydrolysis process plants (350 spray roasters and 50 fluidized beds) have been built all around the world with a capacity from 0,3 up to 25 m³/h of spent solution.

Spray Roasting

In the spray roasting process the Me-chloride concentrate is sprayed by means of a nozzle injection system. The bottom is conical to ensure the flow of oxide to the outlet.
The droplets descend in the reactor, dry up and are pyrohydrolyzed.
The oxide obtained is a powder with a bulk density between 0,2 and 0,8 g/cm³ and a specific surface from 2 to 8 m²/g (BET) for Fe₂O₃ and can have up to 135 m²/g for other oxides.
The Fluidized Bed

In this type of reactor the gas mixture enters via the bottom and provides fluidization of the oxide bed. The concentrated Me-chloride solution is fed onto the bed from the side, no specific injection system is provided.

Oxide granulates obtained by fluidized bed pyrohydrolysis are perfectly shaped spheres with an onion-like structure, resulting from the continuous build up of oxide layers. Typical particle diameters are about 1 mm. The solid density is about 5,4 g/cm³, while the bulk density is around 3,2 g/cm³.

Differences between Spray Roast - and Fluidized Bed - Technology

- Reactor Design
- Process Control
- Process Versatility
- Energy Consumption
- Emissions
- Oxide Product Quality

Fluidized Bed - Oxide

- Particle size: 0,2 - 2 mm
- Specific surface: < 1 m²/g
- Bulk Density: 3,8 kg/dm³

Sprayroast - Oxide

- Particle size: d₅₀ 10 µm
- Specific surface: 3 - 5 m²/g
- Bulk Density: 0,4 - 0,6 kg/dm³
2.2. TENOVA HYDROMET Process

The chemical reaction takes place in 3 basic steps and the main mechanism is a Hydrolysis:

a) Oxidation
b) Fe hydrolysis,
c) HCl and hematite recovery

a) Oxidation step

For the Hydrolysis step is necessary to convert Fe$^{2+}$ to Fe$^{3+}$, which is made through electrochemical oxidation:

\[ \text{-e}^- \quad \text{FeCl}_2 + \text{HCl} \rightarrow \text{FeCl}_3 + \text{Cl}_2 \quad \text{and} \quad 2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3 \]

The electrolytic generation of Cl$_2$ (g) from FeCl$_2$, can be conducted in a modified HCl to Cl$_2$ cell design and ensures a closed loop which does not create any imbalance of Cl$^-$ or Cl$_2$ in the system, the configuration is modular.

b) Hydrolysis step

The Ferric Chloride is heated up to 175 °C under at mospheric conditions:

\[ \text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{HCl} + \text{Fe}_2\text{O}_3 \]

A high strength acid with concentration of around 30% can be produced. The produced ferric oxide powder is a black, fine grained powder with a high specific surface. The bulk density of this oxide is said to be 5 x higher than sprayroasted oxide. The powder will be nearly free of impurities. There is an energy recovery step tied to the recovery of HCl. The matrix in the hydrolysis reactor will accumulate base metal and other impurities. To control impurities, there is a periodic withdrawal of solution, followed by precipitation of base metals, filtration and return of clean matrix to the hydrolysis reactor.

c) Condensation of the produced HCL gas and separation of solids
Very little rinse water is required and the residual moisture has been as low as 4% for the black hematite that they have produced, and is typically in the 5-10% range. There are two stages of filtration with a repulp of the solids produced from the hydrolysis step. The solids are repulped with washing water recovered from the second filtration step, to which some fresh washing water is added in a final washing stage (belt filter). There is a recycle of the washing water within the second filtration system and a portion of the wash water is sent back to the evaporation circuit.

The washed hematite contains < 0.1% Cl and no base metals incorporation.

3. COMPARISON HYDROMET - PYROHYDROLYSIS

Energy consumption & Costs

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ADVANTAGES TENOVA HYDROMET TO PYROHYDROLYSIS

a) Significant lower energy costs
b) Steam can be used as energy source, which can be made from various energy sources
c) No Oxygen required with elevated temperatures and pressures avoiding material- and safety problems.
d) No impurities due to incineration
e) No emission problems, especially dust and HCl
f) High density \( \text{Fe}_2\text{O}_3 \) produced, easy to handle, higher market value
g) Equipment lifetime is longer
h) No red dust in the plant
i) Operational flexibility
j) No limitations in process size
k) Flexible Applications

Outlook

Conventional Pyrohydrolysis will still have its benefits in standard applications in Recovery of Acid from Pickling Lines, due to very high efficiency for HCl recovery (re-use of rinse water)

For hydrometallurgical applications the HYDROMET process has many advantages, the most important lower operation costs. For such applications, considering the module concept of the technology, even high capacities of HCl recovery can be provided at low investment costs.
Fig. 1: Gibbs energy of reaction for some metal chlorides (Kögler, 1997)

Fig. 2: Vapor pressure of several metal chlorides (Van Weert, 1989)
Fig. 3: Thermally decomposable, non-volatile metal chlorides (Krivanec, 1988)

\[
2\text{FeCl}_3 + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{HCl}
\]

Fig. 4: Pyrohydrolysis Regeneration Cycle

RECOVERY RATE > 99.5%