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HYDROCHLORIC ACID IN HYDROMETALLURGY

Fathi Habashi

Department of Mining, Metallurgical, and Materials Engineering
Laval University, Quebec City, Canada
Fathi.Habashi@arul.ulaval.ca

ABSTRACT

Hydrochloric acid (HCl), although more expensive than sulfuric, find uses as a leaching agent in reactions involving iron oxide. The reason for this substitution was the discovery that oxyhydrolysis of ferrous chloride by which HCl can be recycled economically. This avoided the pollution of the environment by ferrous sulfate. It was found further that the rate of leaching of sulfides is faster when HCl is used as compared with sulfuric apparently due to the formation of aqueous chlorine. In case of refractory gold ores, HCl leaching under pressure avoids the use of cyanide solution since gold chloride is produced which can be recovered by standard methods. Hydrochloric acid find also uses in the leaching of scheelite and apatite but its use in leaching clay and anorthosite is questionable.

KEYWORDS

Anorthosite, Ilmenite, Kaolinite, Oxyhydrolysis, Pickling of steel, Refractory gold, Synthetic rutile
INTRODUCTION

Sulfuric acid is the cheapest acid and is used as a leaching agent in many hydrometallurgical processes. However, hydrochloric acid (HCl), although more expensive since it is prepared by reaction of sulfuric with sodium chloride, has replaced sulfuric acid in many reactions involving iron oxide. It replaced sulfuric acid for the first time in 1960s in pickling of steel because of pollution problems (Habashi, 2000). Ferrous chloride produced in pickling can be economically decomposed to ferric oxide and HCl according to:

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

which also shows that the acid can be regenerated but ferrous sulfate cannot be economically decomposed to recover sulfuric acid for recycle. Since then, HCl has been used in many leaching processes. Hydrochloric acid is a corrosive acid and is usually handled in rubber-lined equipment.

REGENERATION OF HYDROCHLORIC ACID

Regeneration of HCl is conducted in fluidized bed or in spray roaster

Fluidized bed oxyhydrolysis

In a fluidized bed, ferrous chloride solution is introduced onto a bed of hot ferric oxide where heating is provided by the hot fluidizing combustion gases (Figure 1). The solution is fed on top of the bed of oxides. The liquid feed wets the outer layer of the hot oxide particles and is quickly evaporated to form a layer of new solid oxide on top of the existing oxide, thereby producing dense homogeneous particles.

Spray roaster oxyhydrolysis

In spray roasters, the ferrous chloride solution is sprayed into an empty cylindrical vessel, while the required energy is supplied by the up flow of hot gases generated in the bottom burners (Figure 2). Spray roasters have large diameters to keep the gas velocities low. If the gas velocity is high, too many particles are elutriated with the off-gas, and the product quality and the efficiency of the roaster drop. The off-gas and oxides leave the roaster counter-currently at 400 to 500°C. The residence time of the sprayed
particles in the high-temperature reaction zone is very short; therefore, very small liquid droplets, which can be quickly heated, should be created by atomization. The fast heat-up results in the formation of a solid oxide crust on the surface of each droplet. As the bulk of the droplet heats, the water content vaporizes and breaks through the oxide shell. Therefore, the spray roasted oxide is composed of very fine “fluffy”, hollow spheres.

Figure 2. Spray roaster

Vapour pressure of hydrochloric acid

The maximum boiling point of HCl at atmospheric pressure is 110°C, and an acid boiling at this temperature is called an azeotropic mixture, i.e., it boils without change. Figure 3 shows vapour pressure of HCl solutions at different temperatures (Habashi, 1999).

Figure 3. Vapor pressure of HCl solutions at different temperatures

HYDROCHLORIC ACID FOR PURIFICATION OF MINERALS

Low grade tin ore

Cassiterite, SnO₂, concentrate especially those from Bolivia contain many impurities and were purified by boiling at 110°C with HCl in autoclaves. This was conducted in rotating spherical autoclaves (Figures 4 and 5) at the Longhorn Smelter in Texas (Habashi, 2014). Tin oxide obtained was amenable to conventional smelting.
Figure 4. Rotary autoclave for removing impurities from cassiterite concentrate

Figure 5. Twenty autoclaves as the one shown in the previous Figure, ten on each side

Low grade niobium ore

Pyrochlore (Figure 6) is the most abundant and complex niobium-containing mineral. It can be represented by the formula $A_{2-m}B_2O_6(O,OH,F)_{1-n}nH_2O$ where $A = Ca, Ba, Sr, Na$ and $B = Nb, Ta, Ti$. Economic ore deposits of this mineral were discovered in the period 1950-1960 at the Araxa and Catalão mines in Brazil and Saint Honoré mine in Quebec. Pyrochlore from Saint Honoré contains calcium, sodium, and fluorine whereas that from Araxa and Catalão contains barium and water. Both contain minimal amounts of tantalum and appreciable amounts of uranium, thorium and rare earths (Toromanoff & Habashi, 1983).

Figure 6. Pyrochlore crystals on quartz

Figure 7. Pyrochlore concentrate

Pyrochlore concentrate containing 57% $Nb_2O_5$ (Figure 7) can be transformed into technical grade $Nb_2O_5$ (minimum purity, 90%) by digestion with 10 mol/L HC1 at 200°C in a pressure reactor for 4 h. The
reaction takes place through the formation of calcium niobate \((\text{Ca}_2\text{Nb}_2\text{O}_7)\) as an intermediate product that forms a non-porous protective layer:

\[
3(\text{Nb}_2\text{O}_5\cdot\text{CaO}) + 2\text{HCl} \rightarrow 2\text{Nb}_2\text{O}_5 + \text{Ca}_2\text{Nb}_2\text{O}_7 + \text{CaCl}_2 + \text{H}_2\text{O} \quad (2)
\]

\[
\text{Ca}_2\text{Nb}_2\text{O}_7 + 4\text{HCl} \rightarrow \text{Nb}_2\text{O}_5 + 2\text{CaCl}_2 + 2\text{H}_2\text{O} \quad (3)
\]

Major impurities in the product are \(\text{Ta}_2\text{O}_5\), \(\text{TiO}_2\) and \(\text{SiO}_2\).

**Preparation of synthetic rutile**

High grade ilmenite (Figure 8) or titanium slag (Figure 9) can be decomposed by 20% HCl at 120°C and 200 kPa; iron is solubilized leaving a material containing about 93% \(\text{TiO}_2\) (Toromanoff & Habashi, 1985):

\[
\text{FeTiO}_3 + 2\text{H}^+ \rightarrow \text{TiO}_{2(\text{impure})} + \text{Fe}^{2+} + \text{H}_2\text{O} \quad (4)
\]

A negligible amount of titanium is lost in solution. Leaching can be conducted at lower temperature, i.e., no autoclaves would be required, if a preliminary oxidation–reduction step is conducted to modify the crystalline structure of the mineral and render it more amenable to leaching. Thus, the ore is first heated in an oxidizing atmosphere to convert as much as possible of \(\text{FeO}\) into \(\text{Fe}_2\text{O}_3\). This is followed by heating in a reducing atmosphere to convert \(\text{Fe}_2\text{O}_3\) into iron which can be leached with HCl. Reduction is necessary to obtain a ferrous chloride solution which is less corroding as compared to ferric chloride. Synthetic rutile (Figure 10) is used to manufacture \(\text{TiO}_2\) white pigment or metallic titanium by the chlorination route. This process does not apply for low grade ilmenite containing appreciable amounts of insoluble matter because these remain with the synthetic rutile thus decreasing greatly its tenor in \(\text{TiO}_2\). Figure 11 shows a general scheme for the production of synthetic rutile.

![Diagram of synthetic rutile production](image-url)
HYDROCHLORIC ACID FOR LEACHING MINERALS

Hydrochloric acid has been used for leaching complex oxide, silicates, sulfides, phosphates, and gold ores.

Ilmenite

A low-grade ilmenite ore containing as low as 11% TiO$_2$ can be dissolved in concentrated HCl at 80°C. After filtration to remove insoluble matter the solution was heated to distil off HCl for recovery. The slurry obtained was filtered to get Ti(OH)$_2$ which was then calcined to obtain TiO$_2$ which analyzes +98% (Figure 12). The solution obtained from the last filtration step could be treated by solvent extraction to get vanadium then undergoes oxyhydrolysis to recover HCl and Fe$_2$O$_3$. Such product would be suitable for the pigment and titanium metal industry (Habashi et al., 2015).

![Figure 12. Direct production of 95% TiO$_2$ from a low grade ilmenite [Magpei process]](image)

A pilot plant has confirmed this process. It is evident that the new leaching technology at ambient pressure is superior to the old electric furnace smelting - autoclave upgrading.

Sulfides

The leaching of sulfides with HCl is faster than leaching with sulfuric of the same normality, all other factors being the same (Figure 13) (Habashi & Toor, 1979; Mizoguchi & Habashi, 1981, 1983; Naito & Habashi, 1984). It is believed that chlorine is formed by the reaction (Kołodziej & Habashi, 1985):

$$2\text{HCl} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Cl}_2(\text{aq}) + \text{H}_2\text{O}$$

Aqueous chlorine is known to be a strong oxidant for sulfides that is why its formation would enhance the dissolution.

![Figure 13. Hydrochloric acid was found to be superior to H$_2$SO$_4$ in leaching sulfides](image)
Gold

Gold has usually been extracted from its ores by cyanide solution. Refractory gold ores are usually treated by different methods, e.g., bacteria, pressure leaching, roasting, etc., to liberate the gold then leach it by cyanide solution. It was found that when refractory gold ores are treated with HCl in an autoclave, gold goes into solution and after filtration it can be precipitated by reduction with charcoal (Habashi, 2009):

$$2\text{Au} + 8\text{HCl} + 1\frac{1}{2}\text{O}_2 \rightarrow 2\text{AuHCl}_4 + 3\text{H}_2\text{O}$$

(6)

$$\text{AuCl}_4^- \rightarrow \text{Au}^{3+} + 4\text{Cl}^-$$

(7)

$$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$$

(8)

$$\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$$

(9)

Overall reaction:

$$4\text{Au}^{3+} + 3\text{C} + 6\text{H}_2\text{O} \rightarrow 4\text{Au} + 3\text{CO}_2 + 12\text{H}^+$$

(10)

Scheelite

Scheelite, CaWO$_4$, is an important source of tungsten. It is decomposed by HCl [2]:

$$\text{CaWO}_4 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{WO}_3\cdot\text{H}_2\text{O}$$

(11)

Sulfuric acid cannot be used because of the formation of insoluble calcium sulfate. The digested mass is washed with water to remove iron and manganese chlorides, the residue is then dissolved in hot NH$_4$OH from which ammonium wolframate is crystallized by evaporation.

Apatite

Phosphate rock is composed mainly of fluorapatite, hydroxyapatite, and carbonato-apatite. Phosphate rock occurs either as a sedimentary deposit, e.g., in Florida and North Africa, or as igneous rock, e.g., in Kola peninsula, Russia. Sedimentary phosphates supply about 85% of the phosphate rock for the industry. Phosphate rock is used for the manufacture of fertilizers and elemental phosphorus.

When phosphate rock is treated with acids water-soluble monocalcium phosphate, citrate-soluble dicalcium phosphate, or phosphoric acid can be obtained. The first two can be used directly as a fertilizer, while the latter is neutralized with ammonia to produce an ammonium phosphate fertilizer. Hydrochloric acid is used sometimes to leach phosphate rock to produce either monocalcium phosphate fertilizer:

$$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 14\text{HCl} \rightarrow 3\text{Ca(H}_3\text{PO}_4)_2 + 7\text{CaCl}_2 + 2\text{HF}$$

(12)

or phosphoric acid:

$$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 20\text{HCl} \rightarrow 6\text{H}_3\text{PO}_4 + 10\text{CaCl}_2 + 2\text{HF}$$

(13)

Calcium chloride is then removed by crystallization and then precipitation as CaSO$_4$ by sulfuric acid whereby HCl is also recovered for leaching:

$$\text{CaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HCl} + \text{CaSO}_4$$

(14)

Phosphate rock of sedimentary origin contains on the average 0.01% uranium while igneous phosphate, contains about 1% lanthanide oxides. Acidic esters of phosphoric acid used alone or in combination with other organic phosphorus compounds are used for extracting these elements.
Production of dicalcium phosphate

Dicalcium phosphate, CaHPO$_4$, can be effectively produced at the mine location by in-situ, heap, or vat leaching using dilute HCl, and can be marketed as a citrate-soluble fertilizer or as animal feed containing 40% P$_2$O$_5$. The flowsheet of the proposed process is shown in Figure 14 [13]. Phosphate rock is leached with 10% HCl to produce a solution of monocalcium phosphate, Ca(H$_2$PO$_4$)$_2$. The solution is then crystallized to get the double salts CaClH$_2$PO$_4$·H$_2$O. The crystals are then separated from the mother liquor and decomposed at 200–250°C to get dicalcium phosphate product:

\[
CaClH_2PO_4 \cdot H_2O \rightarrow CaHPO_4 + HCl + H_2O
\]  

(15)

Figure 14. Proposed method for the production of dicalcium phosphate

In this operation, about 40% of the acid required for the leaching step is recovered for recycle and the remaining 60% can be regenerated by reaction of the mother liquor with H$_2$SO$_4$. If in situ leaching used, then the cost of beneficiation is eliminated.

The following points should be noted (Habashi, 2017):

- H$_2$SO$_4$ cannot be used in this technology because the formation of gypsum will prevent the percolation of the leach solution.
- Only dilute HCl can be used because more concentrated acid will result in the formation of H$_3$PO$_4$ in the upper layers of the bed which when it percolates downwards it will form dicalcium phosphate and thus prevent percolation:

\[
Ca_{10}(PO_4)_6F_2 + 4H_3PO_4 \rightarrow 10CaHPO_4 + 2HF
\]  

(16)

- Monocalcium phosphate solution can also be purified, then treated with ammonia to produce a mixture of dicalcium phosphate and ammonium phosphate:

\[
Ca(H_2PO_4)_2 + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4
\]  

(17)
Ca(H₂PO₄)₂ + 2NH₃ → CaHPO₄ + (NH₄)₂HPO₄  \hspace{1cm} (18)

**Silicates**

Hydrochloric acid has been proposed for leaching kaolinite and anorthosite and pilot plants have been operated to test such processes. Both minerals are lower in Al₂O₃ content than bauxite and both processes use sparging with HCl (Figure 15) to recover aluminum chloride hexahydrate which is then calcined to recover HCl and alumina:

\[
2\text{AlCl}_3\cdot6\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl} + 9\text{H}_2\text{O} \hspace{1cm} (19)
\]

Both processes produce silica as a byproduct while red mud from the Bayer process is a waste product that pollutes the environment. In spite of this advantage, it seems that these processes cannot compete with treating bauxite with NaOH when comparing the ease with which aluminum hydroxide is precipitated and calcined to alumina in the Bayer process and the ease in handling a noncorrosive reagent like NaOH.

![Figure 15. Solubility of AlCl₃.6H₂O in hydrochloric acid (Sawyer & Turner, 1985)](image)

**Kaolinite**

Kaolinite is the major component of clay and a potential source of alumina. It contains about 33–35% Al₂O₃, 45% SiO₂, and 13% H₂O while bauxite the actual source of alumina contains 55–60% Al₂O₃. Dilute acids are effective in solubilizing clay if the clay is first dehydroxylated. For example, to render kaolinite attacked by dilute acids, it is heated at 400–800°C to convert it to metakaolin:

\[
\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3\cdot2\text{SiO}_2 + 2\text{H}_2\text{O} \hspace{1cm} (20)
\]

Metakaolin which is an amorphous aluminum silicate can be leached with acid to extract aluminum selectively leaving behind crystalline SiO₂:

\[
\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 2\text{SiO}_2 + 3\text{H}_2\text{O} \hspace{1cm} (21)
\]

Researchers at the former US Bureau of Mines in 1985 [14], however, extracted alumina from un-calcined kaolinitic clay in 15 minutes by heating it at 200°C using 20–27% HCl:
\[
A_2O_2SiO_22H_2O + 6HCl \rightarrow 2AlCl_3 + 2SiO_2 + 5H_2O
\] (22)

The process is being developed further by Orbite Aluminae in Cap Chat, Quebec Province in Canada and an industrial plant is planned. Aluminum chloride hexahydrate is crystallized from solution by sparging with HCl gas, the crystals of AlCl_3·6H_2O are washed with 36% HCl to remove entrained mother liquor, dried, and decomposed to Al_2O_3:

\[
2AlCl_3·6H_2O \rightarrow Al_2O_3 + 6HCl + 9H_2O
\] (23)

while the mother liquor, mainly ferrous and ferric chloride in HCl, is decomposed at high temperature to recover Fe_2O_3 and HCl (Figure 16) (Boudreault et al., 2013).

Figure 16. Simplified Orbite process

Anorthosite

Anorthosite like clay is widely available and is a potential source of aluminum. In the United States, domestic resources were estimated at 600 billion tons containing about 30% Al_2O_3, 50% SiO_2, and 15% CaO. Anorthosite is a feldspar rock composed of variable amounts of albite (Na_2O·Al_2O_3·6SiO_2 or NaAl(Si_3O_8)) and anorthite (CaO·Al_2O_3·2SiO_2 or CaAl_2(Si_2O_8)). Anorthosite at the White Mountain deposit in Western Greenland was leached by HCl, filtration of insoluble residue, HCl sparging of clear solution to precipitate aluminum chloride hexahydrate, and calcination of the hexahydrate to regenerate HCl and produce alumina. Calcium silicate and amorphous silica in the residue are marketable by-products (Goode et al., 2016).

CONCLUSIONS

A review was given in the use of HCl in hydrometallurgy. The acid is useful for the purification of concentrates, for the treatment of certain complex oxides, for refractory gold ores, and for phosphates. It seems that the treatment of sulfides by HCl while faster than sulfuric acid yet it is not worth to change the technology because of that. On the other hand, the treatment of silicates to get alumina seems to be not economical in comparison with treatment of bauxite by NaOH. Among the reasons are the low tenor of aluminum in the silicates as compared with bauxite, the ease with which Al(OH)_3 is precipitated from NaOH as compared with the precipitation of aluminum chloride hexahydrate by HCl, and the calcination of Al(OH)_3 as compared with the calcination of aluminum chloride hexahydrate to get Al_2O_3. Add to this the corrosion problems and materials of construction issues, the treatment of silicates with HCl becomes even less attractive. More information is available in Proceedings of conferences on Chloride Hydrometallurgy are available (Winand, 1977, Parker, 1982, Peek & Van Weert, 2002).

REFERENCES


