

RECOVERY OF CHEMICALS FROM WASTE IRON SULFATE. A LABORATORY TEST OF THE PRODUCTION OF IRON CHLORIDE AND/OR ELECTROLYTIC IRON

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ABSTRACT

Waste iron sulfate is produced in titanium dioxide manufacture and in steel pickling with sulfuric acid. Many processes have been proposed to use this waste as a source of chemicals or raw materials. The process developed here is based on the reaction with pure or waste calcium chloride (Solvay brine) to obtain iron(II) chloride and gypsum as a by-product. The iron chloride solution can either be directly oxidized to iron(III) chloride by reaction with chlorine or electrolyzed to produce electrolytic iron and gaseous chlorine. The more interesting procedure is to electrolyze one-third of the iron(II) in solution and to oxidize the remainder with the chlorine obtained from the electrolysis.

INTRODUCTION

Iron(II) sulfate is a by-product of titanium dioxide manufacture (ilmenite plus sulfuric acid process) [1-3] and a waste product in steel cleaning by pickling with sulfuric acid. It also appears as a waste from some flue gas treatment processes [4] and slags [5].

The iron sulfate is obtained either dissolved in waste sulfuric acid or in the solid state as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ after crystallization from the acid liquors. The composition of such liquors is up to 300 g/l in iron(II) sulfate and in free sulfuric acid in the case of titanium dioxide manufacture, and up to 460 g/l and 90 g/l in iron(II) sulfate and in free sulfuric acid, respectively, in the case of steel cleaning.

Many technical, ecological, and environmental problems arise when waste iron sulfate (solid or waste solutions) must be discarded, due to the high solubility of iron sulfate in water (ca. 480 g/l) and high acidity of the waste solutions. It is necessary to dilute the waste solutions, or to neutralize the free acid by reaction with calcium salts (carbonates or hydroxide) before discharging the waste.

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Waste iron sulfate can be the source of iron (or iron oxides) and sulfur (or sulfur dioxide or trioxide). Table 1 lists previous reports concerning the recovery of chemicals from waste iron sulfate. Other uses as "substitute raw material" may be summarized as follows:

- (a) fertilizer in agriculture, particularly in vitaculture [25, 26];
- (b) chemicals in hydrometallurgy (leaching of manganese [27] or nickel ores [28] or foundry dusts with high Pb and Zn content [29]);
- (c) raw material in cement (setting modifier [30]) or additive to cement kiln crude mixtures [31], or activator for hydraulic binders;
- (d) anti-corrosion product [32];
- (e) chemicals for precipitation of FeS during water cooling of metallurgical slags; and

TABLE 1

Recovery of chemicals or raw-materials from waste iron sulfate [6]

Recovered chemical or raw-material	Process for recovery	Ref.
H_2SO_4	Recycling of waste pickling solutions after crystallization of solid $FeSO_4 \cdot 7H_2O$	[7]
$SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$	Thermal decomposition (in fluidised bed) + catalysis	[8-10]
H_2SO_4 + iron oxide + synthetic rutile	Chemical process	[11]
H_2SO_4 + Fe (metal)	Electrolysis	[12]
Fe (metal)	Thermal decomposition + reduction	[13]
Iron oxide for pigments and ferrites	Thermal decomposition or precipitation	[14-16]
Magnetite for siderurgy or painting	Air oxidation of waste solutions	[17]
Sodium sulfate for manufacture of glass and pharmaceuticals	Solution reaction	[18]
Magnesium sulfate or $MgSO_4$ + ammonium sulfate for fertilizers	Gas-liquid reaction	[19]
Ammonium sulfate + pigments	Precipitation and gas-liquid reaction	[20]
Calcium sulfate dihydrate (Titanogypsum) for building materials	Reaction with calcium salts	[21-24]
Iron chlorosulfate for waste water purification	Chloration	[2]
Iron(III) chloride + Fe(metal) + gypsum	Solution reaction + oxidation + electrolysis	This paper

(f) for waste water purification either alone or with lime [33–35], or after chlorination [2, 36].

It is well-known that the higher the valency of an ion, the better is its ability to flocculate waste water. So, iron(III) chloride is of more interest than say iron(II) sulfate for this purpose. Another interest of iron(III) chloride is the use of this salt as a reagent for leaching sulfide ores or as a chemical in the manufacture of printed circuits. Electrolytic iron is a source of pure iron.

LABORATORY TRIALS

The process developed on a laboratory scale was tested on a waste solid iron sulfate heptahydrate of composition shown in Table 2, and on an iron sulfate containing waste sulfuric acid liquor from titanium dioxide manufacture. The process developed is shown in the flowsheet depicted in Fig.1, and is based on the following reactions:



Both reactions (2) and (3), or only one of them, may be realized, as discussed below.

To carry out reaction (1), solid iron sulfate is mixed with water at ambient temperature with addition of a small quantity of hydrochloric acid to obtain a solution of about 1 to 1.6 M in iron sulfate at pH 2. To this solution is added, in stoichiometric quantity, an aqueous solution of calcium chloride. At 25°C, calcium sulfate dihydrate precipitates and a FeCl₂ solution (at about 2.5 g/l of CaSO₄ · 2H₂O) is obtained. Calcium sulfate is separated by filtration or by centrifugation and can be used as a raw material in gypsum

TABLE 2

Chemical composition of waste solid iron sulfate used as raw-material (titanium dioxide manufacture waste). This product is about 99% in FeSO₄ · 7H₂O

Element	Content	Element	Content
SO ₄	34–36%	SB	5 ppm
Fe	19–20%	SN	5 ppm
Mn	2500 ppm	Cu	3 ppm
Ti	1500 ppm	Pb	1 ppm
Zn	200 ppm	Mo	1 ppm
Co	30 ppm	Cd	0.2 ppm
Cr	20 ppm	As	0.1 ppm
Ni	20 ppm	Hg	0.01 ppm
V	10 ppm	hydration water	about 45%

plaster manufacture [23, 24], as an additive to portland cement [22], or discarded without particular difficulty.

Sulfuric acid-iron sulfate waste liquors can also be used for reaction (1). In the same way, the calcium chloride solution can be either reagent grade or waste by-product, such as from Solvay soda manufacture. Such a brine is about 0.96 M in CaCl_2 and 1.04 M in NaCl .

The FeCl_2 solution produced in (1), or the FeCl_3 produced in (2), or the water used for washing the precipitated gypsum, can be recycled for solubilization of the waste iron sulfate. The process requires make-up water for dissolving the waste iron sulfate and to wash the by-product gypsum.

Reaction (2) is carried out in a compartmented cell. One of the products is chlorine which can be used in reaction (3). However, small quantities of chlorine can be used to oxidize the FeCl_2 in the anodic compartment to yield FeCl_3 solution with a yield of nearly 100%.

In laboratory trials, graphite was used as the anode and an iron plate as the cathode. Electrolysis was realized at 85°C with a current density of 0.2 A/cm^2 . Under such conditions, the electrolytic yield was greater than 90%

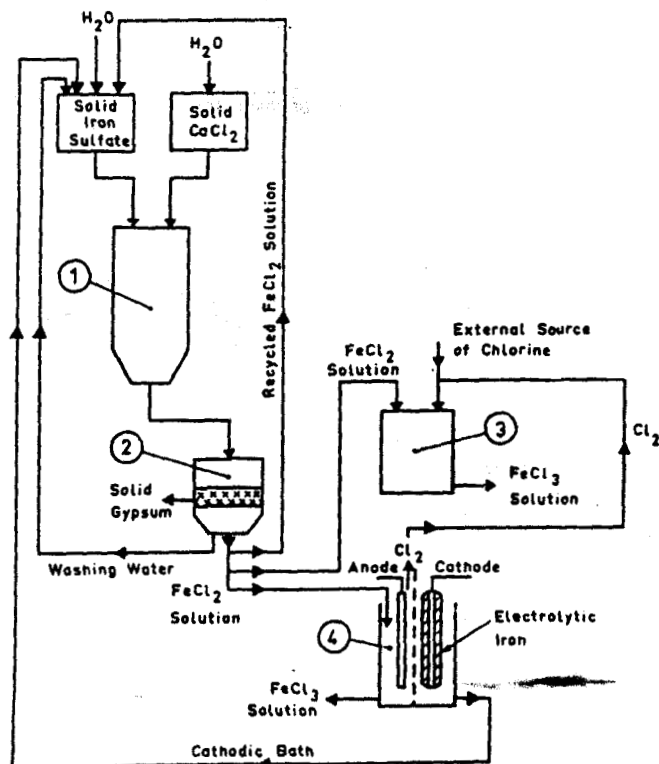


Fig. 1. Diagram of the process of transformation of waste iron sulfate into FeCl_2 solution and/or electrolytic iron. 1 — Crystallization reactor, 2 — Centrifugation or filtration, 3 — Oxidation reactor, 4 — electrolysis cell.

but diminished when the concentration of Fe^{2+} in the cathode compartment was lowered by a factor of two.

Reaction (3) can be conducted either using the chlorine produced in (2) or provided from other sources.

Laboratory tests pointed out that the order of mixing the two solutions for reaction (1) is not important. On the other hand, more interesting results are obtained when (1) is conducted not too far from stoichiometry and with reagent concentrations not more than from 1.0 to 1.6 M. Otherwise, some difficulties arise in calcium sulfate precipitation, such as formation of a pasty body during crystallization or setting of the precipitate, which lead to poor filtration and difficult handling.

Considering possible pollutants, as well as materials balances, it appears that the more practical process is to electrolyze one-third of the FeCl_2 solution and use the chlorine produced to oxidize the other two-thirds. Concentrations of iron(III) chloride obtained under such conditions are about 80 to 135 g/l, according to whether the starting calcium chloride was reagent grade or waste Solvay brine.

POSSIBILITIES FOR SCALE-UP

From a practical point of view, calculations can be made for predicting what may be obtained by treatment of say 100,000 Mg a year of waste solid iron sulfate heptahydrate, which represents the quantity of this waste produced by a mid-size titanium dioxide plant.

Recovery of only FeCl_3 solution

Use of pure CaCl_2 solution (1.6 M in CaCl_2) for reaction (1) produces 430,500 m³ of FeCl_3 solution (135 g/l in FeCl_3 and 31 g/l in NaCl). Use of Solvay brine (0.96 M in CaCl_2) produces 733,300 m³ of FeCl_3 solution (79.5 g/l in FeCl_3 and 31 g/l in NaCl). In both cases, from 333 to 366 m³ of water and 12,760 Mg of Cl_2 have to be furnished.

Recovery of electrolytic iron

Whatever the source of CaCl_2 , about 20,130 Mg of iron and 25,530 Mg of by-product Cl_2 are obtained.

Recovery of both FeCl_3 solution and electrolytic iron

The favored process is to electrolyze one-third of the FeCl_2 solution, as previously described, so consuming all of the by-product chlorine. Then with pure CaCl_2 solution (1.6 M), 6700 Mg of electrolytic iron and 286,660 m³ of FeCl_3 solution (135 g/l) are produced. With Solvay brine, 6700 Mg of electrolytic iron and 486,660 m³ of FeCl_3 solution (79.5 g/l in FeCl_3 and 31 g/l in NaCl) are produced.

Whatever the choice, the quantity of calcium sulfate dihydrate (gypsum) obtained is about 60,000 Mg of maximum purity when reaction (1) utilizes reagent grade calcium chloride, under stoichiometric conditions [23].

CONCLUSIONS

The main interest of the proposed process is to replace the discarding of waste with the possibility of production of useful chemical products. The proposed process is clean in that no important pollutant arises. The process requires a relatively small amount of energy inasmuch as all operations are carried out at low temperatures.

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