Mines Branch Information Circular IC 244

THE HYDROGEN SULPHIDE ROUTE TO SULPHUR RECOVERY FROM BASE METAL SULPHIDES

PART III: THE RECOVERY OF IRON PRODUCTS FROM FERROUS CHLORIDE SOLUTIONS

by

D.A. Reeve* and T.R. Ingraham**

ABSTRACT

A review has been made of the methods that may be used to recover hydrogen chloride and iron products from aqueous acidic solutions of ferrous chloride.

Simultaneous separate reviews have been made of means for recovering hydrogen sulphide from pyrrhotite and for converting hydrogen sulphide to elemental sulphur.

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Direction des mines

Circulaire d'information IC 244

RÉCUPÉRATION DU SOUFRE DES SULFURES DE MÉTAUX COMMUNS PAR LA VOIE DE L'ACIDE SULFHYDRIQUE

PARTIE III: RÉCUPÉRATION DES PRODUITS DE FER DES SOLUTIONS DE CHLORURE FERREUX

par

D.A. Reeve* and T.R. Ingraham**

RÉSUMÉ

Les auteurs ont étudié les méthodes qui peuvent servir à récupérer l'acide chlorhydrique et les produits de fer des solutions aqueuses acidiques de chlorure ferreux.

Ils ont également passé en revue les moyens de récupérer l'acide sulfhydrique de la pyrrhotine et de transformer l'acide sulfhydrique en soufre élémentaire.

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INTRODUCTION

In one of its aspects, the Mines Branch Environmental Improvement Program is concerned with the reduction of sulphur dioxide pollution of the air utilized for the combustion of fossil fuels and for the pyrometallurgical treatment of sulphide minerals. The Program at the present time involves a multi-faceted attack on the problems associated with both of these major sources of sulphur dioxide emissions.

In this three-report series on "The Hydrogen Sulphide Route to Sulphur Recovery from Base Metal Sulphides", an examination is made of the various steps that might be involved in recovering sulphur directly from sulphide minerals via the intermediate step of generating hydrogen sulphide. The hydrogen sulphide route was selected for study because of its inherent flexibility. Sulphur may be recovered directly from hydrogen sulphide by the Claus reaction, in which the H_2S is oxidized with precisely the stoichiometric amount of oxygen:

$$2H_2S + O_2 \rightleftharpoons 2H_2O + 2S \qquad [1]$$

Or, as an alternative, the H_2S may be used to reclaim the sulphur from the sulphur dioxide produced by pyrometallurgical methods of treating sulphide ores:

$$2H_2S + SO_2 \rightleftharpoons 2H_2O + 3S \qquad [2]$$

The technology for sulphur recovery from hydrogen sulphide is well established. The reactions are virtually quantitative and they are effective with both strong and dilute gas mixtures.

The inherent flexibility of the hydrogen sulphide route for producing sulphur is attractive at the present time when attempts are being made to reduce sulphur dioxide pollution levels.

In the first of this series of reports, the methods of generating hydrogen sulphide from sulphide ores were discussed. In the second report of the series, a detailed examination was made of the Claus reaction and the variety of its applications.

The present report, which is the third of the series, reviews the methods of recovering hydrogen chloride and an iron product from ferrous chloride solutions. The problems associated with HCl regeneration and ferrous chloride treatment are likely to occur whenever a base metal sulphide is treated with hydrogen chloride.

HYDROLYSIS OF FERROUS CHLORIDE IN THE SYSTEM $FeCl_{2(s)}-H_2O_{(g)}-O_2$

The recovery of iron oxide from an aqueous ferrous chloride solution is a two-stage process$^{(1)}$: Firstly, partial dehydration of the solution, and, secondly, hydrolysis of the residue to ferric oxide and hydrogen chloride. Because hydrolysis always accompanies the drying, it is difficult to prepare pure anhydrous ferrous chloride$^{(2)}$.

(a) Equilibrium and Kinetic Considerations

On the basis of equilibrium data, Wilska$^{(3)}$ suggested, for a practical process, the following:

(i) The amount of steam to be introduced into the system would be determined by the desired recovery of HCl and by the desired HCl concentration in the condensate.

(ii) When open-flame heating of the decomposition furnace is used, the amount of water vapour that must be introduced into the system will be determined by the moisture content and the available hydrogen in the fuel, and also by the water content of the ferrous chloride. The latter is the sole source of water vapour when indirect heating is used.

Ionin and Nikitina(4) studied the rate of hydrolysis of ferrous chloride in steam and air according to the equation:

$$2FeCl_2 + 2H_2O + 1/2O_2 \rightleftharpoons Fe_2O_3 + 4HCl \qquad [3]$$

They constructed a phase diagram (Figure 1) from the results of Kangro and Peterson(5) and of Stirnemann, reported in Schäfer's papers(6). The diagram shows that ferric oxychloride exists as an intermediate phase between Fe_2O_3 and $FeCl_3$ in the range of temperature from 94 to 528°C. The melting point of $FeCl_3$ is shown as 306°C. On the basis of their experiments and the work of Schäfer(6), they concluded that the sequence of steps in the oxidation and hydrolysis of $FeCl_2$ is as follows:

(i) Solid phase oxidation of $FeCl_2$:

$$2FeCl_2 + 1/2O_2 \rightleftharpoons FeOCl + 1/2Fe_2Cl_6, \qquad [4]$$

(ii) Vapour phase hydrolysis of FeOCl:

$$1/2Fe_2Cl_6 + H_2O \rightleftharpoons FeOCl + 2HCl, \qquad [5]$$

(iii) Solid phase hydrolysis of FeOCl:

$$2FeOCl + H_2O \rightleftharpoons Fe_2O_3 + 2HCl \qquad [6]$$

Ionin, Kozhakova and Nikitina(7) made the corresponding study in steam alone, according to the equation:

$$3FeCl_2 + 4H_2O \rightleftharpoons Fe_3O_4 + 6HCl + H_2 \qquad [7]$$

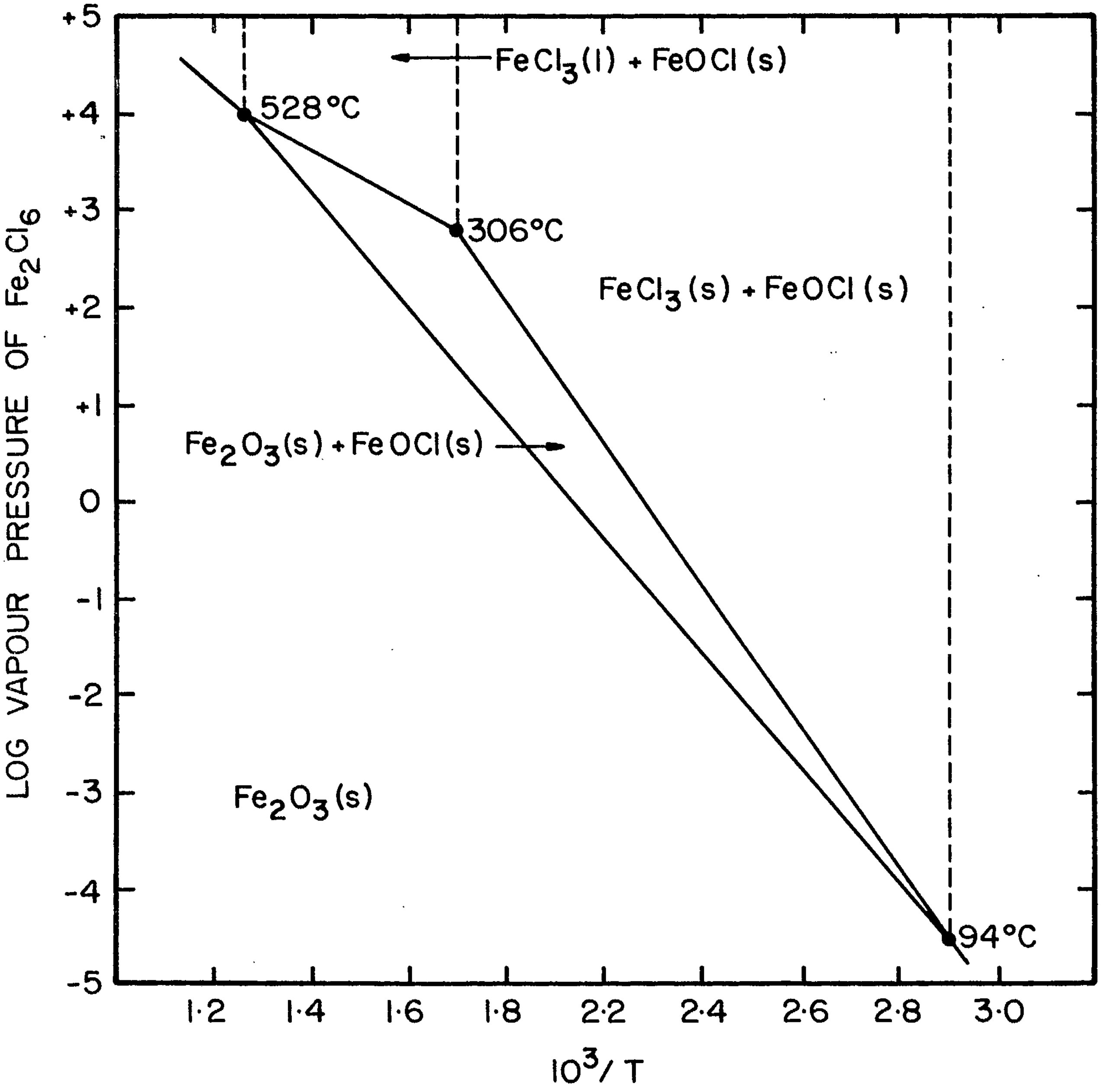

FIGURE 1: The effect of Fe_2Cl_6 pressure and temperature on the stability of phases in the Fe-O-Cl system for temperatures in the range from 94 to 528°C

The equilibrium conditions for this reaction are represented by the equation:

$$K_p = (p^6_{HCl} \cdot p_{H_2})/p^4_{H_2O} \qquad [8]$$

where K_p is the equilibrium constant for reaction [7] and represents partial pressures in atmospheres. Ionin, Kozhakova and Nikitina suggested that the equilibrium constant may be calculated from the following equation:

$$\log K_p = -16530/T + 5.25 \log T - 7.54 \times 10^{-3} T + 4.02 \qquad [9]$$

This equation was used to select temperatures between 450 and 650°C for a subsequent kinetic study of the hydrolysis. They reported that reaction [7] was very complex, and could be represented by the following stages:

(i) Hydrolysis with formation of solid FeO:

$$FeCl_2 + H_2O \rightleftharpoons FeO + 2HCl \qquad [10]$$

(ii) Oxidation of FeO to Fe_3O_4:

$$3FeO + H_2O \rightleftharpoons Fe_3O_4 + H_2 \qquad [11]$$

In both the papers by Ionin et al.(4,7), somewhat unconventional methods of data analysis were used. Because of this, their conclusions are difficult to substantiate. We have analyzed the published data of Ionin et al. by conventional methods and have drawn the following conclusions from their work:

(i) When $FeCl_2$ is hydrolyzed in steam and air, the rate of hydrolysis at the initiation of the reaction increases almost linearly with increasing percentages of air in the steam. After the particles are lightly covered with Fe_2O_3, the rate of hydrolysis then decreases almost linearly with increasing percentages of air in the steam.

(ii) In steam-air mixtures, the rate of hydrolysis of $FeCl_2$ is relatively slow at temperatures below the melting point of $FeCl_3$ (306°C). Above that temperature, the activation energy for the rate-controlling reaction is only 3 kcal/mole. This low value suggests that the rate control is probably vested in the rate of diffusion of either steam or hydrogen chloride across the Fe_2O_3 layer (Equation 3).

(iii) When $FeCl_2$ is hydrolyzed in steam alone, there are two processes that may exert control on the reaction rate simultaneously; a chemical reaction at the interface of the $FeCl_2$ and Fe_3O_4 (Equation 7), and the diffusion of steam across the Fe_3O_4 layer.

(iv) The activation energy for the chemical process established at a constant steam flow rate (36 litres/hour) is 17 ± 0.5 kcal/mole.

(v) The diffusion control is indicated by the linearity of a relationship between the reaction rate and the square root of the steam flow-rate.

(b) Patent Literature

As early as 1921, Tyrer(8,9) patented a method for the production of ferric oxide, suitable for use as a pigment, from ferrous chloride. The ferrous chloride was spread on the floor of a muffle furnace and air, moistened by passing through water at 60°C, was heated to 250-300°C and passed over it. Tyrer reported that the addition of small quantities of salts of copper, magnesium, tin, sodium and potassium had a catalytic effect on the hydrolysis reaction.

In a series of British and French patents in 1928(10,11,12) and in a U.S. patent in 1935(13), Levi and Gray proposed a chlorination method to recover sulphur and ferric oxide from iron-bearing sulphides. They pointed out that this method avoids the formation of sulphur dioxide. The ferric oxide and hydrogen chloride were obtained by heating the ferrous chloride to about 250°C with air or with a mixture of steam and air.

Also in 1928, a British patent by Wescott(14) described a method for decomposing ferrous chloride above its melting point (673°C) with preheated air or oxygen to produce ferric oxide. The ferrous chloride, in dispersed or vaporized form, was burned with air or oxygen at such a temperature (between 830 and 900°C) that a coarsely crystalline oxide was obtained.

In the nineteen 'thirties, Bacon and his co-workers(15-20) patented a chlorination method, similar to that of Levi and Gray described above, for the recovery of sulphur and ferrous chloride from iron-sulphide-bearing materials. The ferrous chloride was treated with steam and air at 440-600°C to produce hydrogen chloride and ferric oxide.

Heinrich(21) patented a process for the manufacture of metal oxides and HCl from metal chlorides and steam. A chloride layer of thickness less than 5 mm was heated for a time not exceeding that necessary for the reaction. This method was claimed to overcome difficulties caused by the vaporization of the chlorides or the formation of oxychlorides and other by-products. To obtain these reaction conditions, the use of a travelling-grate furnace or the outer surface of a rotary drum was suggested.

Both Dechêné(22) and Primavesi(23) suggested the use of superheated steam to hydrolyze ferrous chloride. Primavesi used superheated steam at a temperature of between 200 and 350°C; the final products were hydrogen chloride and ferrous oxide. Wilska(2), however, from theoretical considerations and experimental tests, stated that the temperatures recommended by Primavesi were too low to obtain a satisfactory yield. For the reaction:

$$FeCl_2 + H_2O \rightleftharpoons FeO + 2HCl, \qquad [10]$$

Wilska quoted values of the logarithm of the equilibrium constant ($\log K_p$) to be -8.8 at 200°C, and -5.3 at 350°C. Higher temperatures would thus be required for a successful process. These observations were borne out by the results of Ionin, Kozhakova, and Nikitina(7).

Wilska recommended that a method using both air and steam for the hydrolysis of ferrous chloride would be best in practice. As an example of such a process, that of Strelzoff(24) was mentioned. In this method, balls, about one inch in diameter and made from chrome-nickel alloy steel, were heated in a furnace to about 1000°C and delivered to a rotary kiln along with a concentrated solution of ferrous chloride, or crystalline hydrated ferrous chloride, and air or oxygen. The reaction, which took place between 300 and 650°C, formed ferric oxide, high-strength hydrochloric acid, and water. Wilska pointed out that the grinding effect of the rolling balls brought the gases into contact with the reacting solids and speeded up the reaction. The grinding also removed any oxide scale that would tend to slow down the reaction of the solids.

In a U.S. patent (1952), Loevenstein(25) stated that the decomposition of hydrated ferrous chloride to ferric oxide and dry hydrogen chloride gas can be effected by heating on a hot plate a thin layer of the chloride, dried previously at 120°C to the monohydrate form. Thus, Loevenstein claimed that the oxidation only began after all the chloride had been converted to the monohydrate, the last hydrate water molecule being consumed in the decomposition reaction. Wilska, however, discounted the experimental data presented in this patent as being "useless", because some necessary details had not been reported. Also, from his experiments, Wilska showed that, in contrast to the views of Loevenstein, all the hydrated water (or, at least, the reactive part of it) escaped before complete oxidation had occurred of a ferrous chloride hydrate having the stoichiometric composition $FeCl_2 \cdot 1.7H_2O$. Indeed, at 500°C, characteristic brown fumes of Fe_2Cl_6 began to form.

As well as experiments to discount the patented processes of Primavesi and Loevenstein, Wilska conducted experiments on the hydrolysis of ferrous chloride in a directly-heated rotary kiln. The reaction zone temperature was not monitored, but the temperature of the exit gas from the kiln was in the range 315 to 460°C. An energy balance for the decomposition was calculated, and it was concluded that, because the reaction enthalpy is only 0.5 kcal/mole(3), heat losses caused by radiation owing to the high reaction temperature were far more significant, from economic considerations, than the energy consumed in the actual decomposition reaction. Heat losses accounted for 77% of the total energy requirements.

Achille(26) patented a method for the recovery of iron oxides from iron sulphides by leaching with hydrochloric acid. The ferrous chloride produced in this method was evaporated, and the salt treated with steam or air or oxygen at 125°C to obtain hydrochloric acid and pure iron oxide, the hydrochloric acid being recycled. Ruthner(27) proposed a similar method for the treatment of HCl pickle liquors from the iron and steel industry.

In a process for the beneficiation of iron ores, patented by the United Steel Company, U.K.(28), a precipitate of $FeCl_2 \cdot 2H_2O$ was filtered dried, and hydrolyzed at 350°C in an atmosphere containing steam and air. Similar methods have been described by Weingaertner(29), who advocated hydrolysis of ferrous chloride with steam and air at a temperature between 200 and 400°C in a rotary kiln, and Remond(30), who recommended hydrolyzing ferrous chloride with steam between 500 and 900°C.

In a recent Japanese patent for the recovery of elemental sulphur from pyrite(31), ferric oxide was obtained by oxidizing ferrous chloride with air in the lower hearth of the roaster.

The patents described in this section for the treatment of hydrated ferrous chloride have established the widespread acceptance of the hydrolysis method for the production of ferric oxide and hydrochloric acid from ferrous chloride. It was not until the early nineteen 'sixties, however, when the use of hydrochloric acid began to gain acceptance over sulphuric acid for the pickling of steel strip, that a process became available commercially for the treatment of acidic ferrous chloride solutions.

(c) The Regeneration of Hydrochloric Acid from Pickling Solutions

When steel strip is being hot-rolled before cold-rolling or other forming processes, iron oxide scale forms on the surface. The simplest way of removing this scale is acid pickling. Sulphuric acid was always used as the pickling medium for steel strip because of its availability and cheapness, and because sulphuric acid pickling is amenable to control by rather crude instrumentation. It is, however, an expensive process, costing between \$3.50 and \$6.00 (U.S.)(32) per ton of steel pickled, depending upon equipment age and design. Disposal of waste pickle liquor containing iron sulphate is a serious problem, the usual method being lime neutralization in lagoons, and contract removal. Both of these operations cost about 2 cents per gallon of pickle liquor removed, and pickling one ton of steel with sulphuric acid can yield up to 40 gallons of waste liquor.

The use of hydrochloric acid as the pickling medium eliminates the problem of waste liquor disposal, the descaling rate of the steel strip is faster, and a smaller volume of acid is required (8 lb of hydrochloric acid achieves the same result as 40 lb of sulphuric acid).

Another major advantage of hydrochloric acid pickling over sulphuric is the production of a brighter steel surface which is more easily coated. This improvement is because of a basic difference in the chemistry of the pickling process with the two acids(34).

i. The Ruthner-Dravo Process(32-40)

In June 1964, the first plant in North America for the treatment of spent hydrochloric acid pickle liquors containing ferrous chloride came into operation at the Republic Steel Corporation plant in Gadsden, Alabama. The pickling process, installed at Gadsden, was introduced into the United States by the Dravo Corporation (Pittsburgh), who obtained North American and South American rights to the Austrian Ruthner process (Ruthner Elektrochemische-Metallurgische Industrienanlagen, Vienna). This patented process(41) consists of acid rinsing of the steel strip in a vertical tower, rather than in horizontal vats, followed by neutralizing and washing rinses (Figure 2).

A portion of the acid bath, usually containing about 13% by weight $FeCl_2$, 11% by weight HCl and the remainder water, is continuously withdrawn and fed to a spray roaster where ferrous chloride is hydrolyzed to ferric oxide and hydrogen chloride.

ii. The Nordac-Aman Process

The final stage in the Ruthner-Dravo Process, the spray-roasting of the acidic ferrous chloride solution, is the direct result of process developments from patents filed in Israel(42) and Great Britain(43) by the late J. Aman, and from

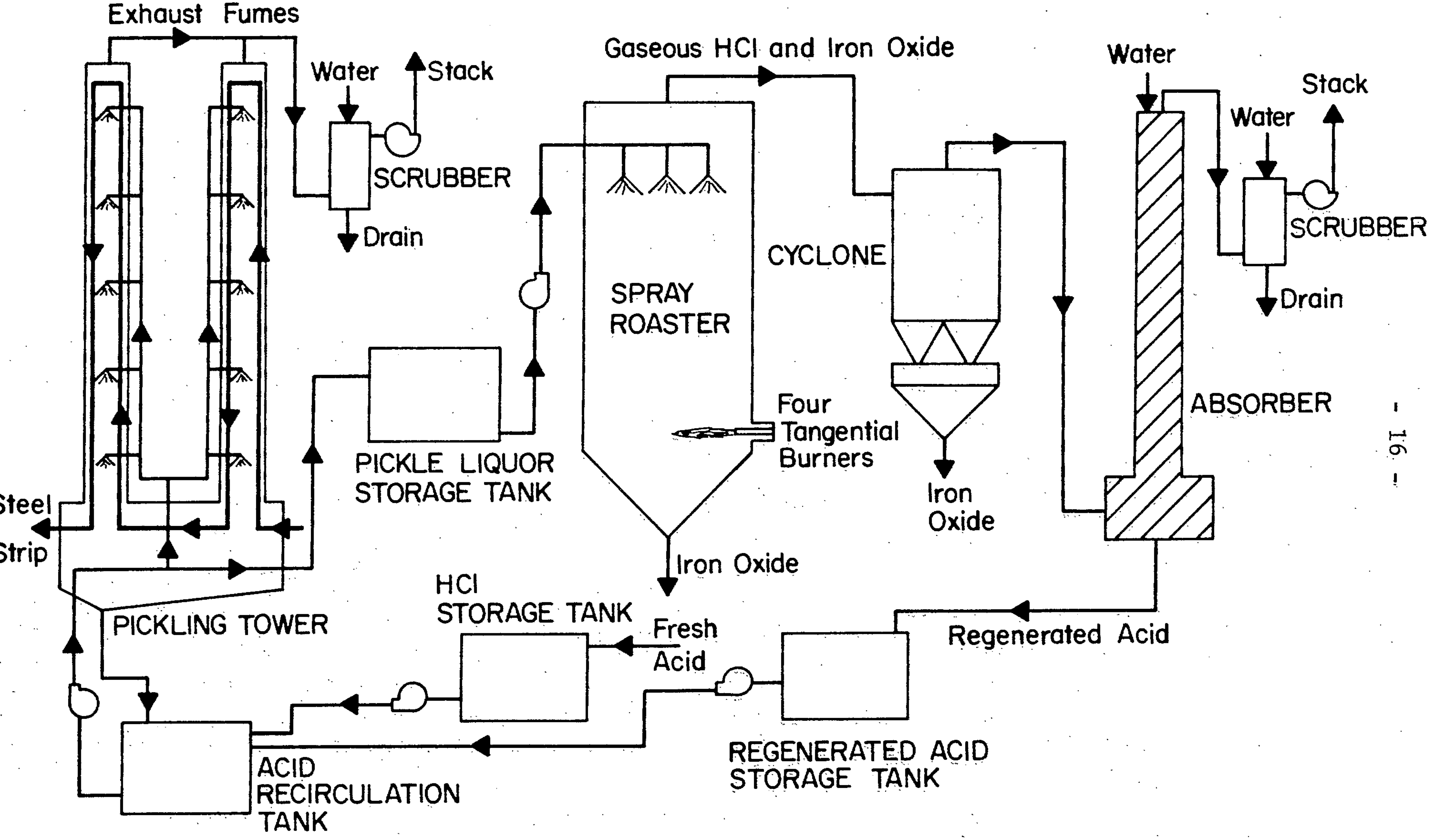

FIGURE 2: The Ruthner-Dravo Process (Flowsheet as used by the Steel Company of Canada, Hamilton, Ontario)

patents filed by the State of Israel(44,45). This fact is not acknowledged in the majority of the descriptions of the Ruthner-Dravo Process.

The spray-roasting process, developed by the Nordac Division of the Woodhall-Duckham Group in the United Kingdom, utilizes a counter-flow, gas-solids reactor, heated by gas-fired or oil-fired burners. Fused hydrates, or aqueous concentrated solutions of thermally decomposable metal chlorides or sulphates, such as $MgCl_2$, $CaCl_2$, $FeCl_2$, $FeCl_3$, $MgSO_4$, $FeSO_4$ and $Fe_2(SO_4)_3$, are atomized into the reactor. Hydrolysis to oxides and acids occurs at temperatures up to 1200°C in a stream of counter-currently flowing hot inert gas, water vapour, or their mixtures. The process is included in Figure 2.

When pickle liquor is sprayed into the roaster, ferrous chloride crystallizes. Water and free hydrochloric acid are quickly evaporated. As the ferrous chloride crystals descend inside the roaster, they encounter a rising temperature gradient and react with the superheated steam to produce iron oxide (mostly Fe_2O_3) and hydrogen chloride. The exothermic roasting reaction proceeds to completion as long as sufficient water and oxygen are present. These conditions normally prevail because of excess air in the combustion gas and water in the pickle liquor.

At the normal exit-gas temperature of between 300 and 400°C, hydrogen chloride is a dry, non-corrosive gas. Special reactor materials are not required, so long as care is taken to insure that metal temperatures are kept above the dewpoint of hydrogen chloride.

After removal of oxide fines in a cyclone, the hydrogen chloride in the roaster exit gases is recovered as hydrochloric acid in an absorption tower system. With a single adiabatic tower (packed column), the concentration of acid obtained from the bottom of the tower is usually about 20% by weight HCl and 80% by weight water; this concentration is close to the ideal represented by the azeotropic mixture. With a multi-tower system, a concentration of HCl of up to 36% by weight can be attained(46).

The roaster is lined with carbon brick, and four high-velocity burners are arranged tangentially just above the conical section. The use of titanium pump components and spray heads, polypropylene filter bags, polypropylene-lined steel pipe, and rubber-lined storage tanks facilitates the handling of hot hydrochloric acid under pressure. Fluorides must be rigorously excluded from the spray-roasting circuit, as these compounds have a disasterous effect on titanium components.

iii. The Stelco Process

At approximately the same time as the Dravo Corporation were introducing their process into North America, a hydrochloric acid recovery system was being developed by the Steel Company of Canada at Hamilton(47). The Stelco system, although making use of the same chemistry as the spray-roasting part of the Ruthner-Dravo Process, kept combustion products separated from reaction products.

Spent pickling solutions were flash-evaporated in air by dripping onto a heated, revolving steel surface. The residue from the flash evaporation was oxidized to ferric chloride, which then underwent a double-decomposition reaction with the superheated steam to produce ferric oxide and hydrogen chloride. These two sequential reactions, describing the mechanism for the thermal decomposition of the ferrous chloride residue, were represented by the equations:

$$FeCl_2 + HCl + 1/4O_2 \rightleftharpoons FeCl_3 + 1/2H_2O \qquad [12]$$

$$FeCl_3 + 3/2H_2O \rightleftharpoons 1/2Fe_2O_3 + 3HCl \qquad [13]$$

According to the patent on the process(48), this mechanism occurred only (i) when the rate of evaporation was controlled to give time for the completion of the double-decomposition reaction [12], and (ii) when the hot-plate temperature was maintained at 510 ± 8°C to prevent sublimation of the intermediate ferric chloride.

The Stelco Process operated on a pilot-plant scale over a 12-month period with only minor difficulties, but in 1965 the Steel Company of Canada installed the Ruthner-Dravo Process, at a cost of two million dollars, at their Hilton Works in Hamilton(49). The acid regeneration part of this plant consists of two duplicate spray-roasting units, each designed to process 21 gpm of pickle liquor containing 13% of ferrous chloride.

iv. The Lurgi Process

In August 1966, a plant for the regeneration of hydrochloric acid from ferrous-chloride-containing pickle liquors, developed by Lurgi Gesellschaft für Wärmetechnik GmbH., commenced operation in Germany(50). In the Lurgi method, acidic ferrous chloride solutions are hydrolyzed in a fluidized-bed reactor, rather than a spray roaster as used in the Ruthner-Dravo Process. The processing sequence is similar to the spray-roasting procedure, except that the Lurgi Process incorporates a pre-evaporator (Figure 3).

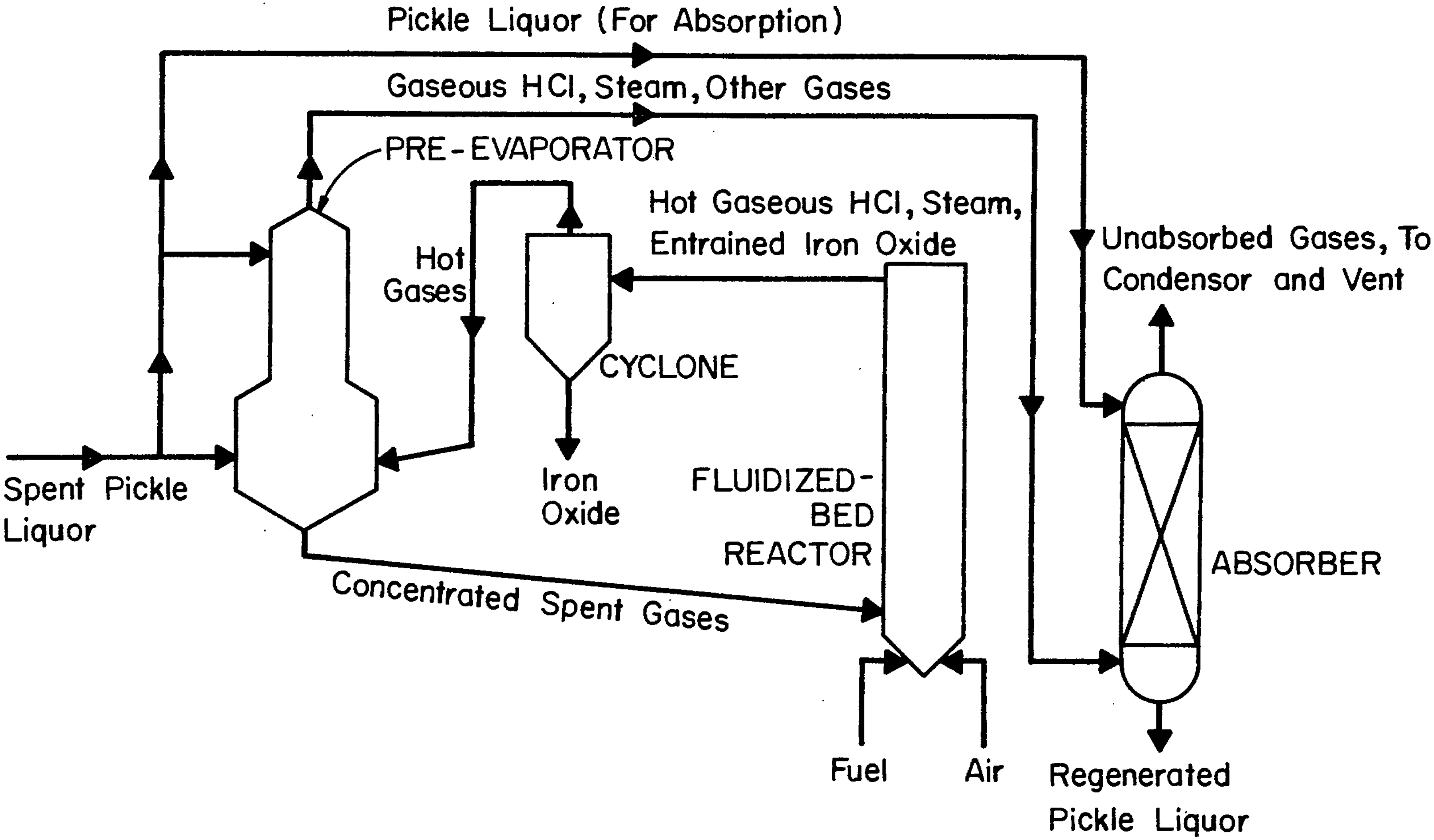

FIGURE 3: Lurgi Process for treating spent pickle liquor

The purpose of the pre-evaporator is to heat the ferrous-chloride-containing bleed stream from the pickling plant by direct contact with gases from the fluidized bed reactor, which is immediately downstream. Concentrated liquor from the pre-evaporator then enters the lower part of the reactor, at an acid concentration of 13% and a ferrous chloride level of 20%. The reactor, containing a fluidized bed of sand, is fired by oil or gas to maintain an operating temperature of about 800°C.

The Lurgi Company claims that the fluidized-bed process saves considerable space over the Ruthner-Dravo Process and is safer because nozzles are not required for spraying the acidic solution into the reactor. Greater operating flexibility is also claimed; the Lurgi plant is able to operate at as little as 10% of its capacity. In addition, the iron oxide by-product has a good bulk density and a very low chloride content.

v. The Turbulator Process

Haveg Industries, of Wilmington, Delaware, is marketing the Turbulator Process(51,52,53) (licensed by Dr. C. Otto and Company, GmbH., Bochum, Germany) for the treatment of pickle liquors having hydrochloric acid concentrations as low as 0.5%.

and as high as 11% by weight, with dissolved ferrous chloride concentrations as high as 35%. Eight turbulator regeneration plants have already been sold in Europe. The equipment includes four main units (Figure 4): a high-turbulence reactor, an air pre-heater, an electrostatic precipitator, and an acid absorption tower.

The chemistry of the Turbulator Process is the same as that of the Ruthner-Dravo and Lurgi Processes already described. As opposed to a spray roaster or a fluidized-bed reactor, the Turbulator Process employs a high-turbulence reactor which consists of four parts: a combustion chamber, a spin-generating chamber, a reaction chamber, and a spraying apparatus.

Fuel, which can be natural gas or light oil, is mixed with the proper amount of air to develop the desired temperature in the combustion chamber. The hot gases from the combustion chamber pass to the spin-generating chamber in which the gases are swirled into a spiral movement. As the spiralling gases pass upward into the reaction chamber, they are forced into a cyclonic, two-directional flow pattern which results in extremely high turbulence within the reaction chamber. Part of the gases leave at the top, while the remainder spirals downward to join the entering gas stream. High heat- and mass-transfer rates, which

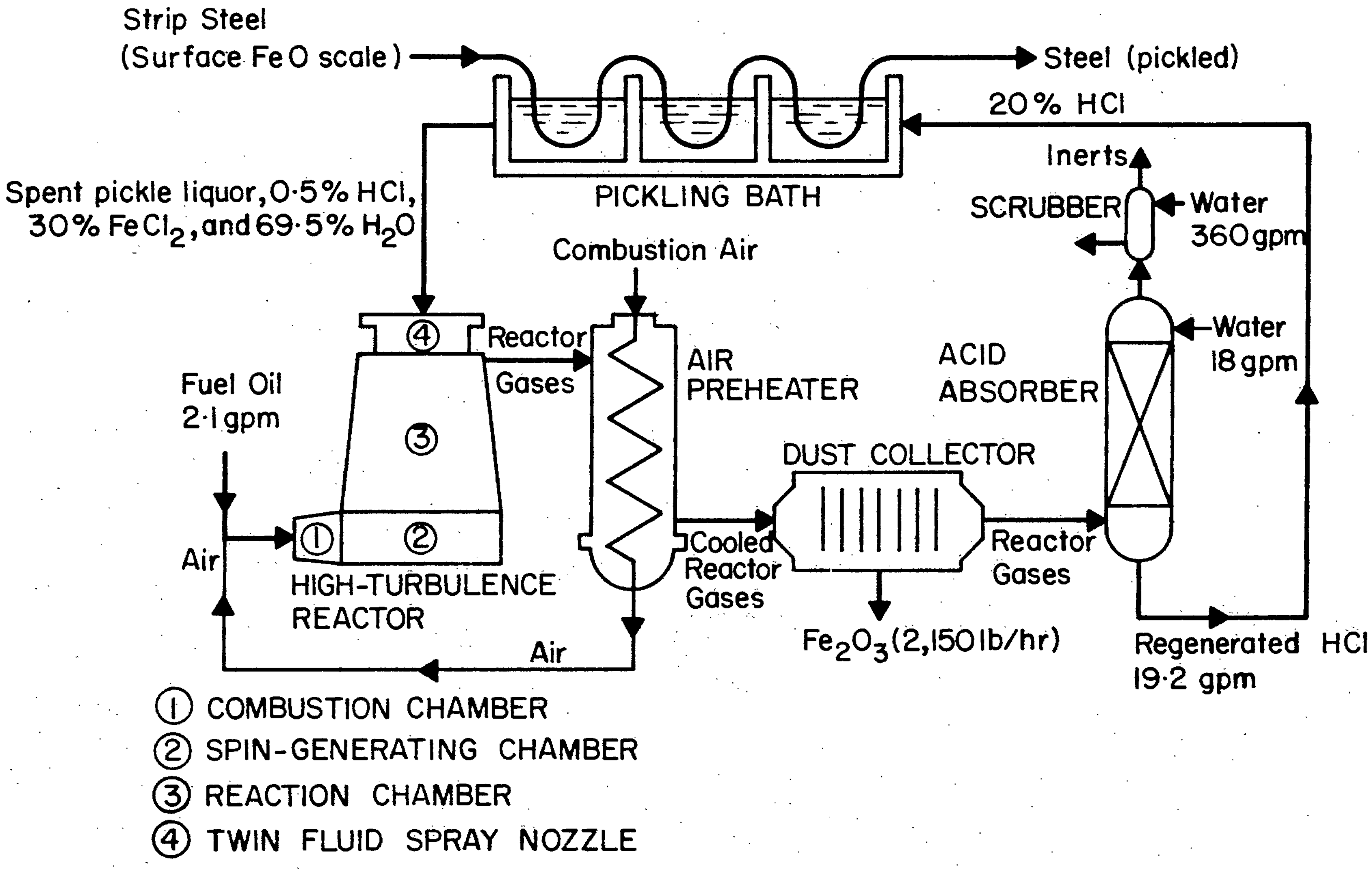

FIGURE 4: Turbulator Process (Haveg Industries, Wilmington, Delaware)

promote temperature uniformity throughout the reactor, occur in the zone of high shear where the oppositely flowing gases meet.

The pickle liquor that is sprayed into the top of the reaction chamber is rapidly vaporized by the upswirling gases and steam. The products of the reaction, which occurs at approximately 600°C, are swept out of the reaction chamber after a retention time of only one-fifth of a second. These hot gases pass to the air pre-heater which cools the reaction products to temperatures that will not cause the corrosion of the mild steel of the electrostatic precipitator.

Iron oxide particles in the 400°C gas stream are removed in the precipitator and an adiabatic absorption column allows for the production of 18 to 20% by weight hydrochloric acid. The unit depicted in Figure 4 processes 1000 gph of pickle liquor containing 30% ferrous chloride, and collects about 2150 lb ferric oxide in that time.

The advantages of the process are claimed to be: (i) a high reaction rate which results in small space requirements, (ii) a high operating flexibility which results in short start-up and shut-down times, and (iii) low maintainance requirements. Haveg Industries supplies ten different-sized systems, with acid recovery ranging from 60 to 2640 gph. The operating cost for a

Type 400 Turbulator Process (regenerating 1056 gph) is given as $0.027 (U.S.) per gallon of hydrochloric acid$^{(54)}$.

IRON RECOVERY BY HYDROGEN REDUCTION OF FERROUS CHLORIDE

a) Equilibrium Studies

Solid ferrous chloride may be reduced by hydrogen according to the following equation:

$$FeCl_{2\,(s)} + H_{2\,(g)} \rightleftharpoons Fe_{(s)} + 2HCl_{(g)} \qquad [14]$$

The equilibrium constant, $K_p = p^2_{HCl}/p_{H_2}$, has been calculated by Sano$^{(56)}$ from experiments done between 496 and 595°C in a gas circulation system. The equilibrium gas composition was determined by condensing the HCl in a liquid-nitrogen trap. Kangro and Peterson$^{(5)}$ used a static method with conventional chemical analysis to establish the partial pressures of H_2 and HCl between 484 and 662°C. In addition, Novikov et al.$^{(57)}$ also used a gas circulation system but analyzed the gas mixture by a thermal conductivity method. Rigg$^{(58)}$ examined all of the foregoing data and suggested that the relationship,

$$\log K_p = -7302/T + 6.29, \qquad [15]$$

would be the best expression for the equilibrium constant over the temperature range 425 to 645°C. We have re-examined all of the data and eliminated those of Sano(56) because, although they have generally the same slope as the others, they are displaced toward lower temperatures by about 30°C from the majority of the data points. We have included the unpublished data points of Govett as reported by Rigg(58) and concluded that the data are best represented by the equation:

$$\log K_p = -37.3168 + 13.0478 \log T - 2781.2/T \qquad [16]$$

The corresponding free energy expression is

$$\Delta G = 12{,}726 - 59.7041\, T \log T + 170.754T \qquad [17]$$

There is only a little scatter of the data points around the line represented by Equation 16 over the range of temperature from 400 to 672°C, the melting point of ferrous chloride.

Equation 16 was used to calculate the equilibrium constant for reaction [14], and also to calculate the equilibrium concentration of HCl that would be developed when a stream of H_2 at one atmosphere total pressure was equilibrated with solid $FeCl_2$. The values are of interest because they represent the maximum concentrations that could be developed in a practical experiment. The results are shown in Table 1.

TABLE 1

Calculations of the Equilibrium Constant and Equilibrium HCl Partial Pressures for The Hydrogen Reduction of $FeCl_2$

Temp. (°C)	K_p (atm)	Max HCl (%)
440	1.03×10^{-4}	1.01
460	1.88×10^{-4}	1.36
480	3.37×10^{-4}	1.82
500	5.91×10^{-4}	2.40
520	1.02×10^{-3}	3.14
540	1.72×10^{-3}	4.06
560	2.85×10^{-3}	5.19
580	4.64×10^{-3}	6.59
600	7.46×10^{-3}	8.27
620	1.18×10^{-2}	10.30
640	1.85×10^{-2}	12.70
660	2.85×10^{-2}	15.51
673	(MELTING POINT)	17.4

From Table 1, it is evident that even at the melting point the gas stream would still carry about 82.6% unreacted hydrogen. A minimum of six recirculations of the hydrogen would probably be required to consume it, even under ideal conditions.

Gravenor, Govett and Rigg(54) have also presented theoretical data for the equilibrium concentrations of HCl that would be developed at a total pressure of one atmosphere by reaction [12]. Their values agree closely with those presented in Table 1.

Schäfer and Krehl(59) calculated the heat and entropy of vaporization at 847°C to be 31.0 kcal/mole and 23.9 e.u., respectively. These authors expressed the temperature dependence of the equilibrium constant for reaction [14] between 932 and 1100°C by:

$$\log K_p = -675/T + 0.20 \qquad [18]$$

At 1016°C, the heat of reaction was estimated to be 3.09 kcal/mole and the reaction entropy 0.91 e.u. The entropy of $FeCl_{2\,(g)}$ was estimated as 89.0 e.u.

Solid ferrous chloride has an appreciable vapour pressure at temperatures near its melting point. The data of Kubaschewski, Evans and Alcock(60) were used to calculate the vapour pressure of the monomer over both solid and liquid $FeCl_2$.

The data for the liquid range were extrapolated into the solid range and the validity of the extrapolation checked against calculations done by Schoonmaker and Porter(61) from their work in a mass spectrometer and the work of Sime and Gregory(62) by the torsion effusion method. The work of Sime and Gregory is in agreement within 4.5 Torr at the melting point while that of Schoonmaker and Porter(61) agrees within 4 Torr. The predicted data are shown in Table 2.

TABLE 2

Calculated Vapour Pressures for Solid and Liquid Ferrous Chloride

Temp. (°C)	Pressure (mm)	Temp. (°C)	Pressure (mm)
550	0.59	700	14.64
600	1.97	750	33.71
650	5.73	800	70.95
673 (mp)	8.50	850	138.24

From the data in Table 2, it is evident that the sublimation of $FeCl_2$ is a substantial possibility at temperatures approaching its melting point. Regis(63) reports growing acicular, hairlike crystals (trichites) of iron by the hydrogen reduction of $FeCl_2$ at temperatures between 600 and 700°C. From his observations of the curvature of the trichites, he concluded that they grow at the base rather than at the tip.

b) Kinetic Studies

Because of their interest in producing metallic iron from $FeCl_2$ by hydrogen reduction, Rigg(58,64,65) and Yannopoulos and Themelis(66) have made extensive studies of the factors that control the rate of the reduction reaction. Despite his three publications on the subject, Rigg(65) concluded recently that there was not yet sufficient information available to design an industrial packed-bed reactor. When all four of his publications are studied, it is evident that there are at least three processes that can control the rate of the reduction. These are:

i. Heat transfer.

ii. The nature of the chemical process in the interface on the surface of the solid $FeCl_2$.

iii. Mass transfer by the sublimation of $FeCl_2$.

It is our impression that control of the rate of the reduction reaction passes successively from one to the other of these processes as the temperature is increased. Our reasons for the conclusions will be developed in the following paragraphs.

i. Heat Transfer

The hydrogen reduction of ferrous chloride is an endothermic reaction. At 550°C, the estimated heat of reaction is 35.4 kcal/mole(58). Because of this substantial heat requirement, and the fact that the heat is required below the temperatures at which radiant heat transfer is significant, pellets of $FeCl_2$ undergo a sharp cooling as the reduction is initiated at low temperatures. This has been clearly demonstrated by Yannopoulos and Themelis(66) who installed small thermocouples within their 1-cm-diameter pellets. Their patterns of temperature decrease are particularly interesting. For a run begun at 610°C, there is a gradual decrease in temperature to about 585°C, followed by a rapid recovery at the end of the reaction. In a run at 640°C, the pellet temperature decreased within the first half minute to 615°C and thereafter recovered slowly. When the run was initiated at 660°C, there was a rapid initial decrease, followed by a rapid recovery as the run progressed. These results demonstrate that at low temperatures, even when the reaction rate is small, the transfer of heat by conduction is so slow that the reaction temperature remains substantially below that of the surroundings for most of the reaction period. Alternatively, at higher temperatures, where the reaction rate is rapid and the necessity for the rapid input of heat is correspondingly greater, the heat is transferred rapidly because of the effects of radiant heat transfer. This behaviour of changing rate with recovery of temperature is shown clearly in Fig. 2 of the 1966 paper by Rigg(64). Although he has chosen to represent the data by a straight line, we believe that they are more accurately represented by two curves that are concave against the time axis. The first rises rapidly and then decreases in the first fifteen minutes; the second rises slowly and then becomes almost linear from twenty minutes until the completion of the reaction. This interpretation of the data is in agreement with the observations of Yannopoulos and Themelis(66) of sharp temperature changes in the same range of temperature.

ii. The Nature of the Chemical Process in the Interface

The data of Rigg(58,64,65) and of Yannopoulos and Themelis(66) show that, in the range of temperature between about

450 and 625°C, barring complications introduced by heat transfer in thick specimens, the reaction interface between the ferrous chloride and the metallic iron moves at a constant rate at a constant temperature. Both sets of experimental work also agree that the reaction rate is proportional to the fraction of the equilibrium pressure of hydrogen chloride that exists at the pellet interface. On the basis of kinetic arguments, one might expect that the rate would be proportional to the square of the hydrogen chloride partial pressure. The fact that the first, rather than the second, power of the HCl concentration is involved may indicate that, kinetically, the following is the more correct representation of the reaction:

$$1/2\ FeCl_2 + H \rightleftharpoons 1/2\ Fe + HCl \qquad [19]$$

The application of Equation 19 to the interface process is supported by earlier experiments of Rigg(58) in which he varied the partial pressure of hydrogen in the gas stream. He found that the reaction rate varied with the square-root of the partial pressure of hydrogen. The acceptance of reaction [19] would imply involvement of dissociated hydrogen, such as would be available from an adsorbed layer of hydrogen on $FeCl_2$.

As a general principle, the activation energies for many heterogeneous reactions can be estimated from the heats of reaction(67). It is not at all unusual for the experimental value to be within ± 1 kcal/mole of the heat of the applicable reaction. In this instance, it would be one-half of the 35.4 kcal reported for the reaction that produces two moles of HCl. That value of 17.7 is in the exact centre of the range of 15.5-19.9 that was suggested by Rigg(58,64,65). It adds further supporting evidence for the contention that the primary reduction process is controlled by a chemical reaction in the interface.

No reasonable explanation has been devised to explain the difference in the activation energy of 17.7 ± 2 kcal/mole reported by Rigg and the value of 27.5 kcal/mole reported by Yannopoulos and Themelis(66). The experimental techniques seem essentially similar. Rigg's suggestion of attributing the difference to an observed induction period does not seem reasonable. The source of the induction period may be traced, according to our earlier arguments, to the strongly endothermic nature of the reaction. The difference may be attributed to the fact that while Yannopoulos and Themelis(66) used carefully dried $FeCl_2$ in their experiments, Rigg appears to have used partly hydrated $FeCl_2$.

iii. Mass Transfer by the Sublimation of $FeCl_2$

In the discussion following Table 2, the sublimation pressures of $FeCl_2$ at temperatures near its melting point were discussed. Pressures of the order of 10 mm are sufficient for profitable metal distillation(68), and a pressure of 8.5 mm of $FeCl_2$ is reached at its melting point. It would therefore be expected that in the higher temperature region the mechanism and rate control of the $FeCl_2$ reduction reaction would involve a gas phase reduction:

$$FeCl_{2\,(g)} + H_{2\,(g)} \rightleftharpoons Fe_{(s)} + 2HCl_{(g)} \qquad [20]$$

Rigg(64) has, in fact, noted the growth of Fe whiskers within his pellets and attributed them to a gas phase transport of $FeCl_2$. The nature of trichite growth from $FeCl_2$ vapour was discussed earlier in this report.

(c) Patent Literature

As early as 1844, Peligot(69) produced high-purity iron by the reduction of ferrous chloride with hydrogen. In 1941, Meissner(70) investigated the production of iron by chlorinating iron oxides with hydrogen chloride and reducing the ferrous chloride crystals in hydrogen. Yannopoulos and Themelis(66) note that Meissner's reduction tests apparently were conducted under conditions of an inadequate hydrogen supply that caused lengthy reduction times.

Several patents concerned with the hydrogen reduction of ferrous chloride for the production of iron powder were credited to the Republic Steel Corporation in the nineteen 'fifties. Graham and Beidler(71) selectively reduced ferrous chloride to iron by reducing with hydrogen at 500-625°C. Crowley, Graham and Beidler(72) reduced gaseous ferrous chloride with hydrogen in a two-stage reaction zone, one part of which was at a temperature less than the boiling point of ferrous chloride (1030°C) and the other part was above the boiling point. Darver and Walters(73) reduced ferrous chloride in liquid form to elemental iron. Molten ferrous chloride was introduced into a chamber containing hydrogen and atomized. An annular stream of nitrogen was also introduced into the chamber to prevent premature contact between the hydrogen and liquid ferrous chloride before atomization of the ferrous chloride. In a patent by Whitehouse and Beidler(74), the production of iron and hydrogen chloride from ferrous chloride vapour and hydrogen was achieved by introducing the hydrogen at 150-200°C (540°C maximum) and the ferrous chloride at 980-1100°C into the reducing zone of the furnace. The reaction was controlled at a temperature of about 680°C.

At the United Steel Company, U.K.(75), ferric chloride, obtained by treating low-grade iron ore with hydrogen chloride, was reduced by hydrogen in two stages using a fluidized-bed technique. Reduction in the first stage was to ferrous chloride at 300-500°C, and, in the second stage, to iron at 500-800°C.

Achille(76) reduced dry ferrous chloride, obtained from the reaction of pyrrhotite and hydrochloric acid, with hydrogen at 650°C.

(d) The Peace River Process

The most promising application of the hydrogen reduction method is a Canadian process developed by the Peace River Mining and Smelting Company, of Edmonton, together with the Research Council of Alberta. This process was to be applied to the production of iron powder from a deposit of sedimentary oolitic iron ore located in the Swift Creek area of the Clear Hills, Northwestern Alberta(54,55). Attempts to physically beneficiate this ore for blast-furnace treatment were unsuccessful, but direct reduction of the ore by the R-N Process, carried out on a pilot-plant scale by the R-N Corporation in Birmingham, Alabama(77), produced a sponge iron suitable for electric furnace smelting.

It was considered uneconomic, however, to establish an iron industry in Alberta based on the direct reduction process, but circumstances favoured a hydrometallurgical method. Such a method was developed and patented(78-84) by the Alberta Research Council. This process, known as the Peace River Process, was later adapted for the production of iron powder from iron scrap(1,85,86,87). A commercial plant, to produce 50,000 tons per year of iron powder from steel turnings from the automotive industry, has been installed by Great Lakes Forgings Limited, a subsidiary of the Peace River Mining and Smelting Company, at Anderdon, near Windsor, Ontario.

The first step in the Peace River Process (Figure 5) is the dissolution of scrap iron in hot acid containing 20 to 25% by weight of hydrogen chloride. The reaction

$$Fe + 2HCl \rightleftharpoons FeCl_2 + H_2 \qquad [21]$$

takes place at 90°C and at atmospheric pressure. The ferrous chloride solution, containing from 3 and 5% residual acid, is pumped to a rotary-drum filter that removes insoluble impurities.

The filtered leach liquor is heated in a double-effect evaporator until the solution is saturated with respect to the tetrahydrate of ferrous chloride. The saturated solution is then

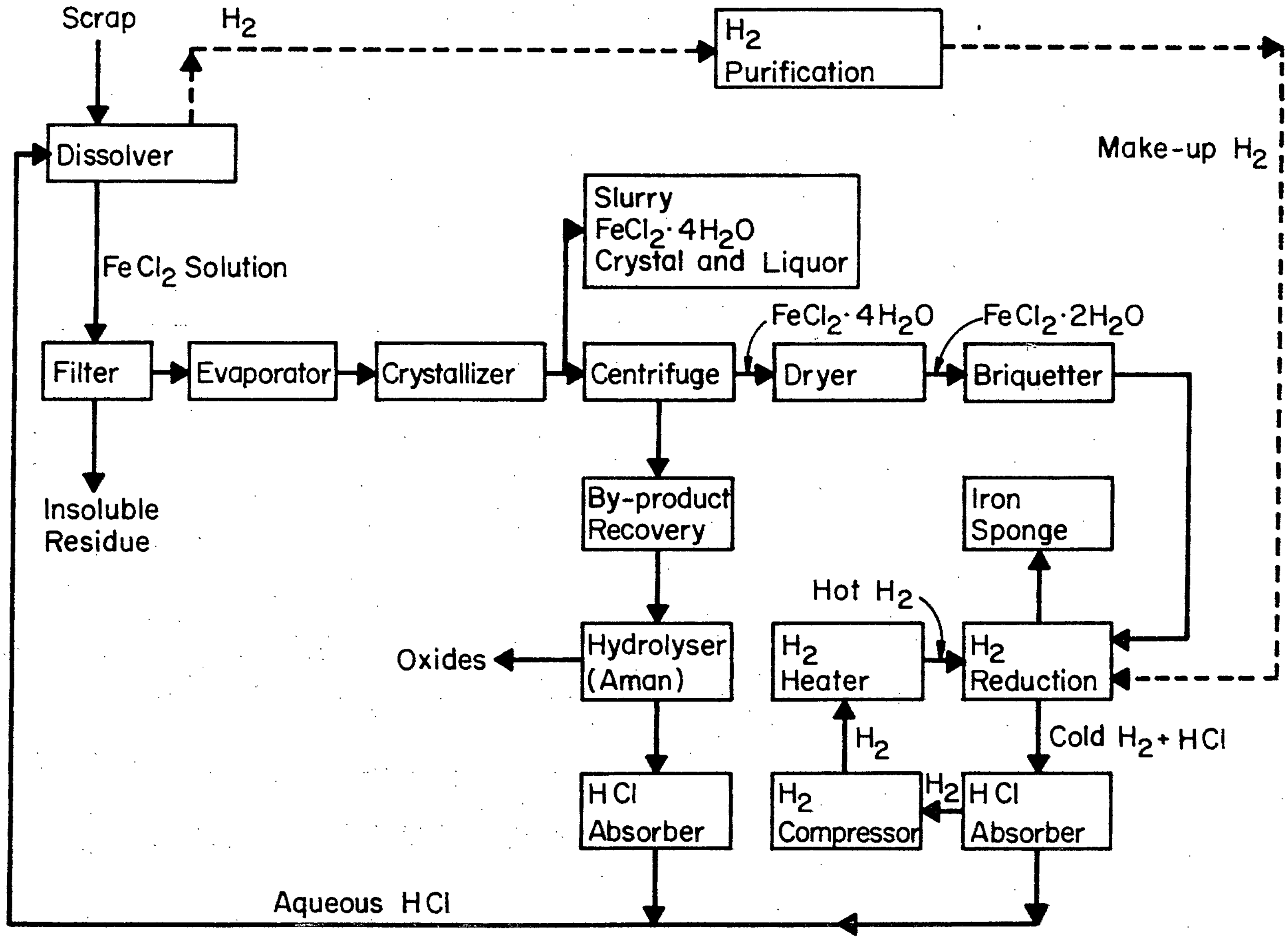

FIGURE 5: Peace River Process for the recovery of sponge iron from scrap

fed into a vacuum crystallizer, where $FeCl_2 \cdot 4H_2O$ crystals form. These crystals are separated from the mother liquor in a centrifuge, and the mother liquor is returned to the vacuum crystallizer. The supernatant liquor from the centrifuge, which contains soluble impurities such as metal chlorides, is sent to a Nordac-Aman spray roaster.

Rubber-lined steel is used in the construction of the equipment described above for handling acid ferrous chloride solutions(86). Piping is made from glass-fibre-reinforced plastic, and either silica iron or graphite is used for the internal parts of pumps. The centrifuge basket is made of titanium wire screen.

The ferrous chloride tetrahydrate crystals from the centrifuge are flash-dried in a Raymond dryer to the dihydrate so that a free-flowing solid is obtained for briquetting prior to the hydrogen reduction. Care has to be taken at this stage not to initiate any hydrolysis, otherwise the material becomes difficult to handle. Hydrolysis can be prevented by drying in the presence of hydrogen or hydrogen chloride.

In the final stage of the Peace River Process, the briquetted ferrous chloride dihydrate is reduced with hydrogen. For this reaction, the value of the equilibrium constant increases with temperature. Thus, if the temperature in the flash dryer (with an atmosphere of hydrogen) is less than in the hydrogen reduction reactor, ferrous chloride will not be reduced in the dryer if gas pressures are suitably controlled.

The reduction is done at temperatures between 600 and 800°C; the heat needed for the reaction is about 35.4 kcal/mole(58), and an additional 23 kcal/mole are required to preheat the feed and evaporate residual water(86). At the melting point of ferrous chloride the gas equilibrium is 17.4% HCl (Table 1), but in practice, only about 10% of the gas leaving the reactor is hydrogen chloride(54). Consequently, it is necessary to recycle hydrogen after absorption of hydrogen chloride.

The hydrogen reduction step is a batch process, taking place inside fixed-bed reactors. Although fluid-bed conditions would be more desirable than fixed-bed, the iron agglomerates at temperatures near 600°C, and a fluidized bed tends to defluidize. After reduction, the sponge-iron briquettes are cooled and broken in a hammer mill. Initially, it was found that after hammer milling, the product contained too high a proportion of fines. However, by seeding the ferrous chloride from the drier with previously-reduced iron powder, aggregrates of powder particles were grown within the sponge. After hammer milling, the comminuted material was found to be suitable for a moulding-grade powder(84).

By changing the amount and particle size of seeding iron powder, and by varying the screen openings of the hammer mill, a variety of iron powders can be produced. They vary in apparent density from 1.8 to 3.3 g/cm^3 (87).

IRON RECOVERY BY ELECTROLYSIS OF FERROUS CHLORIDE SOLUTIONS

In contrast to hydrogen reduction of ferrous chloride, or oxidation with air and steam, few attempts have been made to treat ferrous chloride solutions by electrolysis.

In 1928, Levy and Grey(88,89) recovered iron from a concentrated solution of ferrous chloride at 90-100°C in an electrolytic cell, using a carbon anode surrounded by a solution of sodium chloride, or calcium chloride, or magnesium chloride. A current density of 1.6-4.0/amp/cm^2 was used. British Titan Products(90) recovered iron and chlorine from spent pickle liquors by a method similar to that of Levy and Gray; the anolyte in the electrolytic cell was calcium chloride and a ferrous chloride solution was used as the catholyte.

Sanvordenkar and Tendolkar(91) obtained iron powder by electrodeposition from a ferrous chloride bath. The operating variables were: concentration of ferrous chloride, 25-60 g/l;

pH, 3-5.5; current density, 0.8-1.6 amp/cm^2; and temperature, 20-45°C. The optimum $FeCl_2$ concentration was about 30-35 g/l; a lower concentration gave a spongy powder, while higher concentrations gave a mixture of coherent and loose powder.

In a Russian patent, Shafershtein et al.(92) used an electrolyte consisting of a mixture of ferrous and sodium chlorides in the ratio 6:1. Conditions for electrolysis were: pH, 4-5; current density, 2 amp/cm^2; and temperature, 18-20°C. Tsyganov and Ganiev(93) studied the effects of electrolyte acidity, current density, and temperature on the yields of iron and hydrogen from an electrolyte containing 400 g/l ferrous chloride tetrahydrate and 200 g/l sodium chloride. An increase in acidity of the electrolyte and in current density led to lower iron and higher hydrogen yields, whereas an increase in the temperature of the electrolyte increased the yield of iron but decreased the yield of hydrogen. At a constant current density of 0.01 amp/cm^2 and temperature of 18°C, evolution of hydrogen increased with increasing acidity of electrolyte (corresponding to a drop in pH from 1.87 to 1.10).

SUMMARY AND CONCLUSIONS

The recovery of iron products from ferrous chloride solutions is a two-stage process: (i) the removal of water, and (ii) either hydrolysis or hydrogen reduction of the anhydrous ferrous chloride.

Both hydrolysis and hydrogen reduction of anhydrous ferrous chloride are utilized as the basis of industrial processes. For economic reasons, the electrolysis of ferrous chloride solutions has not been considered for large-scale operations.

The chemistry of the Ruthner-Dravo Process for the hydrochloric acid pickling of steel strip is based on the hydrolysis of ferrous chloride. This process is gaining wide acceptance by the United States steel industry; in 1965, the Steel Company of Canada installed a Ruthner-Dravo pickling plant at Hamilton(49). The Lurgi Process and the Turbulator Process, both of which operate on the same chemical principles as are used in the acid regeneration unit of the Ruthner-Dravo Process, are already in operation in Europe. They have yet to be introduced into North America, probably because the Ruthner-Dravo Process was established and proved before the Lurgi and Turbulator Processes became available.

The ferric oxide recovered from the Ruthner-Dravo Process has a fine consistency, somewhat similar to jeweller's rouge. It has been sold in small quantities at about $55 (Canadian) per ton(94) to ferrite manufacturers, after purification by leaching to remove about 1% of unoxidized ferrous chloride.

These three processes, designed for the regeneration of hydrochloric acid from spent pickle liquors, could be integrated into a base-metal leaching operation. The ferric oxide recovered from such an operation would have a value of about $8 per ton as powder, or $11 per ton as pellets. The inclusion of a reduction step in the process after pelletizing would permit an increase in the price to approximately $150 per ton of iron(94).

The Peace River Process for the hydrogen reduction of anhydrous ferrous chloride is the alternative to these three methods. The evaporating, crystallizing, centrifuging, drying and briquetting stages of this process (Figure 5) necessarily must result in greater costs for installation and operation for it as compared with a spray-roasting type of installation. On the other hand, the primary product from the hydrogen reduction process is a non-pyrophoric iron powder, suitable for powder metallurgy. This iron powder would command an even higher price than would the iron obtained from the hydrogen reduction of the ferric oxide produced in the thermal decomposition method. It is also of interest to note that the ferric oxide produced by the spray roasting (Aman hydrolysis, Figure 5) of supernatent liquor from the centrifuge in the Peace River Process is classed merely as solid waste(83).

In conclusion, the chemical engineering principles of both methods of treating acidic ferrous chloride solutions have been developed from pilot-plant to full-scale successful operation. Just recently, vapour-liquid equilibrium data relating to the recovery of HCl from $FeCl_2$ solutions have been published(95). A spray-roasting type of process would require less capital cost to install than the more complex hydrogen reduction process, but the latter process produces an iron powder which has more than fifteen times the value of the ferric oxide product from the former. Incorporation of either of these processes into a hydrochloric-acid-leach circuit for treating base-metal concentrates would be technologically feasible and, in fact, the Peace River Process was developed originally to treat an Albertan oolitic iron ore that was found to be amenable to hydrochloric acid leaching after a reducing-roast step.

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