STUDIES ON FEASIBILITY OF HYDROCHLORIC ACID RECYCLE AND IRON-II-CHLORIDE RECOVERY IN PICKLING OPERATION IN STEEL CORD INDUSTRY

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Prof. Dr. Tayfur Öztürk

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Timur Doğu

Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Inst. Cevdet Öztin — **Co-Supervisor**

Prof. Dr. N. Suzan Kıncal — **Supervisor**

Examining Committee Members

Prof. Dr. Güniz Gürüz

Prof. Dr. Müjgan Çulfaz

Prof. Dr. N. Suzan Kıncal

Inst. İbrahim Yıldırım

Inst. Cevdet Öztin

ABSTRACT

STUDIES ON FEASIBILITY OF HYDROCHLORIC ACID RECYCLE AND IRON-II-CHLORIDE RECOVERY IN PICKLING OPERATION IN STEEL CORD INDUSTRY

Özdemir, Tonguç

M.S., Chemical Engineering

Supervisor: Prof. Dr. N. Suzan Kıncal

Co-supervisor: Inst. Cevdet Öztin

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During the present study, it was aimed to have process synthesis and design of suitable recycle/recovery options for waste pickle liquors from pickling baths. These processes were compared through the consideration of the economics of the processes. The processes selected were Conversion of HCl to $FeCl_2$, Evaporation Process and Crystallization of $FeCl_2$. The first reclamation process studied was the Conversion of HCl to $FeCl_2$, with that process it was aimed to have all the waste pickle liquor as aqueous $FeCl_2$ solution. In the Evaporation process case, firstly the flowsheet simulations of different processes were completed for data based on composition of waste pickle liquor given in the literature. Final flowsheet was obtained for literature data.

Basing on previous flowsheet development, flowsheet integration for the industrial data was done. There were two cases for this recovery one allows solid formation in the evaporator, while the other not. For the further treatment of liquid product from Evaporation Process without solid formation, containing significant amount of HCl, possible alternative was reacting HCl with Fe to convert HCl to $FeCl_2$. The third alternative studied was Crystallization of $FeCl_2$ Process. Furthermore, the little content of $FeCl_3$ in waste pickle liquor was converted to $FeCl_2$ with hydrogen in the laboratory in order to confirm the possibility of that conversion reaction. The conversion of $FeCl_3$ to $FeCl_2$ is a must to eliminate the accumulation of $FeCl_3$ in the mother liquor. For the crystallization, addition of make-up acid before crystallization unit was chosen to increase the chloride ion concentration that would decrease the $FeCl_2$ solubility. For each alternatives purchased equipment cost was calculated. Fixed Capital Investment (FCI) for each alternative was calculated based on purchased equipment cost. Yearly operating costs were calculated. The alternatives were compared with each other with in the perspective of process economics. The most feasible process was found out to be the as Conversion of HCl to $FeCl_2$ process.

Key words: HCl Recovery, Waste Pickle Liquor, Process Integration

ÖZ

ÇELİK KORD ENDÜSTRİSİNDEKİ PİKLİNG İŞLEMİNDE HİDROKLORİK ASİT GERİ ÇEVRİMİ VE DEMİR-II-KLORÜR KAZANILMASININ FİZİBİLİTE ÇALIŞMASI

Özdemir, Tonguç

Yüksek Lisans, Kimya Mühendisliği

Tez Yöneticisi: Prof. Dr. N. Suzan Kıncal

Ortak Tez Yöneticisi: Öğ. Gör. Cevdet Öztin

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Bu tez çalışması esnasında, atık pikling banyosu sıvılarının uygulanabilir geri kazanım proseslerinin, proses sentezi ve tasarımlarının yapılması amaçlanmıştır. Ayrıca uygulanabilir proseslerin ekonomiksel karşılaştırılması yapılmıştır. Seçilen uygulanabilir prosesler HCl'in $FeCl_2$'ye çevrilmesi, Evaporasyon Prosesi ve $FeCl_2$'ün kristalizasyonu prosesleridir. İlk olarak HCl'in $FeCl_2$'ye dönüştürülmesi prosesi çalışılmıştır. Bu proseste bütün kullanılmamış HCl, Fe ile reaksiyona sokulmak suretiyle sıvı $FeCl_2$ çözeltisi elde etmek amaçlanmaktadır. Evaporasyon prosesinde, literatür atık pikling sıvısı kompozisyonu baz olarak alınarak, değişik akış diyagramı alternatiflerinin bilgisayar simulasyonları yapılmış ve optimum proses akış diyagramı elde edilmiştir. Elde edilen optimum proses akış diyagramına göre, endüstriyel veriler için akış diyagramı entegrasyonu yapılmıştır. Evaporasyon prosesinde geri kazanım için iki alternatif bulunmaktadır, birincisi katı

oluşumuna izin vermeyen geri kazanım prosesi diğeri ise katı oluşumuna izin veren geri kazanım prosesidir. Katı oluşumuna izin vermeyen geri kazanım prosesinde, sıvı fazda kalan HCl 'i bertaraf etmenin yolu HCl'in Fe ile reaksiyona girmesi ve $FeCl_2$ elde edilmesidir. Çalışılınan üçüncü geri kazanım alternatifi ise $FeCl_2$'ün kristalizasyonu prosesidir. Ayrıca laboratuvar ölçeğinde atık pikling banyosu sıvısındaki $FeCl_3$'ün hidrojenle reaksiyonuyla $FeCl_2$ elde edilmiş ve bu reaksiyonun olabilirliği test edilmiştir. $FeCl_3$'ün $FeCl_2$'e indirgenmesi geri kazanılan taze asit içindeki $FeCl_3$ birikimini önlemek için gereklidir. Kristalizasyon prosesinde taze banyo için eklenecek HCl'in kristalizasyon ünitesinden önce eklenmesi fikri uygulanarak $FeCl_2$ çözünürlüğü düşürülmüştür. Bütün alternatifler için ekipman fiyatları hesaplanmıştır. Sabit yatırım maliyeti, ekipman fiyatları baz alınarak hesaplanmış ve ayrıca bütün prosesler için yıllık çalışma maliyetleride hesaplanmıştır. Proses ekonomileri açısından alternatifler kıyaslanmıştır. En ekonomik proses HCl'in $FeCl_2$'e çevrilmesi prosesi olarak bulunmuştur.

Anahtar Kelimeler: HCl geri kazanımı, Atık pickling sıvısı, Proses Entegrasyonu

TO

MY PARENTS AND MY BROTHER

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C	Crystal Amount
C2	Crystal Amount for 2nd Crystallizer
CHF	Conversion of HCl to $FeCl_2$
EPS	Evaporation Process without Solid Formation
EPNS	Evaporation Process with Solid Formation
f	Fraction Recovered in Vapor Fraction
K2	FeO (kg/h)
K3	Fume Flowrate (kg/h)
K4	Waste Pickle Liquor Flowrate (kg/h)
K5	Fe_2O_3 (kg/h)
M	Mother Liquor Flowrate
M2	Mother Liquor Flowrate for 2nd Crystallizer
P_d	Flash Pressure
P_f	Feed Pressure
Q	Heat Duty
T_d	Flash Temperature
T_f	Feed Temperature
WPL	Waste Pickle Liquor
X1	Mole fraction of HCl
X2	Mole fraction of $FeCl_2$
X3	Mole fraction of H_2O
V_f	Feed Vapor Fraction

CHAPTER 1

INTRODUCTION

In steel production, during the cooling process, after hot-rolling, the oxygen in the atmosphere chemically reacts with the hot surface iron on the steel and forms a compound normally referred to as scale. Pickling is the chemical removal of surface oxides or scale from steel by immersion in an aqueous acid solution. While wide variations are possible in the type, strength and temperature of the acid solution used, sulfuric acid and hydrochloric acid are the most common pickling acids for carbon steel. Mixtures of nitric and hydrofluoric acids are generally used for stainless steel. Periodically, these baths must be neutralized and dumped. With increasingly successful efforts being conducted to close the dumps for environmental reasons, disposal costs are becoming prohibitive, forcing steel plants to find alternatives.

Hydrochloric acid is preferred for batch pickling of hot rolled or heat-treated high -carbon steel rod and wire. This acid produces a uniform, light gray surface and decreases the possibility of overpickling, which produces a black smut on the surface. Continuos pickling operations also use hydrochloric acid for producing the very uniform surface characteristics required for both low - and high-carbon steel. The possibility of over pickling is eliminated by short -time operations, which often precede the deposition of a metallic coating. Moreover, hydrochloric acid offers the following advantages over sulfuric and other acids (Wood, 1985):

- Effective pickling can be obtained with iron concentrations up to 13 %.
- Rinsing is easy, because of high solubility of chlorides

- Subsequent electroplated coating are uniform & adherent
- It is safer to handle hydrochloric acid than sulfuric acid, although protective equipment is required
- Cost of heating of bath is less, due to the lower operating temperature

The chief disadvantage of hydrochloric acid is the necessity of a fume control system.

Pre-cleaning is usually advantageous in applications where the acid pickling time is limited to 1 to 20 sec, as in the continuos pickling operation of wire or controlled high-speed batch pickling processes. It is also used for cleaning the materials that are to be electroplated, hot metal dipped, or painted following acid pickling. Pre-cleaning is not required when the surface contamination consists only of rust or scale and pickling time is not critical (Hudson, 1995). Pickling liquors become contaminated with dissolved metals through use, and the pickling efficiency drops, as the metal concentration increases. In the pickling processes without acid recovery fresh concentrated acid additions are made from time to time to rejuvenate the bath but eventually it becomes spent, due to the accumulation of metal ions, and must be discarded. Pickling speed varies continually throughout the life of the bath and it is difficult to avoid over and under pickling. While most pickle liquor is relatively inexpensive, the indirect cost associated with pickling may go well beyond the cost of acid consumed. This indirect cost includes:

- Cost of neutralizing chemicals (Consumption of NaOH)
- Ultimate disposal of resulting solid waste
- Lost production time that occurs while spent acid is removed and replaced
- Quality control problems due to over and under – pickling as bath composition changes
- Reduction in productivity resulting from the inhibiting action of dissolved metals
- Labor to make up fresh acid
- Labor for removal and disposal of spent acid

Recovery of spent pickle liquors can potentially reduce many of these costs. The advantages of recovery system can be outlined as

- Elimination of down time to dump and replace spent pickle liquor.
- Elimination of shock loading on the waste treatment system that occurs when a spent bath is dumped
- Elimination of clogging in pipes and pumps by ferrous chloride crystals
- Consistent pickle liquor composition and pickling performance with increase in productivity.

In this study it was aimed to synthesise and design selected possible recovery alternatives, which are easily applicable, compact, robust, easy to operate. The alternatives were compared with each other by economical evaluation. In order to find out which alternative to be selected for addition of recovery unit for pickling operation.

The way of approach for the solution of problem divided the thesis into three sections, in the first section the experimental methods and results were given, in the second section the process design and synthesis methods and results were given and finally the economical methods and results were given.

In order to design a recovery system for waste pickle liquors (WPL), the $FeCl_2$-HCl-H_2O system should be studied. The relevant physical equilibrium data, for the $FeCl_2$-HCl-H_2O system is given in Chapter 2. The recovery alternatives, for waste pickle liquors, available in the literature are reviewed in Chapter 3. Experimental methods and experimental results are given in Chapter 4. The synthesis and design of the process alternatives is discussed in Chapter 5. Economical evaluation of the processes is given in Chapter 6. The results are evaluated and compared in Chapter 7 and the conclusions are summarised in Chapter 8.

CHAPTER 2

PHYSICAL EQUILIBRIUM DATA

The physical equilibrium data on $FeCl_2$-HCl-H_2O system is required for the present study to design any recovery system for WPL. To recover HCl from WPL, the components should be separated. Vapor-liquid equilibrium data is required for evaporation and solid-liquid equilibrium data is required for crystallization.

HCl-H_2O system:

Hydrogen chloride is highly soluble in water and this aqueous solution is non-ideal. The vapor–liquid equilibrium phase diagram generated by the Aspen Plus Chemical Engineering Computer Simulation Program is shown in Figure 2.1. As can be seen in Figure 2.1, HCl+H_20 system forms an azeotrope at HCl mole fraction of 0.11 (20.5 wt % HCl) and vapor-liquid equilibrium line is very smooth in the region of HCl concentration lower than azeotrope composition. Ferrous chloride solubility in water at 0°C is 33.2% (Schimmel, 1952). Introduction of $FeCl_2$ into binary HCl+H_2O solution has salting out effect on HCl, increasing its concentration in the vapor phase, as shown in Table 2.1 (Susarev, *et. al.*, 1976).

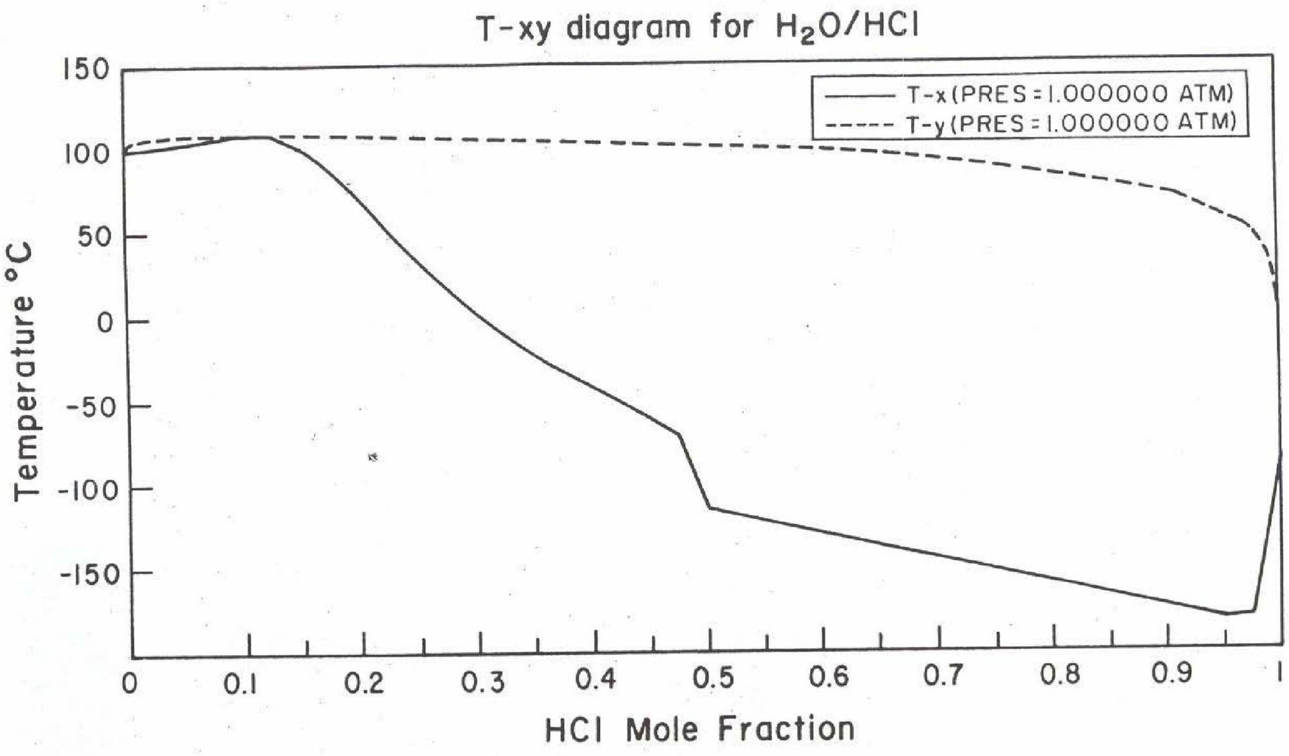

Figure 2.1. T-xy Diagram for HCl-H_2O system

Table 2.1. Data on Liquid-Vapor Equilibrium in System of $FeCl_2$-HCl-H_2O at 25°C (Susarev, *et. al.*, 1976)

Liquid Phase HCl (mole %)	Liquid Phase H_2O (mole %)	Liquid Phase $FeCl_2$ (mole %)	Vapor Phase HCl (mole %)	Vapor Phase H_2O (mole %)
1	98	1	0.0	100.0
2	97	1	0.0	100.0
3	96	1	0.0	100.0
4	95	1	0.0	100.0
1	97	2	0.0	100.0
2	96	2	0.01	99.99
4	94	2	0.1	99.9
6	92	2	0.5	99.5
8	90	2	2.0	98.0
10	88	2	6.6	93.4
12	86	2	21.1	78.9
1	96	3	0.0	100.0
2	94	4	0.1	99.9
4	92	4	0.6	99.4
6	90	4	2.5	97.5
2	92	6	0.6	99.4

Ferrous chloride binds water molecules in HCl solutions and raises the activity and the vapor pressure of HCl (Ionin and Kozhakova, 1973). For the $FeCl_2$-HCl-H_2O system, concentrations of HCl have dehydrating effect upon the ferrous chloride hydrates. The $FeCl_2$ content in solutions saturated with respect to $FeCl_2.4H_2O$ decreases with the increase of the HCl concentrations in the binary solvent $HCl+H_2O$. The solubility of $FeCl_3$ in HCl-H_2O is very high (Linke, 1958). Heat of solution for $FeCl_2$ is 2.7 kcal / mole (Mullin, 1961). The solubility of ferrous chloride in HCl solutions containing 3, 12, 20 % HCl is a linear function of temperature in 5-40 °C range. The solubility of $FeCl_2$ (wt%) is,

= Constant 1 + Constant 2 * Temperature (Franke, *et. al.*, 1973).

The values of constants are given in Table 2.2.

Table 2.2. Solubility constant values for $FeCl_2$ (Franke, *et. al.*, 1973)

HCl Concentration (wt%)	3	12	20
Constant 1	**31.4**	**17.6**	**7.18**
Constant 2	**0.14**	**0.15**	**0.16**

The isotherms of the system of $FeCl_2$-HCl-H_2O are shown in Figure 2.2, based on data taken from Schimmel (1952). The solubility diagram of the $FeCl_2$-$FeCl_3$-H_2O system at 25°C is shown in the Figure 2.3 (Schimmel, 1952). Addition of $FeCl_3$ to the $FeCl_2$ decreases the $FeCl_2$ solubility, as can be seen from Figure 2.3.

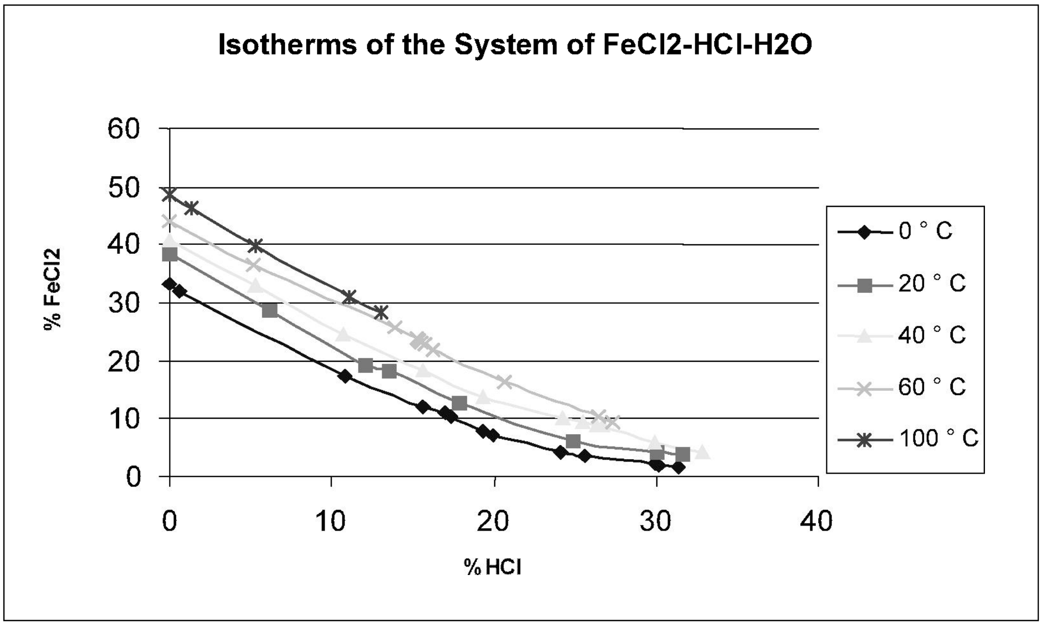

Figure 2.2. Isotherms of the $FeCl_2$-HCl-H_2O System (Schimmel, 1952)

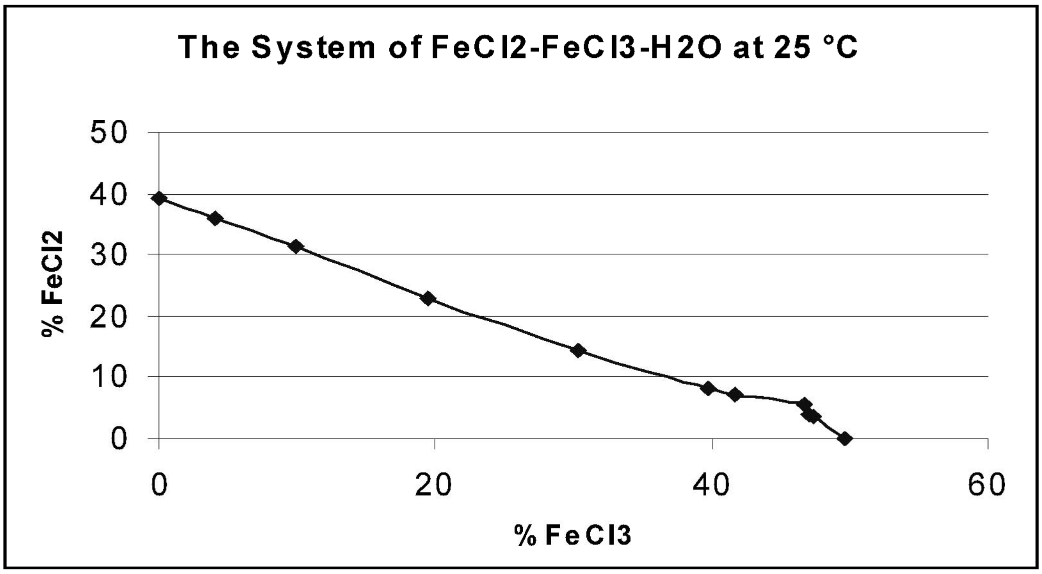

Figure 2.3. Isotherm of $FeCl_2$-$FeCl_3$-H_2O at 25°C (Schimmel, 1952)

The equation;

$$\log\left[\frac{p_{HCl}}{P_{H2O}}\times\frac{X3(2X1+3X2+X3)}{X1(X1+2X2)}\right]=21.94\times(X1+3X2)^{4/3}-0.93$$

relating the vapor pressures of $FeCl_2$-HCl-H_2O system, was developed by Chen et. al. (1970). In this paper vapor contains only HCl and H_2O, so P_{H2O} is P_t-P_{HCl}. The data, given by Stone (1997), for H_2O vapor pressure of pickling baths at 70 °C are tabulated in Table 2.3.

Table 2.3. Vapor Pressure of H_2O at different Pickling Bath HCl Compositions

Weight fraction of HCl	P_{H2O} (mmHg)
10	203.8
12	195.7
14	189.1
17	175.6

CHAPTER 3

METHODS OF REUSE & RECOVERY OF HCl

The processes of reuse and recovery of HCl from WPL are reviewed in this chapter. These processes are Lurgi Process, Dravo Process, Evaporation Process, Recovery by Ion Exchange, Oxyprecipitation, Crystallization Process and Conversion of HCl to $FeCl_2$ Process.

3.1. LURGI PROCESS

This process for the recovery of hydrochloric acid from spent pickling liquors was developed in Germany. The process regenerates the acid in a fluid bed.

The purpose of Lurgi system of regeneration is to restore the balance so that the acid leaving in the pickling liquor remains constant. The theory of this system is to treat a continuos-bleed stream from the circuit to remove iron from the liquor system at the same rate as it is being pickled in the vats. Spent pickle liquor is fed to a pre-evaporator and heated with gases from the regeneration reactor, which is the next in the flow plan, as shown in Figure 3.1. Concentrated liquor from the pre evaporator then enters the lower part of the reactor, at an acid concentration of about 13% and a ferrous chloride level of 20%. This reactor contains a fluidized bed of sand and is fired by oil or gas to provide and maintain an operating temperature around 800°C. Evaporation products leave the top of the vessel together with unreacted components of solution plus the combustion products from the fuel. A cyclone removes ferrous oxide from the stream then the hot gases enter the pre evaporator, as stated above. The overhead product from the evaporator, leaving at about 122°C contains not only the water vapor plus the hydrogen chloride and combustion products from the fluidized bed reactor, but also some hydrogen chloride that vaporizes directly from the entering plant liquor. To place the regenerated acid back to the pickle liquor circuit, the gas mixture from the pre evaporator enters the bottom of an adiabatic absorption tower, where hydrogen chloride is absorbed by another bleed stream of the pickle liquor. The resulting liquid stream that is returned to the pickling plant contains 12% acid and about 70 g/liter iron. Meanwhile, unabsorbed gases go to a condenser, and the gases that do not condense are vented to the atmosphere (Besselievre and Schwartz, 1976).

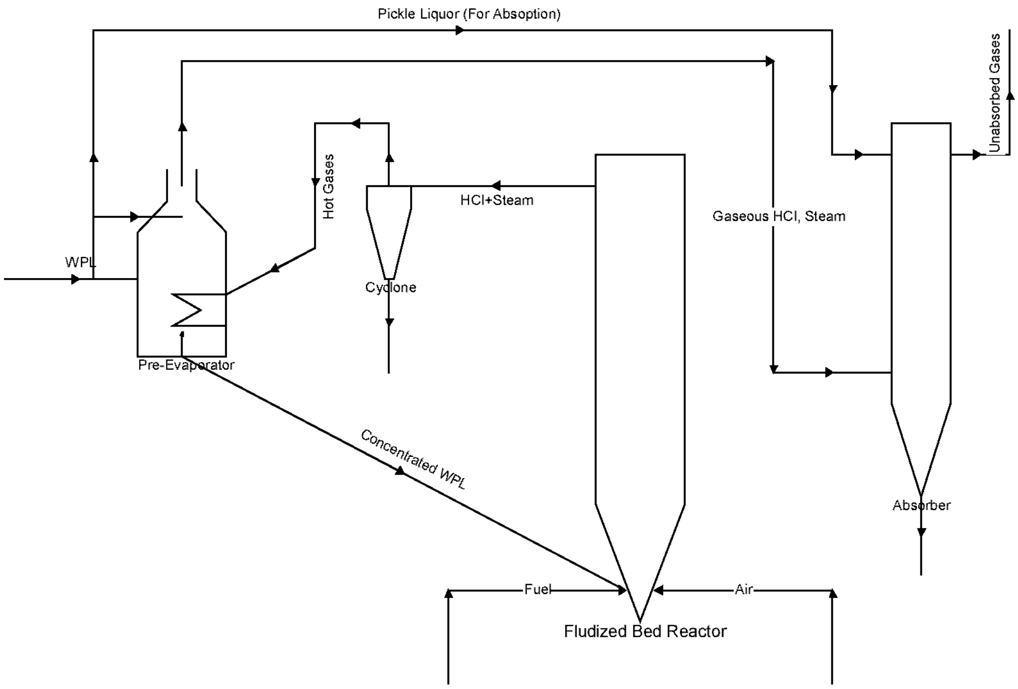

Figure 3.1. Flowsheet of Lurgi process

Dravo Process is similar in most respects to the Lurgi process except that Dravo process uses a spray roaster instead of fluid-bed regeneration step and does not use a pre-evaporator (Besselievre and Schwartz, 1976).

3.2. EVAPORATION PROCESS

This process is based on the separation of volatile components from the solution when the solution is heated to boiling. In this HCl recovery system, illustrated in Figure 3.2, waste acid is heated until the water and acid vaporize leaving only the concentrated iron chloride. Iron chloride solution is pumped to a storage tank for sale or disposal, or is dried to obtain crystals. WPL HCl composition is always smaller than azeotropic composition of HCl+H_2O system. In the evaporation process, HCl concentration in the vapor phase is greater than the initial WPL HCl composition because of non-volatile iron chloride. The water and acid vapor are cooled and condensed in the acid condenser, then returned back to the pickling bath. The remaining water vapor moves into the condenser and is scrubbed of any residual acid. This scrubbed solution can be reused as rinse water in the pickling process. This technology will allow industry to recover HCl at the source, eliminating disposal costs. Moreover a non-hazardous, marketable by-product -iron chloride- is generated. This by-product can be used in fertilisers, animal feeds, and wastewater treatment (Cullivan, 1995).

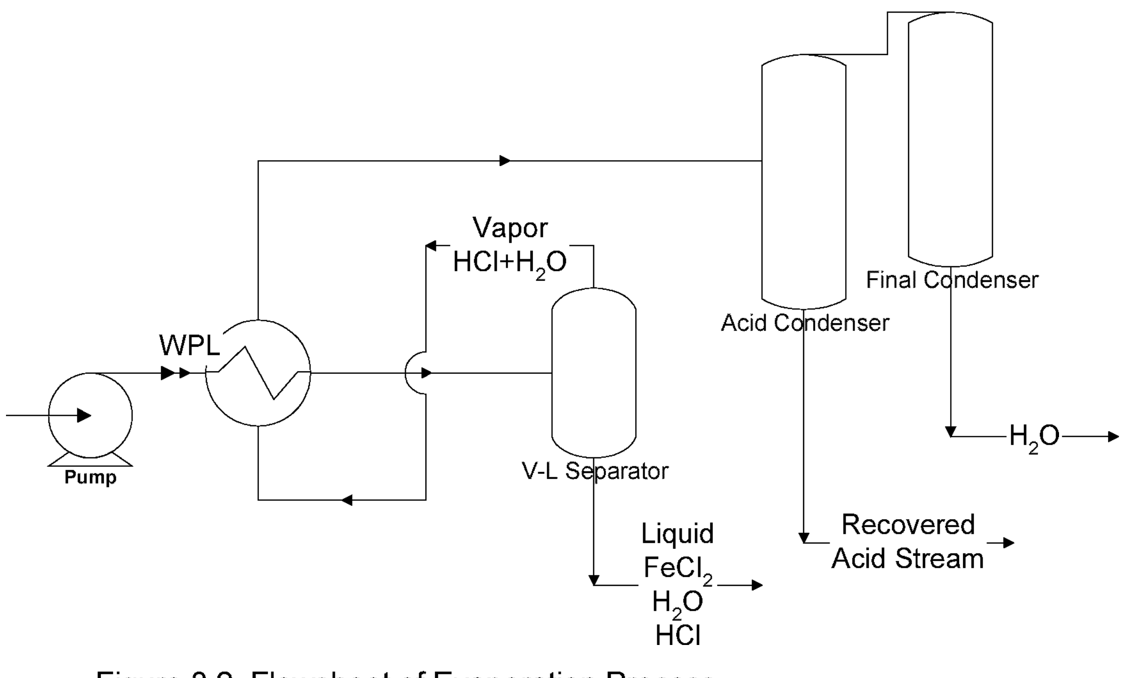

Figure 3.2. Flowsheet of Evaporation Process

The process produces concentrated iron chloride by-product, which can further be processed into a crystalline form or sold as a liquid for agricultural use. Spent hydrochloric acid ranges between 5 and 15 percent iron concentration. The evaporative process heats the solution to extract the acid and water from the spent waste. Only a super concentrated ferrous chloride solution remains.

A pump forces the spent hydrochloric acid into heat exchanger. This spend acid solution then extracts heat from the acid and water vapors generated in the evaporative process by means of a heat exchanger. The pre-heated spent acid solution then enters the evaporation loop.

The water and acid in the spent acid mixture begin to vaporize at about 102 °C. They are continually driven from the waste solution until the temperature reaches the point of saturation at which point the saturated liquor is removed from the evaporator.

The acid and water vapors are driven from the evaporator separator through the heat exchanger and into the acid condensers. The condensing acid vapor combines with some of the condensing water vapor as it descends through the acid condenser. The remaining water vapor continues its journey into final condenser, where it is sub-cooled. The final condensate is reused as rinse water in the pickling process or is returned to the pickling tank with the concentrated acid (Cullivan, 1995).

3.3. RECOVERY BY ION EXCHANGE

Certain ion exchange resins have the ability to sorb strong acids from solution, while excluding metallic salts of those acids. The process is reversible in that the acid can be readily desorbed from the resin with water. It is possible, by alternately passing contaminated acid and water through a bed of resin, to separate free acid and metallic salt. There are two steps in ion-exchange recovery process - the upstroke stream and the downstroke stream. During the upstroke, contaminated acid is pumped into the bottom of the resin bed. Acid is sorbed by the resin particles and the remaining deacidified metallic salt solution is collected from the top of the bed. Next, during the downstroke, water is pumped into the top of the bed, desorbing the purified acid from the resin so that a purified acid product is collected from the bottom of the bed. The total cycle typically takes approximately 5 minutes to complete and continuously repeats itself (Brown, 1990).

3.4. OXYPRECIPITATION

Oxyprecipitation is carried out using air as oxidizing agent and ammonia as a basic agent, until all the Fe^{+2} in the solution has been eliminated (Negro, *et. al.*, 1993). Oxyprecipitation is the treatment of waste acid with NH_4OH and oxygen that leads to the formation of different mixtures of iron oxides where all the Fe^{+2} is eliminated and the ammonium chloride solutions can easily be decomposed to hydrochloric acid and ammonia. The reactions are given as,

$$4\,NH_4OH + 1/2\,O_2 + 2\,FeCl_2 \longrightarrow 4NH_4Cl + 2H_2O + Fe_2O_3$$

$$NH_4Cl \longrightarrow NH_3 + HCl$$

The precipitates have a number of industrial applications. Oxyprecipitation process has been done in the laboratory scale, experimental set-up of which is shown in Figure 3.3 (Negro, *et. al.*, 1993). The process has not been industrially applied yet, the data in the literature is not enough to carry out the process design.

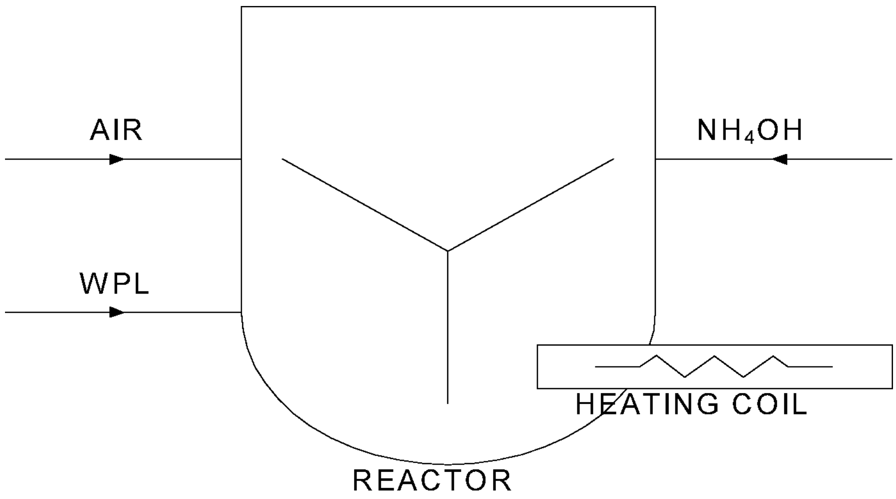

Figure 3.3. Oxyprecipitation Reactor

3.5. CRYSTALLIZATION

The $FeCl_2$ crystals formed at low temperatures are then removed from the pickle liquor, which then permits reuse of the free hydrochloric acid remaining within the regenerated pickle liquor in normal pickling operations. The crystallization process is carried out in a crystallizer. A crystal de-watering centrifuge is used to separate wet ferrous chloride crystals from supernatant pickle liquor. The chilled regenerated pickle liquor within recovered acid tank is then transferred back to the pickling line by pumping, as can be seen in Figure 3.4. The make-up hydrochloric acid is fed to pickling baths. The recovered acid contains 12 weight percent of $FeCl_2$. The low temperature, low energy requirements of the process makes the process economically superior to any known high-temperature closed loop regeneration process (Lurgi Process) (Peterson, 1991).

$FeCl_3$, that is present in WPL, has high solubility even in very low temperatures (Linke, 1958). In this case, accumulation of $FeCl_3$ in mother liquor is inevitable for crystallization process.

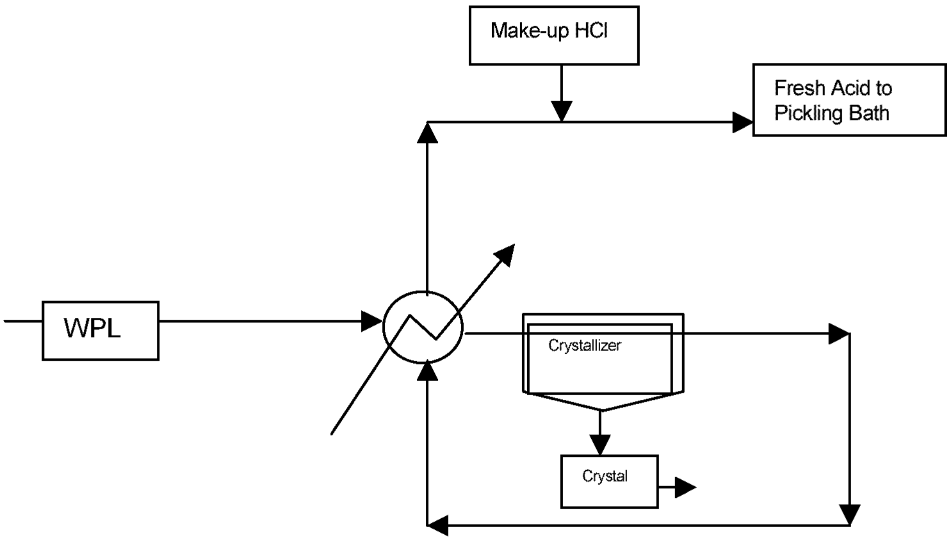

Figure 3.4. Flowsheet of Crystallization Process

3.6. CONVERSION OF HCl TO $FeCl_2$

The production of $FeCl_2$ starts with the reaction between Fe and HCl. Iron, either in the metallic or in the iron oxide form, reacts with HCl to produce $FeCl_2$. The reaction between HCl and Fe is complete. The reaction should be carried out at atmospheric pressure in a reaction vessel under conditions such that stoichiometric excess of iron always present to ensure the complete conversion. The residence time is reported to be any time ranging from two minutes to 30 hours preferably from 3 hours to 15 hours and the temperature of the ferric chloride solution produced advantageously ranges from 40°C to 100°C, and preferably from 60° to 90°C (Clair, 1995). Industrially, solutions of $FeCl_2$ are prepared by dissolving iron in hydrochloric acid or by reducing $FeCl_3$ solutions with iron. Moreover, $FeCl_2$ solution can also be prepared by passing hydrogen over heated $FeCl_3$ and $FeCl_2$ is sold as 30 weight percent $FeCl_2$ as aqueous solution in the market (Elvers, et. al., 1985).

CHAPTER 4

EXPERIMENTAL METHODS AND DATA EXTRAPOLATION

As has been explained in Chapter 2, the solubility data were available in the temperature range between 0°C to 100°C. Shown in Figure 2.2, the solubility of $FeCl_2$ decreases with the decrease in temperature. The solubility data for lower temperatures were required to design crystallization process. Data from Schimmel (1952) was taken and $FeCl_2$ solubilities at temperatures lower than 0°C was estimated with computer program that uses least-squares regression method for estimation. The estimation method derives a curve that minimizes the discrepancy between data points and the curve. This technique is called least squares regression method. In order to see the reliability of estimated data experiments were carried out.

4.1. EXPERIMENTS ON T-x DIAGRAM

Samples with the composition given in the Table 4.1 were taken from an existing plant, Beksa-steel cord manufacturer located in İzmit. It operates 24 hours per day and 7900 hours per year and produces 24000 tons of steel cord per year. Samples were taken and 14, 17 ml 36% HCl was added to the 100-ml samples 1 & 2 respectively, in order to increase the HCl concentration in the solutions. So that, the mother liquor after crystallization would have the approximate HCl concentration of fresh acid. Then crystallization operation was carried out in the Bosh mark crystallizer at –33°C. The total iron concentration, zinc concentration, aluminium concentration in the solution was determined with atomic absorption spectroscopy made by Philips, Unicam PU 9 model. Fe^{+2}, Fe^{+3} composition was determined with analytical (wet) chemistry. Fe^{+2} concentration was determined via titration with $KMnO_4$ after 1ml of sample mixed with 250 ml distilled water and with Zimmerman-Reinhardt reagent, which is a solution of Mn(II) in fairly concentrated sulfuric acid and phosphoric acid. After total Fe concentration was determined with the following procedure. 1ml sample was added to 5 ml HCl and it was boiled then 0.3 ml $SnCl_2$ was added. After 7 ml of 5 weight percent $HgCl_2$ was added, precipitation occurred. 100 ml distilled water was added with 40 ml Zimmerman-Reinhardt reagent. And titrated with $KMnO_4$. Fe^{+3} concentration was found with the difference between total Fe concentration and Fe^{+2} concentration (Usanmaz, 1991). The amount of HCl in the solution was determined by titration of solution with Na_2CO_3. Also the HCl content was determined via titration with NaOH these two method gave the parallel results. The crystallization experiments were carried out at –33°C.

4.2. EXPERIMENTS ON CONVERSION OF $FECl_3$ TO $FECl_2$

Because of high solubility of $FeCl_3$ at crystallization temperature, crystallization process ends up with the $FeCl_3$ accumulation in the recovered acid stream, if WPL contains $FeCl_3$. In order to eliminate accumulation of $FeCl_3$, it should be converted to $FeCl_2$, which has lower solubility than $FeCl_3$. There are many possible reactions for the reduction of the $FeCl_3$ to $FeCl_2$ in the literature. But the reduction reaction to be selected should not introduce another component to the WPL. This type of reaction is achievable via the reaction of $FeCl_3$ with hydrogen. The experimental set-up is given in Figure 4.1. 100 millilitres of WPL was placed in a closed container with gas inlet and outlet, hydrogen was fed continuously for 10 minutes with 420 millilitres (200 %). Volumetric flowrate of hydrogen was 0.7 ml/sec. The experiment was carried at 70°C. For the real system a packed column can be used. In real process, usage of excess hydrogen can also be applied, unused hydrogen gas can be returned back to the reducing column.

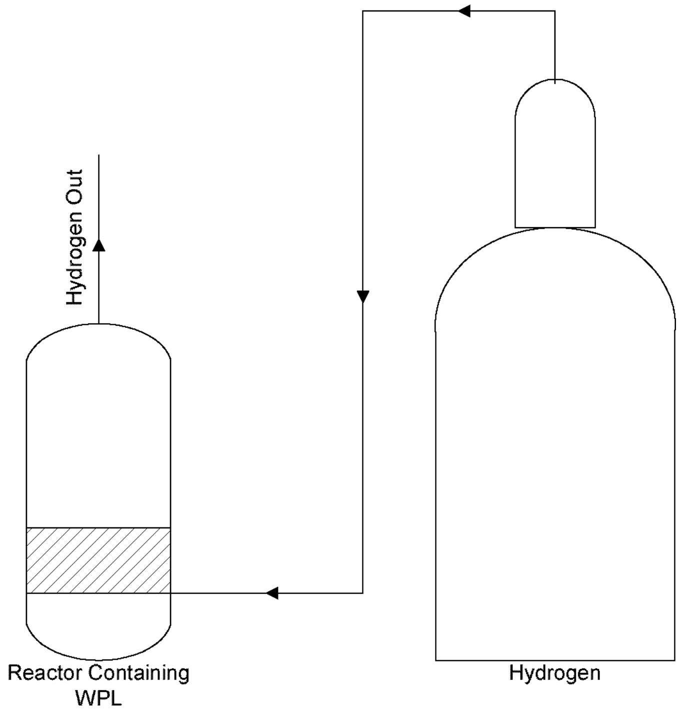

Figure 4.1. The Experimental set-up of $FeCl_3$ to $FeCl_2$ reduction

4.3 EXPERIMENTAL RESULTS AND DATA EXTRAPOLATION

Samples, with properties tabulated in Table 4.1, were crystallized. The crystallization experiments were carried out at –33°C. Experimental results are tabulated in the Table 4.2, % HCl in the table gives the HCl composition in mother liquor and % $FeCl_2$ % $FeCl_3$ gives $FeCl_2$ and $FeCl_3$ solubility in the mother liquor after crystallization.

Table 4.1. WPL Sample Properties

	Sample 1	**Sample 2**
HCl, wt %	13.57	13.54
Fe, wt %	8.05	7.53
FeCl , wt %	17.05	13.63
FeCl , wt %	1.57	1.87
Zn, ppm	1.01ppm	0.97 ppm
Al, ppm	0.78ppm	0.58 ppm
Density, g/cm	1.24	1.23

Table 4.2. The composition of equilibrium solution at -33 °C

	% HCl	% FeCl	%FeCl	Density (g/cm)
Sample 1	20.3	3.1	1.7	1.15
Sample 2	20.7	2.4	2.0	1.14

The solubility data from Schimmel (1952), shown in Figure 2.2, was extrapolated to low temperatures. The solubility graph based on estimated data is shown in Figure 4.2. The sample was containing FeCl , different from the FeCl -HCl -H O system. As can be seen in the Figure 2.3, addition of FeCl to FeCl decreases the FeCl solubility linearly up to 40% FeCl composition. The slope of that linear curve is 0.814, that is increase of 1% FeCl composition in the FeCl -FeCl system decreases the FeCl solubility by 0.814%. With that data, 0.814 fold of FeCl composition was added to the found solubility of FeCl to find out the FeCl solubility in the FeCl -HCl -H O system. The corrected experimental data are tabulated in Table 4.3. Experimentally found solubility values are tabulated in Table 4.3 for comparison with estimated data which are pointed on Figure 4.2. The solubility of FeCl at 20.3 and 20.7% HCl compositions (the compositions at which experiments were carried out) were taken from Figure 4.2 and tabulated in Table 4.3. As can be seen from Table 4.3 estimated data are consistent with experimental data.

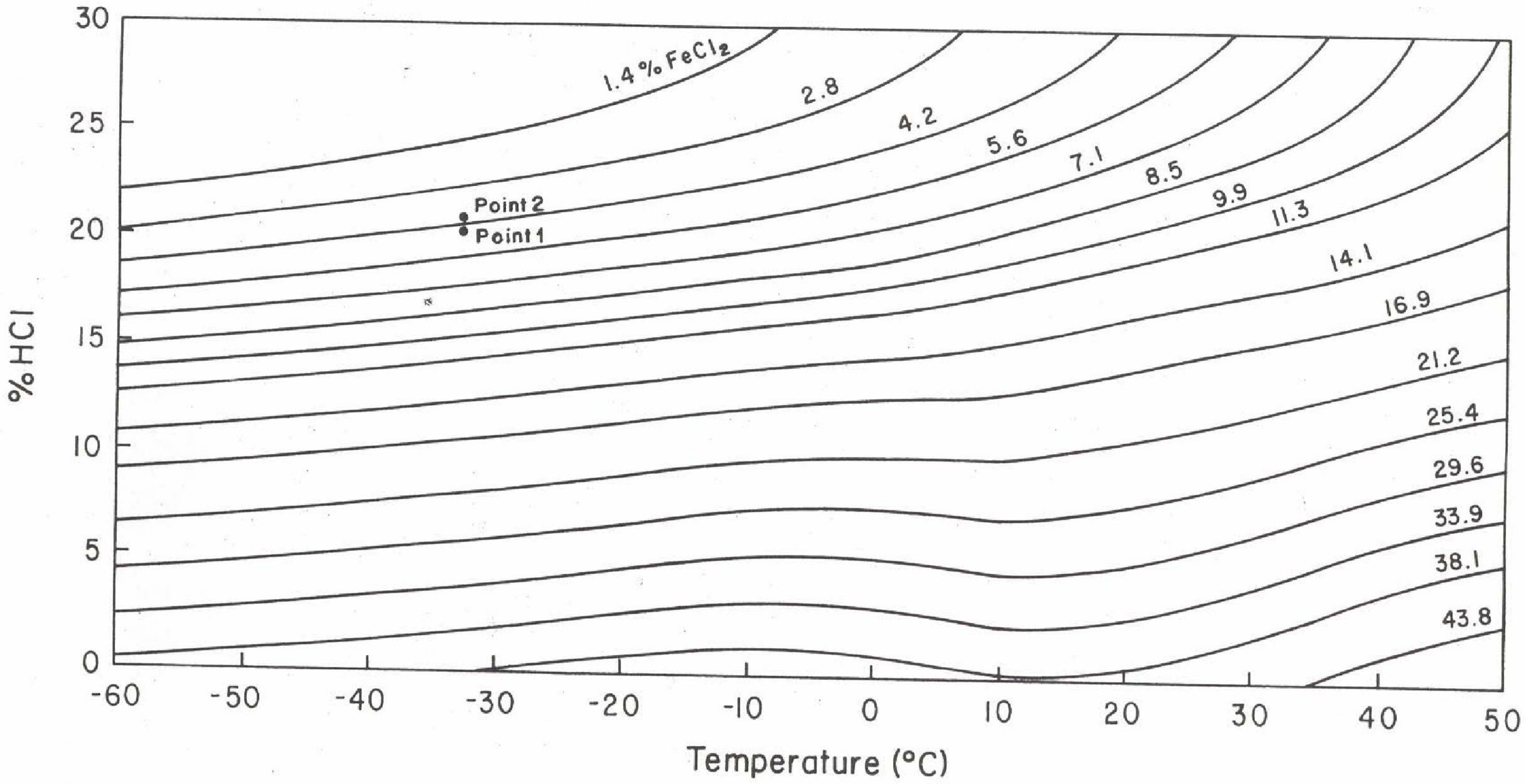

Figure 4.2. Estimated Solubility Curve of $FeCl_2$ in the $FeCl_2$-HCl-H_2O System

Table 4.3. Comparison of $FeCl_2$ solubility in the $FeCl_2$-HCl-H_2O system, based on results from Experimental Data with Estimated Data at –33°C

	$FeCl_2$ solubility (weight %) in the $FeCl_2$-HCl-H_2O system based on Estimated Data	$FeCl_2$ solubility (weight %) in the $FeCl_2$-HCl-H_2O system based on Experimental Data
Point 1	4.5	4.5
Point 2	4.1	4.0

The hydrogen was used as reducing agent for the conversion of $FeCl_3$ in the waste pickle liquor to $FeCl_2$. The result of the experiment for the reduction of $FeCl_3$ to $FeCl_2$ taken place at 70°C is given in Table 4.4.

Table 4.4. Experimental Results of Reduction of $FeCl_3$ to $FeCl_2$

Components	Initial Compositions	Composition After Reduction
Fe^{+2}, wt %	7.48	7.76
Fe^{+3}, wt %	0.28	0
Density, g/cm^3	1.25	1.28

CHAPTER 5

PROCESS SYNTHESIS AND DESIGN

5.1 METHOD OF ATTACK

Recovery alternatives were reviewed from literature in Chapter 3. Assessment of these alternatives were done, in order to select the alternatives to be studied for process synthesis and design.

Lurgi Process and Dravo process are very complex, beside they require high temperatures about 800 °C this means high energy cost. These two processes convert $FeCl_2$ to iron oxides. Then the free chlorine gas react with water to produce HCl. Lurgi process employs a fluid bed into which the WPL is injected. The oxide remains in the fluid bed for several hours at about 800 °C, and as new liquor is added, the oxide produced deposits on particles already present in the fluid bed, so producing particle growth. The oxide is removed continuously from the reactor to maintain constant level. Because of long residence time and high temperature, the fluid bed reactor produces a dense, coarse oxide. On the other hand, the reactor requires high capacity and it is expensive. In the Dravo process, the disadvantages are that the reactor is very big and oxide produced has a low bulk density, which may present handling problems. For evaporation such high temperatures as in Lurgi and Dravo Processes, is not required. As can be seen, these two processes are not easily applicable and may not give a compact design for recovery process.

Oxyprecipitation is also very complex it requires addition of ammonium chloride that costs extra money. What is more, oxyprecipitation has not been industrially applied. That is why oxyprecipitation was not studied further. Recovery via ion exchange would certainly be affected from the dissolved and suspended contaminants in the waste pickle liquors.

The criteria for selection of process alternatives were simplicity, adaptability, compactness, robustness, and easy process conditions to operate. The recovery alternatives selected, that fit these criteria were

- Conversion of HCl to $FeCl_2$
- Evaporation Process
- Crystallization of $FeCl_2$.

Process synthesis and design was done for these selected alternatives. The data taken from the pickling bath was selected as design basis for the present study, since such an operating data for the composition of waste pickle liquor would be more reliable. Data set (giving the main and pre-pickling bath compositions of HCl, Fe^{+2}, and Fe^{+3}), tabulated in Table APP1, were taken for 68-hour period. Water vapor pressure was found from Stone (1997) and vapor pressure of HCl was found from equation given in Chen et. al. (1970). The mass fraction of HCl was found from the ratio of vapor pressures. Total, Fe^{+2}, Fe^{+3} and Cl^- balances were written and solved for WPL, Fume, Fe0, Fe_2O_3 flowrates. The details of mass balance are given in Appendix B.

Flowsheet development was done for each alternative based on the physical equilibrium data available from literature or data generated from the simulation program. Experiments were carried out to see the reliability of estimated data for low temperature solubilities. The details of the experiments are given in the Chapter 4.

The energy requirement of each process was found from simulations. The process equipment were designed. Thermal design of heat exchangers and evaporator was done using the Kern method (Kern, 1950), the heat exchanger design procedure is given in APPENDIX G. 10% heat loss to environment was assumed while exchangers are designed. A Visual Basic macro program was developed and used to speed up the shell and tube heat exchanger design. Dirt factor for each exchanger arrangement was calculated by the computer program, the heat exchanger arrangements with lower dirt factors than the required dirt factor were eliminated, the remaining heat exchangers were compared on the basis of their costs. Costs for each heat exchanger arrangement was calculated via the heat exchanger cost estimation method taken from Cheremisinoff (1986). The method is based on using correction indexes to estimate cost of heat exchangers basing on a unit heat exchanger cost. The pressure drops of each exchanger for shell and tube side was calculated. The operating cost of each exchanger was also calculated and the optimum exchanger is found out as the one with minimum yearly total cost. The costs calculated were corrected with cost index for 1997. The heat exchanger with lowest cost was selected as the optimum heat exchanger to be used. The heat exchanger cost also includes lining cost since the WPL is corrosive. The cost of plate type heat exchangers, which have same heat duty, inlet and outlet temperature specifications with shell and tube heat exchangers designed, was taken from Alfa-Laval (Plate –type heat exchanger Producer Company) in order to compare the cost of two types of heat exchangers. The plate type heat exchangers were more expensive, and therefore shell and tube heat exchangers were used in the process synthesis. Storage tanks for each recovery alternative has design capacity of 20 days of storage.

Pumps were designed to have capacity that can pump the WPL for 500 m and elevate 5 meters. Since the pump capacity requirement was low, same pump design specification was used for all pumps. Pump design calculations are shown in the APPENDIX F.

Crystallizer cost were taken from Peters and Timmerhaus (1991), this gives the cost of crystallizer depending on the capacity of the crystallizer. Stainless steel was selected as the material of construction for the crystallizers. The surface of the crystallizers are lined with rubber (Petterson, 1990). The cost of each crystallizer was found out depending on capacity of the each crystallizer.

The centrifugal filter, made of stainless steel, cost was found from Peters and Timmerhaus (1991), which relates the cost of centrifugal filter to bowl diameter. Bowl diameter of 10 in. (25.4 cm) selected with respect to solid holding capacity of filter. The power required, given in Peters and Timmerhaus (1991), to run the filter was 3.5 kW.

For $FeCl_3$ reducer packed column design was done. Ceramic intalox packing material was selected for its high corrosion resistance. 20 mm H_2O pressure drop in the packed bed was acceptable (Sinnot, 1993). Column diameter and column height were calculated following the calculation procedure given in Sinnot (1993). Then, the cost of $FeCl_3$ reducer, a packed column, was taken from Peters and Timmerhaus (1991), which relates the cost per foot height to column diameter.

The cost of industrial refrigeration is determined by the operating temperature and the capacity of the crystallizer (Timmerhaus, 1991). The cost of industrial refrigeration for crystallization processes using two and three crystallizers were same, because the refrigeration heat duty of these two processes were same.

The reactors were designed for 10 h retention time. Capacity of each reactor was determined based on the flowrate of feed to reactor, after the cost for each reactor was determined related with their capacity from Garret (1989). The costs taken were for reactors with jacket, made of stainless steel. Fe-storage tank that would store the scrap iron for the Conversion of HCl to $FeCl_2$ Process has a design capacity of 20 day of storage.

Mixing tank that mixes recovered HCl with make-up HCl was designed for a capacity of 1 h of storage, materials of construction selected was stainless steel with teflon lining. The same design capacity was used for all mixing tanks. The flares, used for burning, selected are guyed, made of steel with 12.2 m (40 ft) elevation. The cost for each flare was taken from Garret (1989).

5.2. DESIGN BASIS

In order to go further in the present study, pickling bath operating data were required. It was intended to have real data from pickling baths. The data, tabulated in APPENDIX A, were taken from an existing plant that has three pickling baths with similar operating conditions. Temperature of pickling baths was at 70°C and the fresh acid composition that was fed to the baths was 18.7% HCl. The mass balance of the bath was done. For each data set, given in Appendix A, the WPL flowrate, fume flowrate, fume HCl mass fraction, FeO and Fe_2O_3 amount coming from wire surface were calculated. Then the average flowrate of WPL and average composition of WPL were calculated. According to mass balance calculations, shown in Appendix B, the design basis for the recovery system is tabulated in Table 5.1. Moreover, the compositions of samples taken from the baths are tabulated in Table 5.1, and the values are comparable.

Table 5.1. Design Basis Waste pickle liquor composition (weight %), Compared with Composition of Samples taken from Pickling Baths

Components	Design Basis Composition (weight %)	Composition of Sample 1 (weight %)	Composition of Sample 2 (weight %)
% HCl	**10.50**	**13.57**	**13.54**
% $FeCl_2$	**15.85**	**17.05**	**13.63**
% $FeCl_3$	**1.22**	**1.57**	**1.87**
% H_2O	**72.43**	**67.81**	**70.96**
Mass Flowrate (kg/h)	**256**		

The Capacity of the Plant is 24000 tons steel cord /year

5.2.1. CURRENT SITUATION

In the plant, where the Pickling baths data was taken, steel cord, hose reinforcement wire and spring wires are produced. Wire rod is the raw material for these products. At the first step wire rod is elongated. In the second step, wire is heat treated in order to obtain the original structure that was changed during elongation. During heat treatment an oxide layer forms over the wire rod. The oxide layer should be eliminated, this is done via pickling operation, dissolving oxides in the acid baths. The flow diagram of the pickling operation is shown in the Figure 5.1. Fume is the vapor (containing HCl+H_2O) leaving the pickling baths. Pickling Baths are continuously fed by fresh acid (at 70 °C and 18.7% HCl composition) and operate as semi-batch reactors. As the main pickling bath is fed with fresh acid, acid from main pickling bath overflows to pre-pickling bath at the same time contaminated acid in the pre-pickling bath goes to WPL tank. Acid and wire go counter currently as can be seen in the Figure 5.1. As time passes $FeCl_2$ and $FeCl_3$ concentration in the baths become high. Acid can not further clean the surface of the wire. In this case baths are dumped and charged with fresh acid. After pickling operation the rod is further elongated and in some cases plated with copper and zinc, depending on the end usage of product.

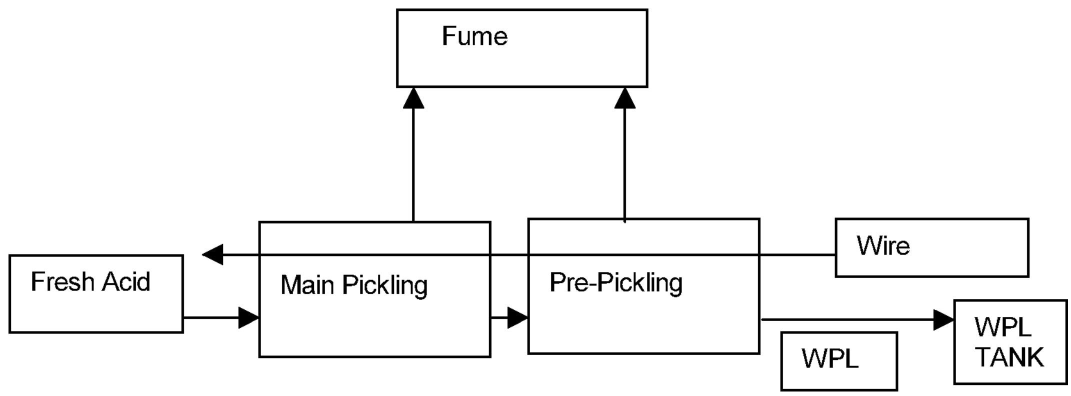

Figure 5.1. Flow Diagram of Pickling Baths

Dumped WPL is sent to waste treatment unit where it is reacted with NaOH to neutralize HCl and convert iron chloride to insoluble iron oxides. Solid waste is handled and transported and further disposed to landfill area. Liquid waste is discharged. This way is not an environmentally friendly way to manage the waste. The fresh feed is heated in the pickling baths with steam that causes extra energy to be used. The amount of NaOH used, amount of solid and liquid waste formed for one year is given below,

The Capacity of the Plant is 24000 tons steel cord /year

Annual Waste Pickling Liquor: 2028 tons/year

NaOH for neutralization: 454 tons/year

Total Solids after Filtration (at 50% moisture): 2026 tons/year

Total Liquids to be drained: 455 tons/year

HCl neutralized: 213 tons/year

Instead with the recovery unit the, potential gains can be listed as:

HCl that can be recovered: 213 tons /year

Total Fe^{++} that can be recovered: 150 tons/year

Total $FeCl_2$ that can be produced (including conversion of HCl to $FeCl_2$): 691 tons/year

5.3. EVALUATION OF SELECTED PROCESS ALTERNATIVES

Present study is concentrated on the three alternatives that are Conversion of HCl to $FeCl_2$, Evaporation Process and Crystallization of $FeCl_2$ Process.

5.3.1. CONVERSION OF HCl TO $FECl_2$

In this reclamation, it is aimed to convert all the unused HCl to $FeCl_2$ via addition of scrap iron. In that way the waste pickling liquor becomes $FeCl_2$ solution which can be used in many areas such as in dye and waste water treatment that is why it can easily be marketed. The reaction below will take place in this process.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

For the present study, reaction temperature was selected as 70°C, same as the feed temperature, which is within the optimum temperature range of 60°-90°C given in Clair (1995). One consideration of this process is the formation of explosive hydrogen gas. The hydrogen formed may be managed in different ways depending on the amount formed. H_2 can be burned for energy or can be used in the reduction process of Fe^{+3} to Fe^{+2}. H_2 is utilized for burning in this recovery alternative. Bubbles of hydrogen gas formed during the process would mix the solution in the reactor.

This process requires a reactor, a heat exchanger, a tank and a pump, the flowsheet of the process is shown in Figure 5.2. The resistance time reported to be any time ranging from two minutes to thirty hours preferably from 3 hours to 15 hours by Clair (1995). Reactor retention time was taken as 10 hour, based on this information given by Clair (1995). The calculation of the reactor energy balance is given in the APPENDIX C.

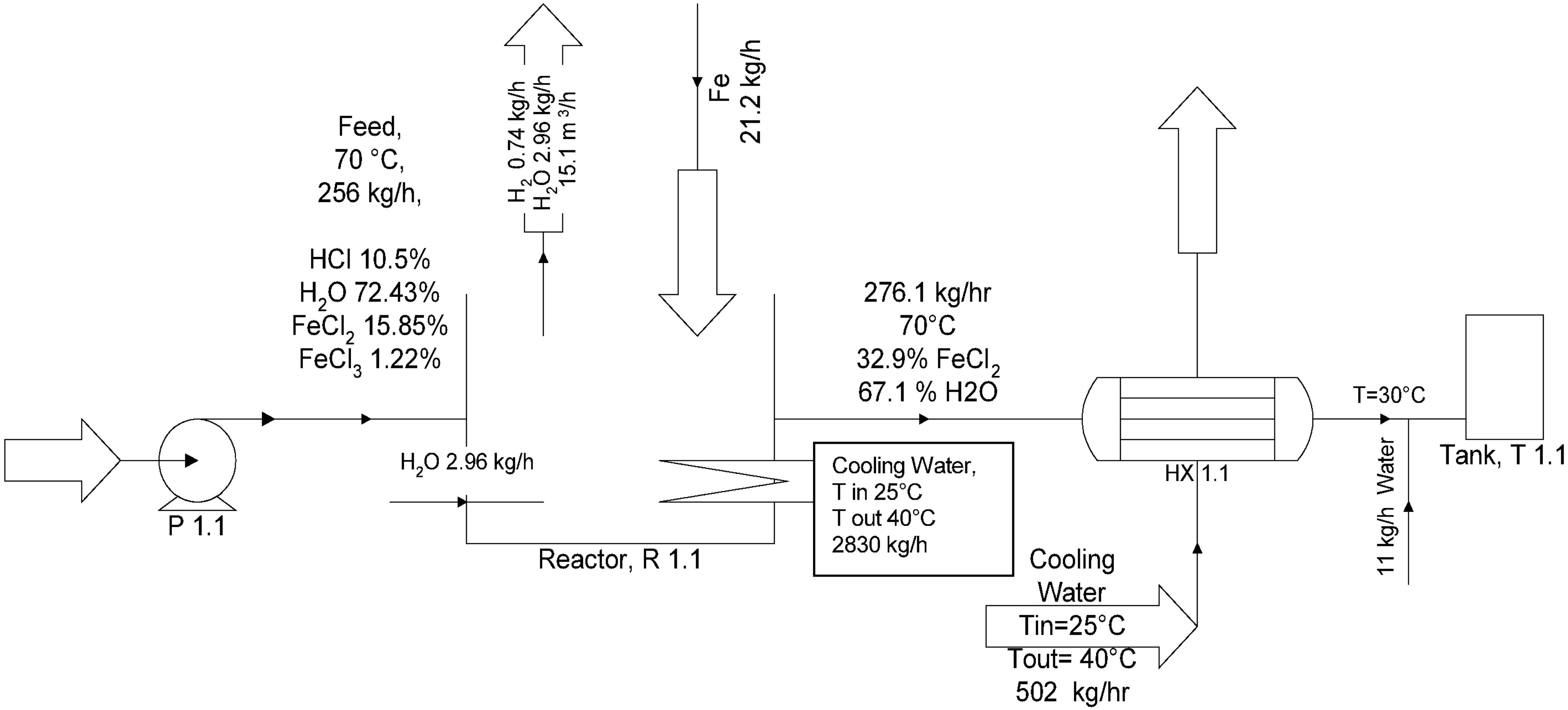

Figure 5.2. Flowsheet of Conversion Process of HCl to $FeCl_2$

The process equipment list is tabulated in Table 5.2.

Table 5.2. Equipment List for the Conversion of HCl to $FeCl_2$ Process

No	Equipment Code	Name	Function	Cost ($)
1	HX 1.1	Heat Exchanger	Cools the $FeCl_2$	5 100
2	P 1.1	Pump	Pumps WPL	700
3	T 1.1	Tank	Stores $FeCl_2$	33 200
4	R 1.1	Reactor	Converts HCl to $FeCl_2$	16 800
5	Fl 1.1	Flare	Flares H_2	2450
6	T 1.2	Fe-storage Tank	Stores Scrap Iron	3 750

Optimum Heat Exchanger design result for that recovery alternative is tabulated in Table 5.3.

Table 5.3 Heat Exchanger design result for the Conversion of HCl to $FeCl_2$

Type	**1-4 HE**
Tube Length, m	**2.44 (8 ft)**
Tube OD, cm	**3.8 (1.5 inch)**
Pitch (cm)	**4.76 (1 7/8 inch)**
No of Tubes	**34**
Shell ID, m	**0.74 m (29 inch)**
Uc, W/m^2 K	**465.6**
Ud, W/m^2 K	**63**
Ac, m^2	**5.4**
Design Area, m^2	**9.9**
Rd	**0.001367**
Rd req	**0.001019**

Cost $	**5100**

$FeCl_3$ may also react with Fe to form $FeCl_2$, for the present study; it was assumed that HCl reacts only with Fe to form $FeCl_2$.

5.3.2. EVAPORATION PROCESS

5.3.2.1. PRELIMINARY EVALUATION OF POSSIBLE FLOWSHEET ARRANGEMENTS

Vapor formation is achievable via heating or flash operation. For the evaporation process, different process alternatives were studied and simulated in order to come up with the best flowsheet arrangement of this recovery alternative. Moreover, it was tried to see the efficiency of flash operation in the separation of WPL that is why some process alternatives include flash operation. Before plant data became available, literature WPL composition data 5% HCl, 20% $FeCl_2$, 75% H_2O (weight basis) with flowrate of 100 kg/h, was taken as basis for these flowsheet simulations. Simulations were done with Aspen Plus.

The important criteria for the selection of best flowsheet arrangement are

- Heat duty

- % HCl recovery.

% HCl recovery depends on heat supplied to the WPL, pressure and temperature of feed and flash column.

In the first alternative, feed was heated to saturated liquid at high-pressures (2,4,6,10 atm) and than flashed adiabaticaly to low pressures (0.1,0.6,1 atm), the flowsheet is shown in Figure 5.3. The results of simulations are given in Table APP.9. %HCl recoveries ranged from 1% to 4.5%. It was seen that, the process is not efficient and applicable.

As it was seen in the first alternative only flash operation was not efficient; heat is supplied in the second case. In the second process alternative as can be seen in the Figure 5.4, simulation of the recovery process was done when the WPL is saturated liquid at different feed pressures (1, 2, 3, 4, 6, 8, 10 atm) and flashed to different flash pressures (0.1, 0.3, 0.5 atm) with different fractions of vapor formation (0.3, 0.45, 0.6) by the help of heat supplied within the flash unit. For all simulations the required amount of heat was obtained. The results of simulations are given in Table APP.10.

The % HCl recovered ranged from 13% to 78%. As the result of second alternative simulations, it was concluded that the fraction recovered in that case is still low and the process alternative is not applicable, and flash operation alone is insufficient even at high pressures.

In the third case, heat supplied in the previous case was given directly to the feed, which would partially vaporize the feed, as indicated in Figure 5.5. The feeds with different pressures (4,8,10 atm) are heated and vapor– liquid mixture is obtained and flashed to low pressures (0.1,1 atm). The results of simulations are given in Table APP.11. % HCl recovery ranged from 1% to 71%.

In the fourth alternative, given in Figure 5.6, the feed as vapor-liquid mixture with high-pressure (10 atm) was first flashed to 1 atm. Vapor was separated and liquid was flashed again. The results of simulations are given in Table APP.12. % HCl recovery was 78.4%.

In the fifth alternative, the feed (1, 2 atm), as vapor-liquid mixture, is first separated in a vapor-liquid separator. Liquid is flashed to 0.1 atm. It was seen that addition of a flash column did not significantly improve the separation efficiency. Flowsheet is given in Figure 5.7. The results of simulations are given in Table APP.13. The % HCl recovery ranged from 75% to 99.9%.

In the sixth process alternative, it was decided to eliminate the flash column present in the fifth alternative. The flowsheet is given in Figure 5.8. The results of simulations are given in Table APP.14. % HCl recovery ranged from 68% to 90%. The 90% HCl recovery was the highest HCl recovery that can be achieved without solid formation in the evaporator. Even 99.9 % HCl recovery can be achieved with alternative six, if the temperature of the heat exchanger is increased. That is why alternative 6 was selected as the best process applicable.

Conclusive remarks on the flowsheet simulation studies indicate, flashing the WPL from high pressure is not efficient, flash column does not increase the separation efficiency, best alternative is sixth alternative process that does not have a flash column.

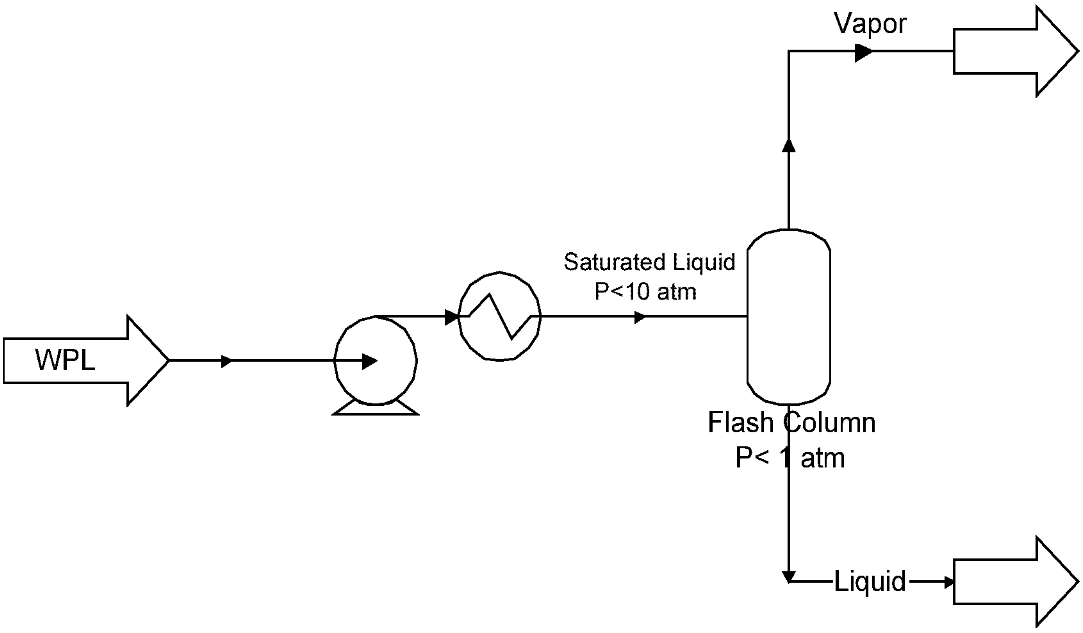

Figure 5.3. Flowsheet for Alternative –1 in Evaporation Process

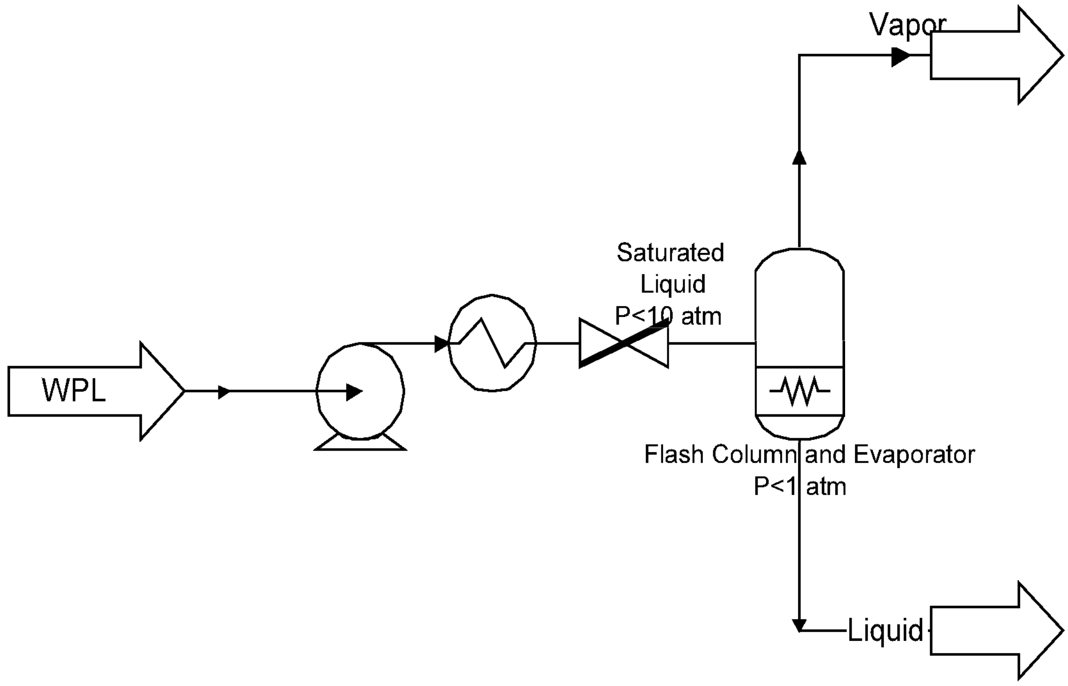

Figure 5.4. Flowsheet for Alternative –2 in Evaporation Process

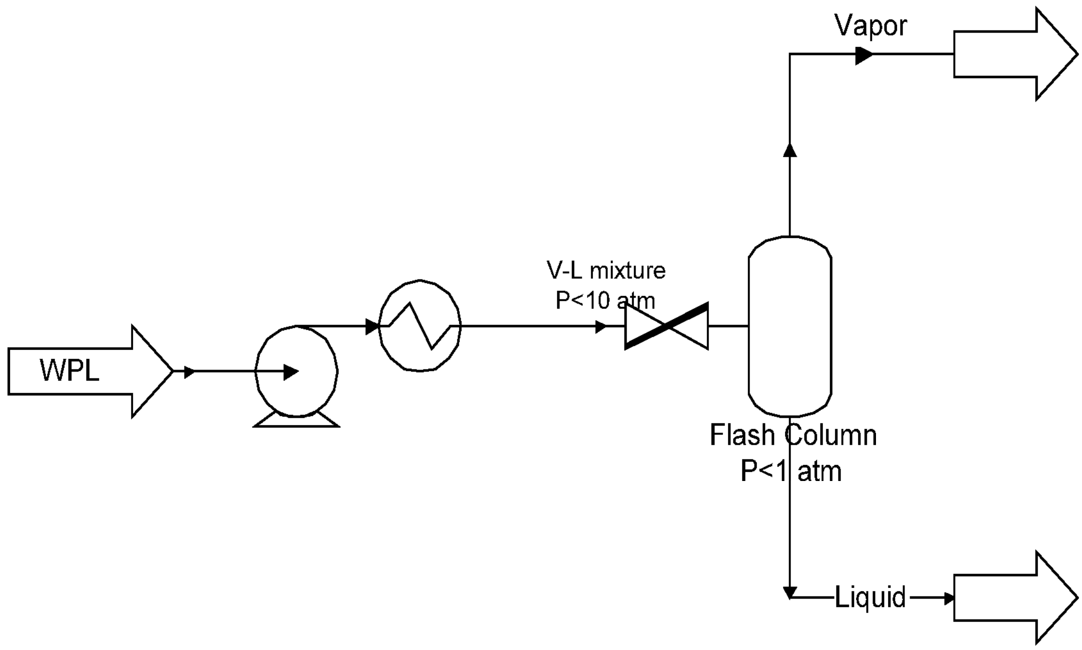

Figure 5.5. Flowsheet for Alternative –3 in Evaporation Process

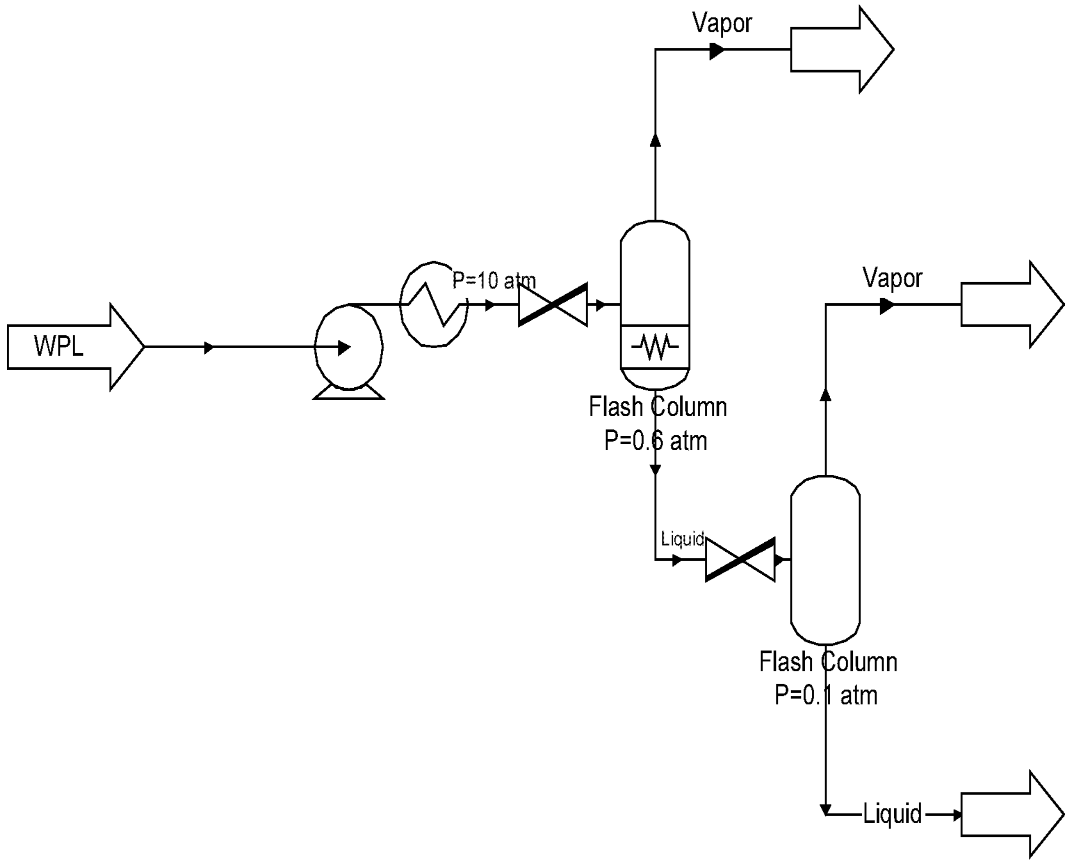

Figure 5.6. Flowsheet for Alternative –4 in Evaporation Process

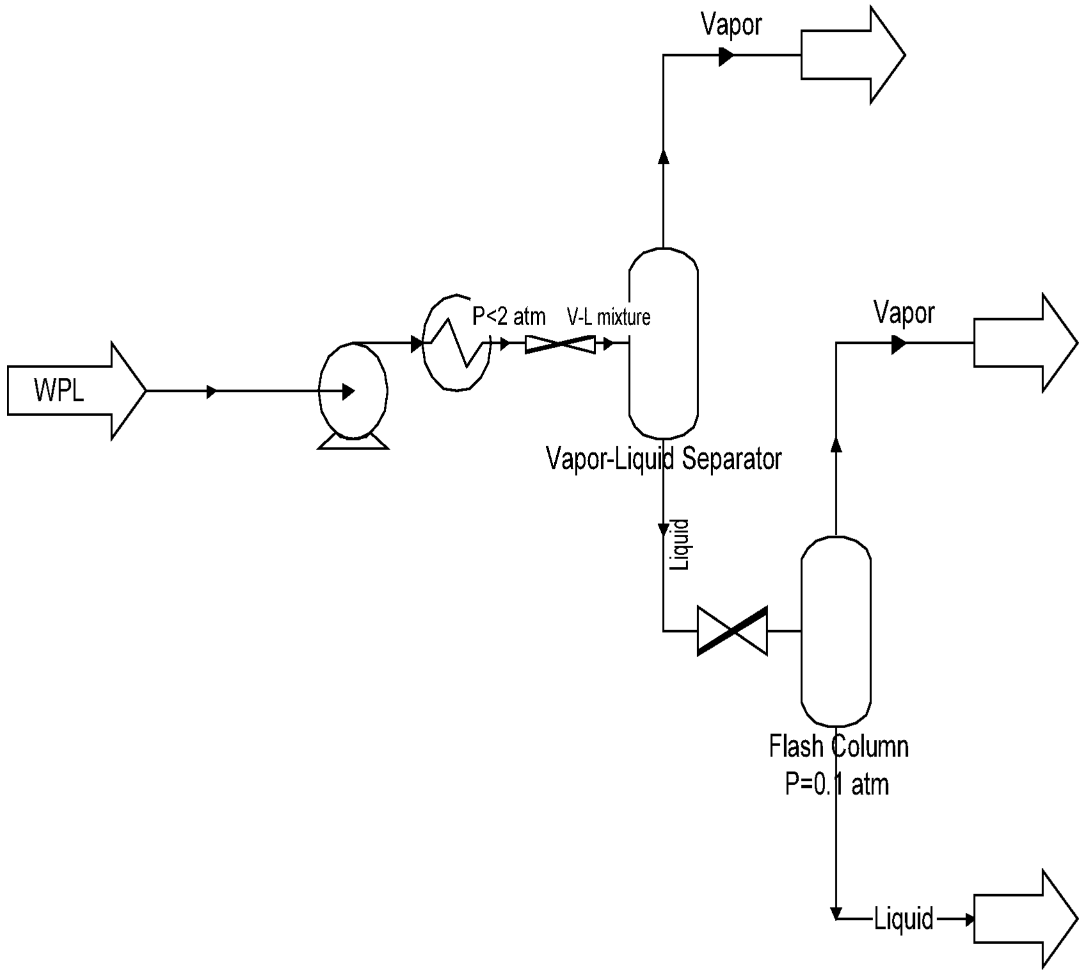

Figure 5.7. Flowsheet for Alternative –5 in Evaporation Process

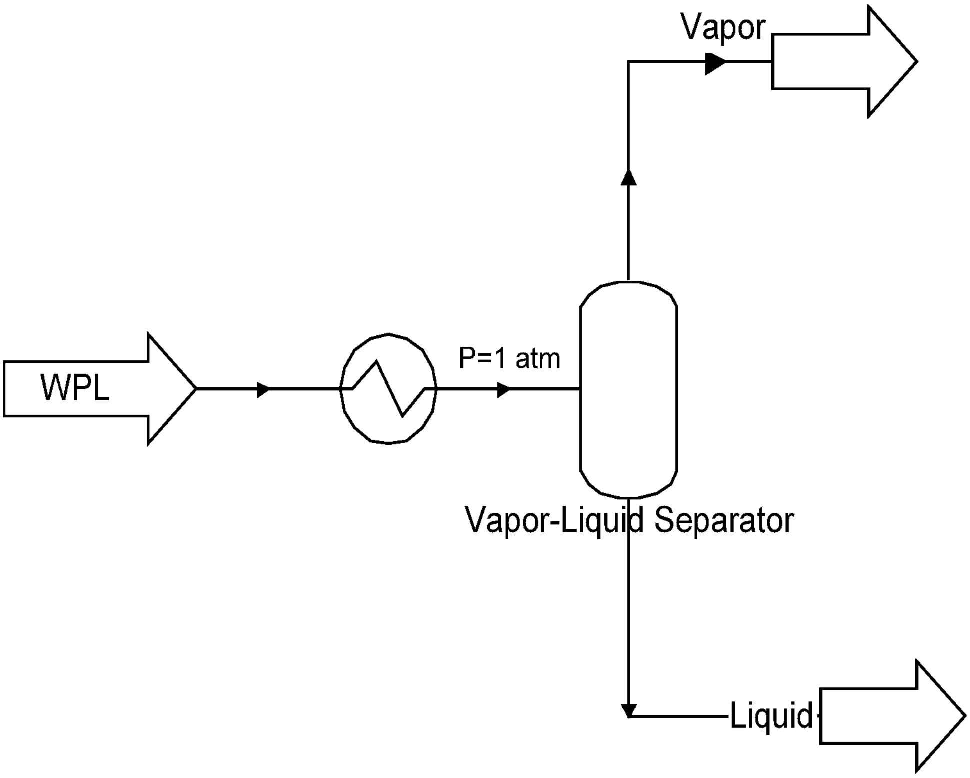

Figure 5.8. Flowsheet for Alternative –6 in Evaporation Process

5.3.2.2. DETAILED PROCESS SYNTHESIS

The process synthesis was done for the sixth flowsheet alternative. In the present study the process design of evaporation process was carried out for two cases, namely allowing for solid formation in the evaporator so as to recover more HCl and not allowing solid formation in the evaporator to simplify process. When considerable amount of HCl was left in the liquid phase, it was converted to $FeCl_2$ via Fe addition as was done in the conversion of HCl to $FeCl_2$ Process. Otherwise no need for further treatment.

5.3.2.2.1. NO SOLID FORMATION IN THE EVAPORATOR (EPNS)

The integrated system consists of three heat exchangers, an evaporator, a reactor, two pumps and two tanks and a valve. The flowsheet of the process is given in Figure 5.9 and the equipment list of this process is tabulated in Table 5.4. 72.5 % HCl recovery was achieved in this alternative. Some amount of water would be added to the liquid phase from the evaporator then would be cooled to 30 °C. The vapor phase from the evaporator is divided into two streams and one stream is used to heat up the feed stream, as can be seen in Figure 5.9. Cooling water cools the other stream to such a temperature that when the combined recycle stream is mixed with fresh acid and water so that the final temperature would be 70 °C. The liquor leaving the evaporator contains about 7.2% HCl.

The HCl in the solution was reacted with iron to convert it to ferrous chloride.

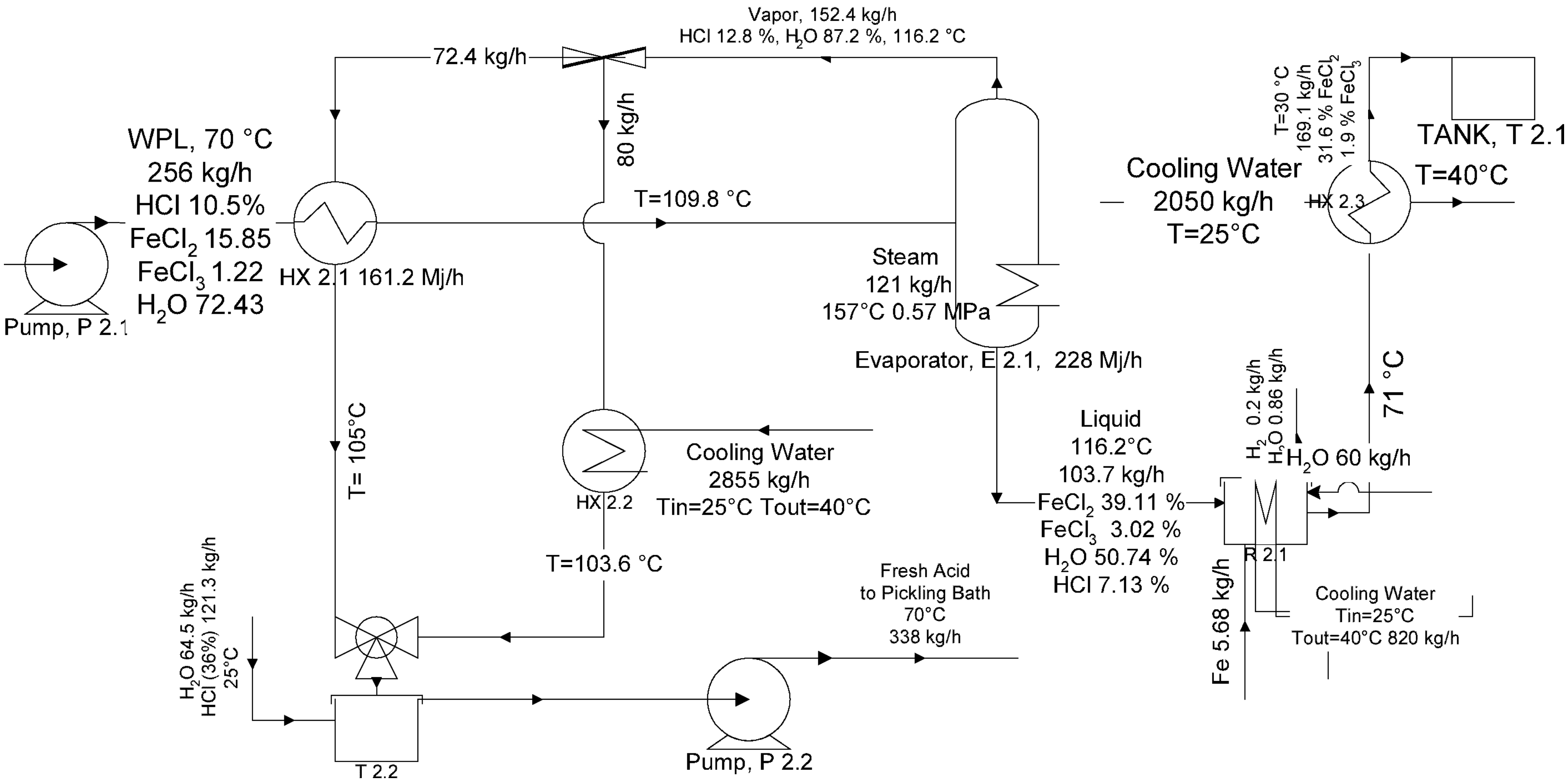

Figure 5.9. Flowsheet for Evaporation Process without Solid Formation

When iron is added to convert all the HCl to $FeCl_2$, H_2 gas is evolved. The energy balance for that process is given in APPENDIX E.

Table 5.4. Equipment list for the Evaporation Process with no Solid Formation

No	Equipment Code	Name	Function	Cost ($)
1	HX 2.1	Heat Exchanger	Heats WPL	41 300
2	HX 2.2	Heat Exchanger	Cools Vapor ($HCl+H_2O$)	4 100
3	HX 2.3	Heat Exchanger	Cools $FeCl_2$	1 850
4	E 2.1	Evaporator	Evaporates the WPL	6 700
5	P 2.1	Pump	Pumps WPL	700
6	P 2.2	Pump	Pumps Fresh Acid	700
7	T 2.1	Tank	Stores $FeCl_2$	20 800
8	R 2.1	Reactor	Converts HCl to $FeCl_2$	12 000
9	T 2.2	Mixing Tank	Mixes fresh acid with recycled acid from heat Exchangers	2 100
10	Fl 2.1	Flare	Flares H_2	800
11	V 2.1	Valve	Arranges Flowrate of Vapor from Evaporator	1 070

Then the $FeCl_2$ solution can be diluted for further concentration adjustment, to have the same concentration in all recovery alternatives. The tank design capacity is 20 days storage of capacity. In this recovery process H_2 is evolved, that H_2 can be flared or can be reacted with chlorine gas to produce HCl. If HCl is produced, it can be used to supply HCl make-up. Production of HCl is the possible process improvement for the designed process. In the present design, it is planed to flare the H_2. The heat exchanger design results for this recovery alternative is tabulated in Table 5.5 and Table 5.6.

Table 5.5. Double Pipe Heat exchanger designed for the Evaporation Process without solid formation (EPNS)

	HX 2.3
Type	**Double pipe**
U, $W/m^2 °C$	**2285**
Ad, m^2	**0.18**
Linear length, m	**3.05 (10 ft)**
Cost,$	**1 850**

Table 5.6. Heat Exchanger Design of Evaporation Process without Solid Formation (EPNS)

	HX 2.1	HX 2.2	EVAP 2
	1-1 HE	**1-4 HE**	**1-4 HE**
Tube Length, m	**4.88 (16 ft)**	**1.22 (4 ft)**	**1.22 (4 ft)**
Tube OD, cm	**3.18 (1.25 inch)**	**3.18 (1.25 inch)**	**1.9 (0.75 inch)**
Pitch (cm)	**3.97 (1 9/16 in)**	**3.97 (1 9/16 in)**	**2.54 (1 in)**
No of Tubes	**193**	**37**	**82**
Shell ID, cm	**73.7 (29 inch)**	**38.7 (15.25 inch)**	**33.7 (13.25 inch)**
Uc, W/m2 K	**185**	**376.5**	**336.5**
Ud, W/m2 K	**154.4**	**143**	**241**
Ac, m2	**78.2**	**1.7**	**4.3**
Design Area, m2	**94**	**4.50**	**6**
Weight, kg	**371.7**	**49**	**42.5**
Rd	**0.001081**	**0.0044**	**0.00118**
Rd req	**0.001019**	**0.001019**	**0.00102**
Cost $	**41 300**	**4 100**	**6 700**

5.3.2.2.2. ALLOWING FOR SOLID FORMATION IN THE EVAPORATOR (EPS)

The integrated recovery system consists of three heat exchangers, an evaporator, two pumps, two mixing tanks, a valve and a storage tank. Required amount of water would be added to the liquid phase from the evaporator, then it would be cooled to 30 °C. The vapor phase from the evaporator is divided into two streams one of which is used to heat up the feed stream. The other stream is cooled to reach the temperature that has enough energy to have fresh acid stream at 70 °C when mixed with make-up HCl stream, additional water required for desired acid composition and the other divided stream. The liquor leaving from the evaporator contains about 0.84% HCl. The equipment list for this process is given in Table 5.7. Integrated flowsheet of the process is given in Figure 5.10.

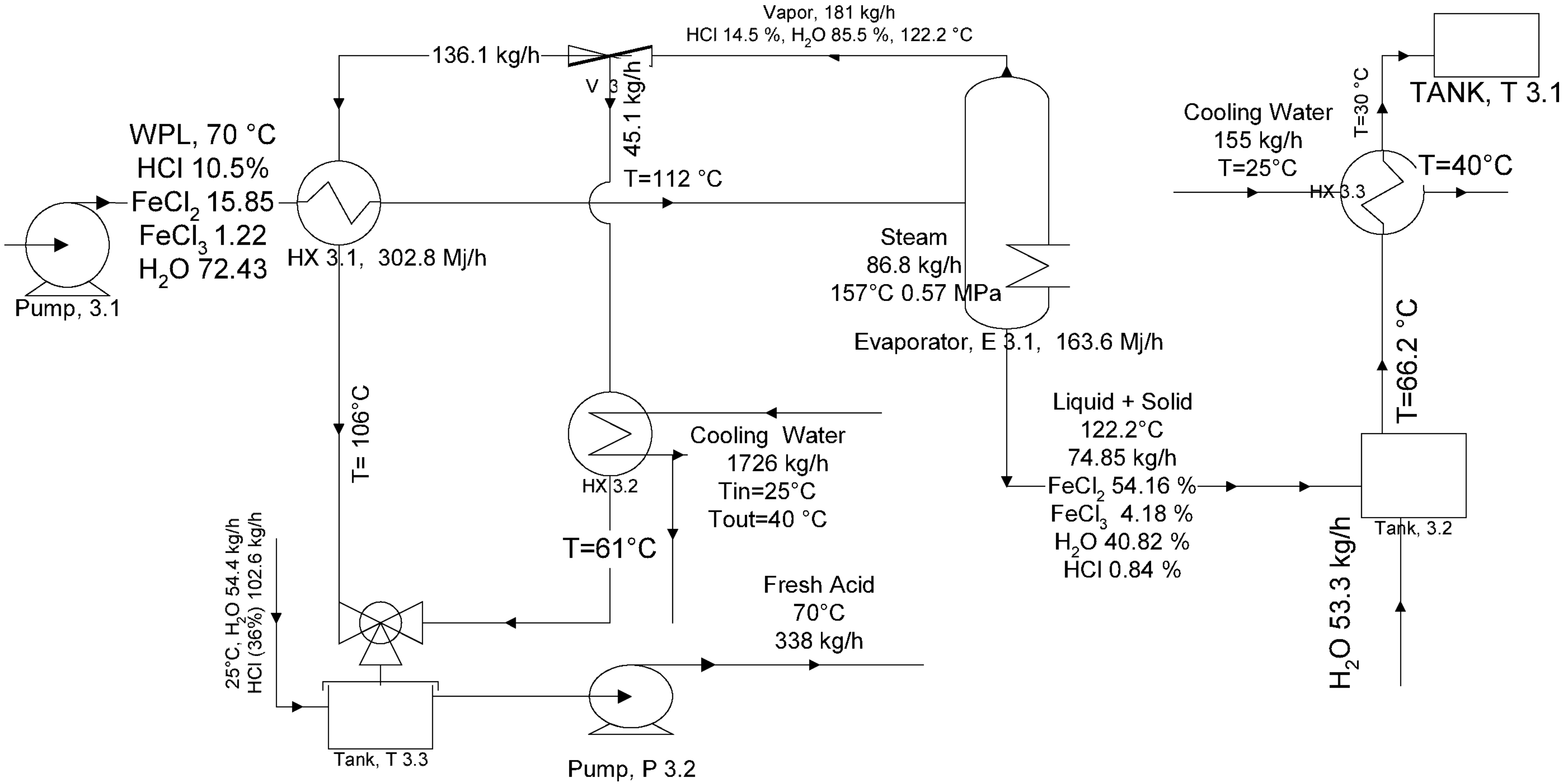

Figure 5.10. Flowsheet for Evaporation Process with Solid Formation

Table 5.7. Equipment List for the Evaporation Process with Solid Formation in the Evaporator

No	Equipment Code	Name	Function	Cost ($)
1	HX 3.1	Heat Exchanger	Heats WPL	46 800
2	HX 3.2	Heat Exchanger	Cools $HCl+H_2O$	3 450
3	HX 3.3	Heat Exchanger	Cools $FeCl_2$	1 900
4	E 3.1	Evaporator	Evaporates the WPL	6 150
5	P 3.1	Pump	Pumps WPL	700
6	P 3.2	Pump	Pumps Fresh Acid	700
7	T 3.1	Tank	Stores $FeCl_2$	17 450
8	T 3.2	Mixing Tank	Mixes $FeCl_2$ with water	2 200
9	T 3.3	Mixing Tank	Mixes fresh acid from heat Exchangers	2 100
10	V 3.1	Valve	Arranges Flowrate of Vapor from Evaporator	1 070

The heat exchanger design results for this recovery alternative is tabulated in the Table 5.8 and Table 5.9.

Table 5.8. Double Pipe Heat exchanger designed for the Evaporation Process with solid formation (EPS)

	HX 3.3
Type	**Double pipe**
U, W/m2°C	**748**
Ad, m2	**0.4**
Linear length, m	**6.1 (20 ft)**
Cost, $	**1 900**

Table 5.9. Heat Exchanger Design of Evaporation Process with Solid Formation (EPS)

	HX 3.1	HX 3.2	EVAP 3
	1-4 HE	**1-4 HE**	**1-2 HE**
Tube Length, m	**4.88 (16 ft)**	**1.22 (4 ft)**	**1.22 (4 ft)**
Tube OD, cm	**2.54 (1 inch)**	**3.18 (1.25 inch)**	**3.18 (1.25 inch)**
Pitch (cm)	**3.18 1.25 in**	**3.97 1 9/16 in**	**3.97 1 9/16 in**
No of Tubes	**311**	**22**	**40**
Shell ID, cm	**994 (37 inch)**	**30.5 (12 inch)**	**38.7 (15.25 inch)**
Uc, W/m2 K	**144.7**	**412**	**311**
Ud, W/m2 K	**124.8**	**145**	**236**
Ac, m2	**130.4**	**1**	**3.7**
Design Area, m2	**151.2**	**2.7**	**4.9**
Weight, kg	**474.2**	**39**	**49**
Rd	**0.0011**	**0.0044**	**0.001024**
Rd req	**0.001019**	**0.001019**	**0.001019**
Cost $	**46 800**	**3 450**	**6 150**

5.3.3. CRYSTALLIZATION PROCESS

The recovery of waste pickling acids can also be achieved by means of crystallization. The aim should be existence of minimum $FeCl_2$ in the recovered acid stream. The lower the temperature, the lower the ferrous chloride solubility would be in the recovered acid stream because of inverse solubility of $FeCl_2$ with temperature. As it was mentioned in Chapter 2, hydrogen chloride has common ion effect on iron chloride solubility that is; the solubility of iron chloride decreases as HCl concentration increases. Low iron chloride solubility is achieved at low temperatures and at high HCl concentrations.

In the present study, a new approach, which was not encountered in the literature so far for the crystallization type of recovery systems, was applied. As a new approach, make up acid is added to the pickling baths directly before crystallization. Moreover, in the present study, as a second new approach, addition of make-up HCl was done with the usage of 36 % HCl before crystallization, by this way both decrease in temperature of crystallized stream and also decrease of solubility of $FeCl_2$ was achieved. Although the WPL + 36 % HCl stream require water addition, water is added after the crystallization in order for not to dilute the WPL+36 % HCL mixture that would cause more $FeCl_2$ to remain in solutions. As the third new approach, the water to be added was in the form of live steam, which would be injected into recovered acid stream to heat up the recovered acid stream, by this way use of a heat exchanger is eliminated.

In the crystallization recovery process, Fe^{+3} in the waste pickle liquor should be reduced to Fe^{+2} because high solubility of $FeCl_3$ in the HCl and H_2O would cause the accumulation of $FeCl_3$. It is the fist time that applies reduction of $FeCl_3$ to $FeCl_2$. After the reduction of $FeCl_3$ the make-up acid and water at room temperature is added to waste pickle liquor and the mixture is cooled to about 60°C. Further the mixed stream is crystallized. Surface cooled crystallizer is suitable for the first stage of crystallization and direct-contact crystallizer should be used for the second stage because of very low operating temperature (Perry, 1984).

The designed process has the following new advantages over the other ones that are designed before,

1. HCl is added before crystallization to lower the $FeCl_2$ solubility

2. $FeCl_2$ in the regenerated acid is lower than the previously designed ones

3. Steam is injected to the fresh acid to heat it to bath temperature this process eliminates the usage of an additional heat exchanger

4. Reduction of $FeCl_3$ to $FeCl_2$ was suggested.

Flowsheet integration was done on these new approaches. The mass balance of the crystallization process should be done before flowsheet integration. The mass balance of the system is given in the APPENDIX H. Make –up acid is added directly to the WPL in order to increase the HCl composition that would decrease the $FeCl_2$ solubility in the crystallization operation. The amount of make –up HCl is calculated in APPENDIX H. Crystallizer temperature was selected as –57°C, since with reciprocating or rotary type of compressors two-stage plants are practical from about –28.9°C to –57.7 °C. In this temperature range two-stage system can enable power savings (Perry, 1984). In the crystallization recovery process, instead of using one crystallizer, more than one crystallizer was used in order to save energy. Here, the comparison of using 2 and three crystallizers for recovery process is done.

Crystallization Using Two Crystallizers;

In order to decrease the energy requirement of the process the refrigeration system is divided in to two parts, in the first crystallizer; WPL is cooled to –40 °C with the mother liquor of the second crystallizer, the flow diagram is shown in the Figure 5.11. Crystals formed in the first crystallizer are separated and the mother liquor is further cooled to –57°C as can be seen in the Figure 5.11. Water is further added for final HCl concentration adjustment. The mass balances for the first and second crystallizers are given in APPENDIX H.

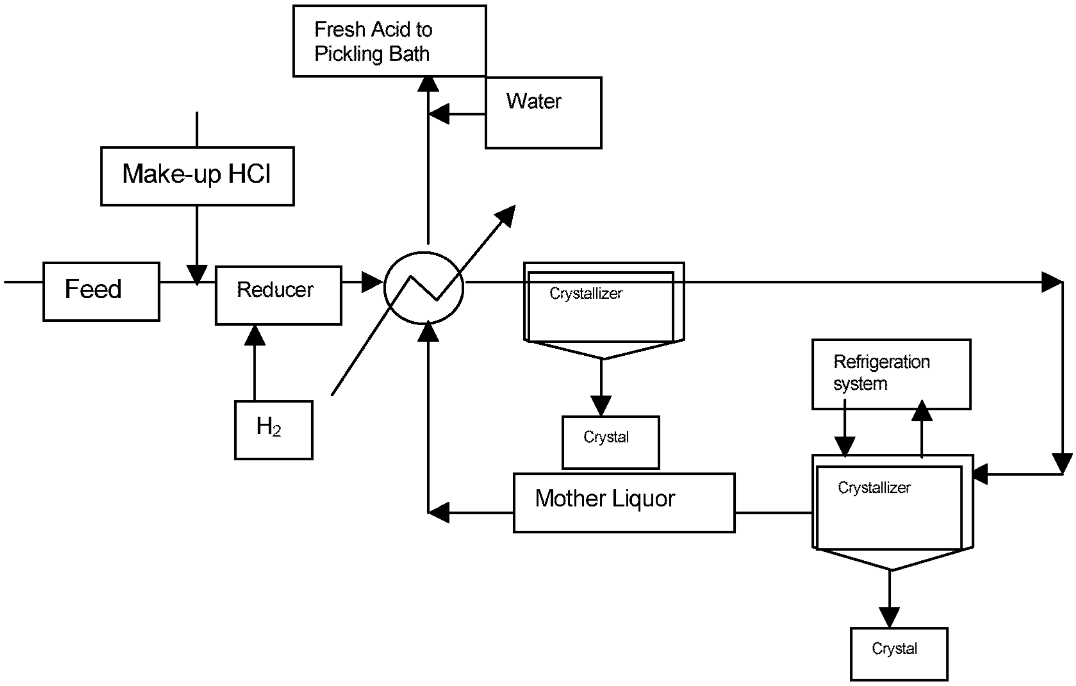

Figure 5.11. Flow diagram for Crystallization Using Two Crystallizers

Crystallization Using Three Crystallizers;

In order to decrease the heat duty of the heat exchanger of the Crystallization Using Two- Crystallizers Process, one more crystallizer can be added to the crystallization system. These two processes would be compared by the economics of processes in this section in order to end up with final crystallization process, on which flowsheet integration would be done. The flowsheet of the process is given in the Figure 5.12, As can be seen in the figure feed is cooled by the mother liquor originally coming from Crystallizer III. Mother liquor of Crystallizer III is previously heated in the HX-B. Heat duty of the only one heat exchanger in the case of Crystallization Using Two- Crystallizers Process is divided into two parts. The economies of these two processes should be compared in order to end up with flowsheet integration for the crystallization case.

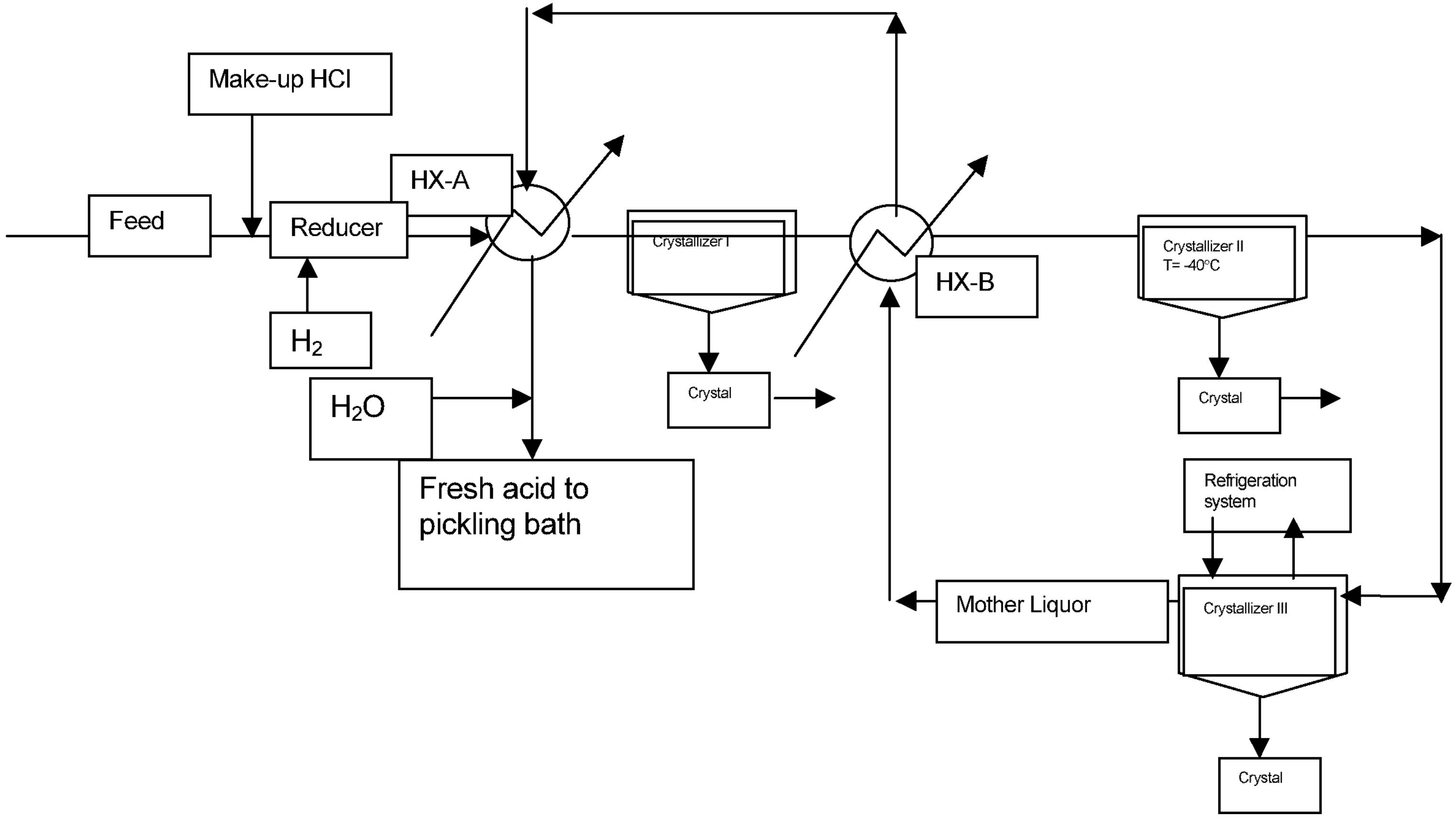

Figure 5.12. Flow diagram for $FeCl_2$ Crystallization Process Using Three Crystallizers

The integrated crystallization system would consist of heat exchanger, crystallizer, filter, pump, and Fe^{+3} reduction column. The crystallizer should be made of stainless steel with teflon lining that is resistant to corrosion.

Crystallization can be done in two, three or more stages. The two cases that are using two and three Crystallizers for the crystallization process are compared via purchased equipment cost of these two processes. The costs of equipment for these cases are tabulated in Table 5.10 and Table 5.11.

Table 5.10. Equipment Cost of Crystallization Recovery Process, when two crystallizers are used for the recovery process

Equipment	Cost ($)
HX 4.1	**23 300**
Crystallizer-1	**45 800**
Fe^{+3} Reducer	**4 200**
Crystallizer-2	**42 800**
Filter	**22 500**
Industrial Refrigeration	**42 000**
Tank	**11 000**
3 Pumps	**2 100**

Purchased Equipment Cost =193 700$

Table 5.11. Equipment Cost of Crystallization Recovery Process, when three crystallizers are used for the recovery process

Equipment	Cost ($)
HX.A	**5 600**
HX.B	**21 900**
Crystallizer-1	**45 800**
Fe^{+3} Reducer	**4 200**
Crystallizer-2	**43 900**
Crystallizer-3	**42 800**
Filter	**22 500**
Industrial Refrigeration	**42 000**
Tank	**11 000**
3 Pumps	**2 100**

Purchased Equipment Cost = 241 900 $

These two processes have the same operating cost, the difference comes from the purchased equipment cost. As can be seen Using two crystallizers is more economical. The process integration will be done on the Using two crystallizer recovery process. The integrated flowsheet of the process is given in the Figure 5.13, as can be seen in the Figure 5.13,1.85 % $FeCl_2$ composition is achieved in the recovered acid stream, this value is lower than the value given in Petterson (1991) which was about 12% $FeCl_2$ in the recovered acid stream.

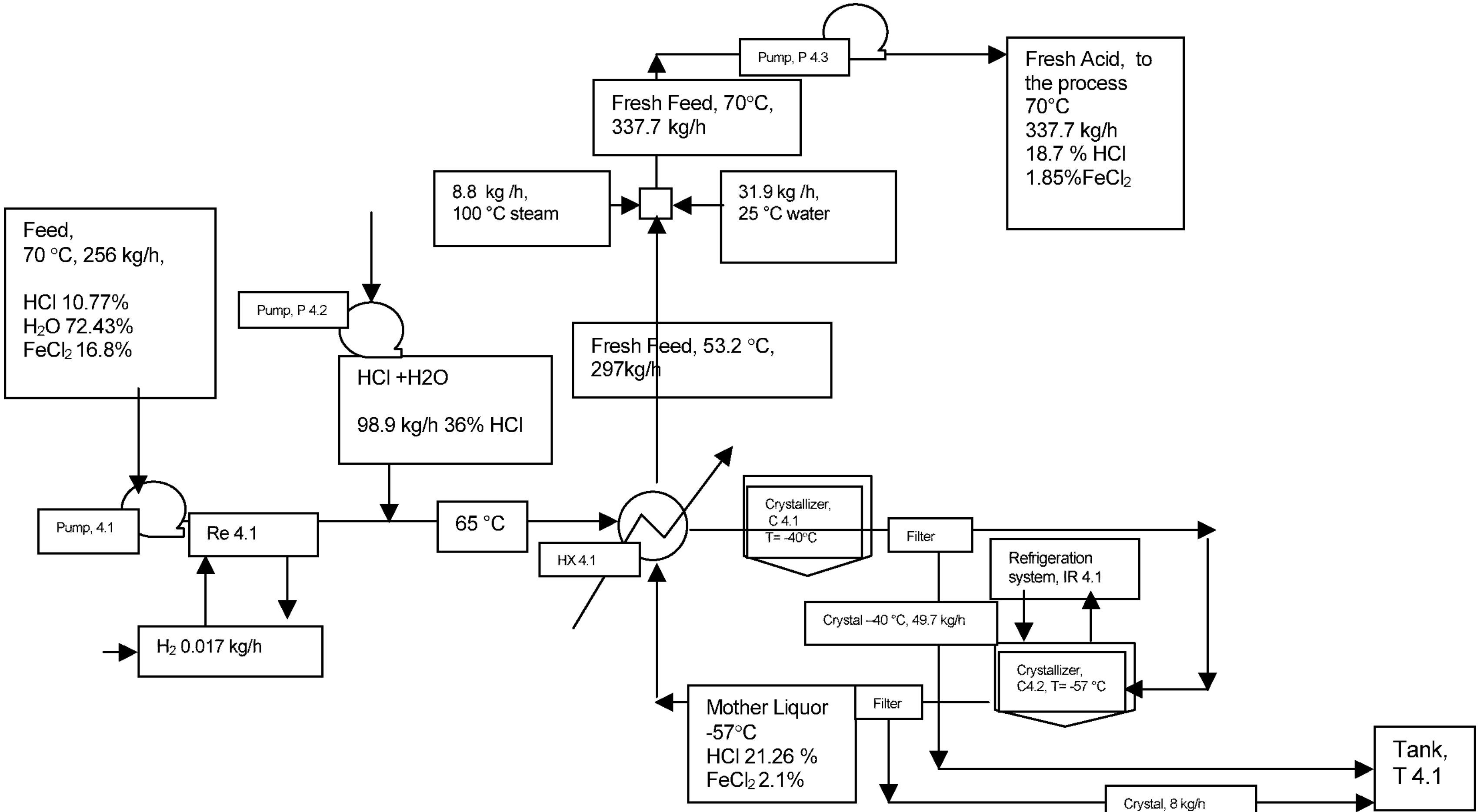

Figure 5.13. Flowsheet of $FeCl_2$ Crystallization Process Using Two Crystallizers

Equipment list for the crystallization process is tabulated in Table 5.12.

Table 5.12. Equipment List for the Crystallization Recovery Process

No	Equipment Code	Name	Function	Cost ($)
1	HX 4.1	Heat Exchanger	Cools the feed	23 300
2	C 4.1	Crystallizer-1	Crystalizes the WPL	45 800
3	Re 4.1	Fe^{+3} Reducer	Reduces Fe^{+3} to Fe^{+2}	4 200
4	C 4.2	Crystallizer-2	Crystalizes the mother liquor from Crystallizer-1	42 800
5	Fi 4.1	Filter	Filters the crystals	22 500
6	IR 4.1	Industrial Refrigeration	Crystallizes the mother liquor	42 000
7	T 4.1	Tank	Stores $FeCl_2$	11 000
8	P 4.1	Pump	Pumps WPL	700
9	P 4.2	Pump	Pumps make-up HCl	700
10	P 4.3	Pump	Pumps Fresh Feed	700

Heat exchanger design results for the crystallization process is tabulated in Table 5.13.

Table 5.13. Heat Exchanger Design Results for Crystallization Process

	HX 4.1
Tube Length, m	4.88 (16 ft)
Tube OD, cm	3.18 (1.25 inch)
Pitch (square)	3.97 (1 9/16 inch)
No of Tubes	106
Shell ID, cm	59.1 (23.25 inch)
Uc, W/m2 K	49.05
Ud, W/m2 K	43.56
Ac, m2	45.70
Design Area, m2	51.54
Rd	0.00257
Rd req	0.002
Cost $	23 300

CHAPTER 6

ECONOMICAL EVALUATION

6.1. ECONOMICAL METHOD OF ATTACK

After the process synthesis and design have been completed, the recovery alternatives were ready to compare with each other. Purchased equipment cost for each alternative was calculated. US Dollar was used for the cost and prices. Plant overhead costs and general expenses, insurance, taxes were not calculated for all process alternatives for economic comparison of processes. Fixed Capital Investment for each alternative was calculated according to the Table 6.1, obtained from Peters and Timmerhaus (1991), which estimates of capital investment basing on purchased equipment cost.

Using the purchased equipment cost as basis for the estimation of the fixed capital investment is a well – known shortcut solution, however it might have led to a very conservative (if not totally pessimistic) estimation. Yet this could be taken as a supplementary evidence for the reliability of the analysis.

The equipment costs were taken from Peters and Timmerhaus (1991) and heat exchanger costs are calculated with the method given in Cheremisinoff (1986). Piping requires teflon lining for corrosion resistance, which was estimated as three fold of piping cost. Lining cost was included for the estimation of fixed capital investment. Tanks were designed for 20-day capacity to collect the liquid by-product. The cost of one spare pump was added for each pump during the calculation of purchased equipment cost. That is, the number of pumps to be bought is two fold of required number of pumps.

Table 6.1. Estimation of Capital Investment Cost

I. Direct Costs = Material and Labor involved in actual installation of complete facility *(70-85 % of Fixed Capital Investment) (taken as 80 %)*
A. Equipment + Installation + Instrumentation + Piping +Electrical +Insulation +Painting
1.Purchased Equipment Cost *(Estimated)*
2.Installation, including insulation and painting *(25-55 % of Purchased Equipment Cost) (taken as 50%)*
3.Instrumentation and Control, installed *(6-30 % of Purchased Equipment Cost) (taken as 30%)*
4.Piping, installed *(10-80 % of Purchased Equipment Cost) (taken as 60%)* + Lining
5.Electrical,Installed*(10-40 % of Purchased Equipment Cost) (taken as 40%)*
B. Buildings, process and axillary *(10-70 % of Purchased Equipment Cost) (taken as 10%)*
C. Service facilities and yard improvements *(40-100 % of Purchased Equipment Cost) (taken as 40%)*
D. Land (1-2% of Fixed –Capital Investment) *(ignored)*
II. Indirect Cost = Expenses which are not directly involved with material and Labor of actual installation complete facility*(15-30 % of Fixed –Capital Investment) (taken as 20%)*
III. Fixed-Capital Investment = Direct Cost +Indirect Cost
IV. Working Capital Investment *(1 month Raw Material Cost* + *1 month Manufacturing Cost* + *1 month Production Cost)*
V. Total Capital Investment =FCI + WCI

Operating Cost, that includes chemical cost, energy cost, transportation cost, disposal cost, for each alternative was calculated. 10% heat loss is included for steam energy cost. Each alternative was compared with each other the most economical alternative was determined by tabulating cash flow diagram relative to the current situation. That is the net earning value was determined via cash flow diagram when the current process is shift to the each recovery process alternative.

6.2. ECONOMICAL EVALUATION

Equipment costs for each alternative is tabulated from Table 6.2 to Table 6.5.

Table 6.2. Equipment Cost of Process Alternative of Conversion of HCl to $FeCl_2$

Equipment	Cost ($)
Reactor	**16 800**
Tank	**33 200**
2 Pumps	**1 400**
HX.1.1	**5 100**
Flare	**2 450**
Fe-Storage Tank	**3 750**
Purchased Equipment Cost	**62 700**

Table 6.3. Equipment Cost of the Case of Evaporation Process without Solid Formation

Equipment	**Cost** ($)
HX.2.1	**41 300**
HX.2.2	**4 100**
HX.2.3	**1 850**
4 Pumps	**2 800**
Tank	**20 800**
Valve	**1 070**
Evaporator	**6 700**
Flare	**800**
Reactor	**12 000**
Mixing Tank	**2 100**
Purchased Equipment Cost	**93 520**

Table 6.4. Equipment Cost of the Case of Evaporation Process with Solid Formation

Equipment	**Cost** ($)
HX.3.1	**46 800**
HX.3.2	**3 450**
HX.3.3	**1 900**
4 Pumps	**2 800**
Tank	**17 450**
Valve	**1 070**
2 Mixing Tank	**4 300**
Evaporator	**6 150**
Purchased Equipment Cost	**83 920**

Table 6.5. Equipment Cost of Crystallization of $FeCl_2$ Recovery Process

Equipment	**Cost** ($)
HX.4.1	**23 300**
Crystallizer	**45 800**
Fe^{+3} Reducer	**4 200**
Crystallizer	**42 800**
Filter	**22 500**
Industrial Refrigeration	**42 000**
Tank	**11 000**
6 Pumps	**4 200**
Purchased Equipment Cost	**195 800**

The chemical cost that was taken from the factories, such as Akkim, producing these chemicals is given in price row in the Table 6.6 for each process alternative. The cost of cooling water was calculated via the assumption of 1/40 of the cooling water is lost while it is cooled in the cooling tower. The electricity cost was taken from Peters and Timmerhaus (1991).

Table 6.6. Annual Chemical Cost for Process Alternatives

Process Alternative		HCl	NaOH	H_2	Fe	Process Water	COST of CHEMICALS (1000 $)/YR
	Price $/1000 kg	**100**	**230**	**87 120**	**405**	**0.264**	
CHF	**1000 Kg/year**	**1389**	**-**	**-**	**168**	**111**	
	Cost (1000$/year)	**138.9**	**-**	**-**	**5.4**	**0.0**	**144.3**
EPNS	**1000 Kg/year**	**960**	**-**	**-**	**45**	**986**	
	Cost (1000 $/year)	**96.0**	**-**	**-**	**1.5**	**0.3**	**97.8**
EPS	**1000 Kg/year**	**812**	**-**	**-**	**-**	**858**	
	Cost (1000 $/year)	**81.2**	**-**	**-**	**-**	**0.2**	**81.4**
Crystallization	**1000 Kg/year**	**783**	**-**	**0.14**	**-**	**-**	
	Cost (1000 $/year)	**78.3**	**-**	**11.9**	**-**	**-**	**90.2**
Current Situation	**1000 Kg/year**	**1389**	**454**	**-**	**-**	**-**	
	Cost (1000 $/year)	**138.9**	**103.8**	**-**	**-**	**-**	**242.7**

Energy cost for each alternative includes steam cost and electricity cost. Unit cost of electricity and steam (at 0.57 MPa and 157 °C) are given in Table 6.7, these data were obtained from Peters and Timmerhaus (1991). In addition, yearly total energy cost for each alternative are tabulated in Table 6.7.

Table 6.7. Annual Utility Cost for each alternative

	Steam (0.008 $/kg)		Electricity (0.07 $/kWh)		Cooling Water (0.085 $/1000 kg)		
	kg/h	**Cost ($/year)**	**kW**	**Cost ($/year)**	**kg/h**	**Cost ($/year)**	**Total Cost ($)**
CHF	29	1 700	1	538	83	56	2 294
EPNS	121	7 176	2	1 075	143	96	8 347
EPS	87	5 148	2	1 075	47	31	6 254
Crystallization	8.8	522	7.8	4 166	-	-	4 688
Current	29	1 700	-	-	-	-	1 700

Working capital investment was calculated based on estimation given in the Peters and Timmerhaus (1991), which estimates working capital investment as the sum of raw material cost of 1-month supply, manufacturing cost of 1 month's production and production cost for 1 month operation. Total capital investment was ultimated to be the summation of working capital investment and fixed capital investment. Annual fixed cost was fixed capital investment per one operating year. Based on the Purchased equipment cost FCI, WCI was calculated according to Table 6.1, the results are tabulated in Table 6.8.

Table 6.8. Fixed Capital and Working Capital Investment of Process Alternatives

	CHF	EPNS	EPS	Crystallization
Purchased Equipment Cost (1000 $)	63	94	84	196
Fixed Capital Investment (1000 $)	353	526	472	1101
Working Capital Investment (1000 $)	42	35	29	42
Total Capital Investment (1000 $)	395	561	501	1143

Annual fixed cost for the current proses was taken as zero as it was fully depreciated and practically speaking its market value is zero.

Process life was assumed as 10 year. Annual operating cost for each recovery alternative was calculated. Annual operating cost includes chemical cost, energy cost, transportation cost of solid waste, disposal cost of solid waste and make-up cooling water cost. Chemicals include HCl, NaOH, Fe, process water and H_2. Annual income comes from the marketing of ferrous chloride. The composition of by-product ferrous chloride was designed to give the same composition for all alternatives in order to have the same basis for the annual income of all recovery processes. Energy and chemical cost for each process alternative includes the entire chemical and energy need of recovery process, if the current process is replaced with recovery process. Total annual cost was calculated as the summation of annual fixed cost and annual operating cost. Total annual sales for each recovery alternative was calculated. Annual direct cost and total annual sales for each alternatives is tabulated in Table 6.9.

Table 6.9. Annual Direct Cost and Total Annual Sales

	CHF	EPNS	EPS	Crystallization	Current
The Chemicals (1000 $)	144.3	97.8	81.4	90.3	242.7
The Utility Cost (1000 $)	2.3	8.3	6.3	4.7	1.7
Transportation Cost (1000 $)	-	-	-	-	31.3
Disposal Cost (1000 $)	-	-	-	-	48.6
Overhead Cost	-	-	-	-	-
Labor Cost	-	-	-	-	-
Total Annual Cost (1000 $)	146.6	106.1	87.7	95.0	324.2
Total Annual Sales (1000 $)	156.0	95.7	72.5	65.8	-

Net annual expense was the difference between total annual cost and total annual sales. Net annual income for each recovery alternative was calculated as the difference between total annual cost of current process and net annual expense of each process. Moreover, payout period and percent return on investment and cash to be accumulated by the end of process life was calculated. From that result the most economical process was determined for the design basis.

The formulas for payout period and % return on investment given in Peters and Timmerhaus (1991) were used:

Payout Period = Depreciable FCI/(avg. profit/yr+ avg. depreciation/yr)

% Return on Investment = Yearly Profit/Total Initial Investment

Economical comparison of process alternatives is tabulated in Table 6.10.

Table 6.10. Comparison of Process Alternatives

	CHF	EPNS	EPS	Crystallization	Current
Purchased Equipment Cost (1000 $)	**63**	**94**	**84**	**196**	**-**
Fixed Capital Investment (1000 $)	**353**	**526**	**472**	**1101**	**-**
Working Capital Investment (1000 $)	**42**	**35**	**29**	**42**	**-**
Total Capital Investment (1000 $)	**395**	**561**	**501**	**1143**	**-**
Annual Fixed Cost (1000 $)	**35**	**53**	**47**	**110**	**-**
Annual Operating Cost (1000 $)	**147**	**106**	**88**	**95**	**324**
Total Annual Cost, TAC (1000 $)	**182**	**159**	**135**	**205**	**324**
Total Annual Sales, TAS (1000 $)	**156**	**96**	**72**	**66**	**-**
Net Annual Expenses, NAE=TAC-TAS (1000$)	**26**	**63**	**62**	**139**	**-**
Net Annual Income when the Current Process is replaced, (Current TAC-NAE) (1000 $)	**298**	**261**	**262**	**185**	**-**
Payout Period, year	**1.1**	**1.7**	**1.5**	**3.7**	**-**
% Return on Investment	**76**	**47**	**52**	**16**	**-**

6.3. CASH FLOW DIAGRAM FOR PROCESS ALTERNATIVES

The tabulated values in the Table 6.11 show the net income that would be earned when the recovery process is applied instead of current process for the 10 years period (process lifetime). That net income includes saving that would be done in the chemicals, in the transportation cost, in the disposal cost of current waste, also the gain that would come from the marketing of $FeCl_2$. Moreover both the Fixed Capital Investment and the operation cost of each recovery processes are considered as expenses. The cash flow during ten year is determined, if the current process is shifted to each recovery process alternative. Cash flow relative to current process is calculated from the expression;

Cash Flow Relative to Current Process = - FCI - WCI + Year *(Annual Operating Cost + Annual Sales Revenue – Annual Operating Cost of Current Process).

Table 6.11. Cash to be accumulated through 10 years for process alternatives

Year	CHF	EPNS	EPS	Crystallization
	Cash Flow (1000 $)	**Cash Flow (1000 $)**	**Cash Flow (1000 $)**	**Cash Flow (1000 $)**
0	- 705	- 561	- 501	-2 203
1	- 372	- 247	- 192	-1 908
2	- 38	67	117	-1 613
3	295	380	426	-1 317
4	629	694	735	-1 022
5	962	1 008	1 044	- 727
6	1 296	1 321	1 353	- 432
7	1 629	1 635	1 662	- 137
8	1 963	1 949	1 971	158
9	2 296	2 262	2 280	453
10	2 630	2 576	2 589	748

Cash to be accumulated by the end of 10 Years for each alternative is tabulated in Table 6.12.

Table 6.12. Cash to be accumulated by the end of 10 Years for each Alternative

Process Alternative	Cash to be accumulated by the end of 10 Years (1000 $)
CHF	2 630
EPNS	2 576
EPS	2 589
Crystallization	748

CHAPTER 7

DISCUSSION

Conversion of HCl to $FeCl_2$ process via addition of Fe to WPL, instead of neutralising WPL with NaOH, seems to be a very practical and feasible approach for handling of WPL. $FeCl_2$ can be marketed through dye, ink, pigment markets (Kroschwitz, J.I., 1995). $FeCl_2$ could be dried and sold as crystals or as solution. Also the $FeCl_2$ can easily be converted to $FeCl_3$, by means of chlorinating the $FeCl_2$ (Clair, 1995). $FeCl_3$ is widely used in wastewater treatment as flocculation agent (Kroschwitz, J.I., 1995). Feasibility of conversion of HCl to $FeCl_2$ process depends strongly on the marketability of $FeCl_2$. If the plant is placed in the region where one of waste water, dye, pigment or fertilizer industries exists, the conversion of unused HCl to $FeCl_2$ process would be the most economical way to handle the waste from pickling baths. Hydrogen evolved during the conversion reaction of HCl to $FeCl_2$ can be reacted with chlorine gas to produce HCl. Some part of make-up HCl required for the pickling baths can be produced via this HCl production way. This additional process was not studied in the present study, but it is a good idea for further studies. HCl can be produced by the following reaction,

$$H_2 + Cl_2 \longrightarrow 2HCl$$

On the design basis used, 42 % of make-up acid requirement of pickling baths can be produced.

In the Evaporation Process, if more concentrated HCl than the recovered acid HCl concentration is desired, in this case usage of a partial condenser after the evaporator is suitable.

Since, when HCl and steam mixture partially condenses the liquid phase would be the richer in the acid. Hydrogen chloride can be concentrated by this way.

Addition of NaOH instead of Fe to the liquid product from the evaporator in the case of evaporative recovery without solid formation can also be applied. In this case, NaOH to be added for neutralization and transportation cost of solid waste to landfill area implies additional cost.

Evaporative recovery with solid formation is more economical than evaporation process with no solid formation, but operation of an evaporator with solid formation is more difficult.

The solubility data of $FeCl_2$-HCl-H_2O system was estimated for low temperatures. Experimental data were compared with estimated data, the estimated data fit the experimental data well. In the crystallization operation, new approaches were developed. The present process integration is different from the early applications that normally crystallizes part of $FeCl_2$ and circulates waste pickle liquor with high amount of $FeCl_2$. Solubility of $FeCl_2$ is reduced in the present study via the addition of 36 % HCl before crystallization operation was carried out. The make–up acid is added as 36 % HCl rather than addition of acid concentration required. This lowers the $FeCl_2$ concentration. Different from the early applications which circulates about 12 % $FeCl_2$ (Peterson, 1991), the $FeCl_2$ concentration in the recovered acid stream is reduced to 1.85% in the present study. In addition, as a new approach two-stage crystallization is used in the present study. Part of water requirement of regenerated acid stream is fed as steam that would raise the fresh acid stream temperature to 70°C by this way usage of one heat exchanger is eliminated. When the crystallization process is adapted, pickling process conditions should be reconsidered since the fresh feed would contain some dissolved $FeCl_2$. $FeCl_3$ is reduced to $FeCl_2$ by means of hydrogen. This operation has not been applied until now for this type of operations, accumulation of $FeCl_3$ in the pickling bath is prevented via reduction reaction. $FeCl_3$ can adhere to the surface of wire. Without existence of $FeCl_3$ in the pickling baths, the adverse effect of $FeCl_3$ on pickling operation would be eliminated with the integration of crystallization process.

As can be seen in the economical comparison of using two and three crystallizers for recovery process, using two crystallizers is more economical than using three crystallizers. However, usage of hydrogen gas may not be appropriate for plant safety.

Crystallization process is more difficult to operate compared with other recovery processes. The process requires –57°C temperature, if very low $FeCl_2$ solubility is desired. Moreover, crystallization process requires the most expensive purchased equipment cost in the process alternatives studied during the present study. What is more, the other disadvantage of crystallization process compared with other recovery alternatives is that, in the crystallization process the existence of $FeCl_2$ is not eliminated. Existence of $FeCl_2$ would hinder the pickling efficiency.

Economical comparison of recovery alternatives was done via "Return on Investment" and "Payout Period" analysis. Although "Payout Period" and "Return on Investment" are rather simple and short-cut methods, they are considered as acceptable methods specifically for this study since,

a) The total initial costs are relatively low,

b) The same project life is assumed for all process alternatives,

c) All process alternatives have similar trends for cash flow (ie. constant cash flow).

Nevertheless equivalent annual cost analysis with an acceptable discount rate, for example 20 %, would give same result.

For comparison purposes, only the major components of the operating cost were taken into account as the other components are likely to be either comparable or not to bring a significant additional burden for all process alternatives. Tax is not only a delicate matter but also very difficult for assessment. Taking into account the environmental effects of this study one may accept a tax exemption (through incentive regulations) both for investment and production stages, which will justify our approach.

CHAPTER 8

CONCLUSIONS

In the waste management, the purpose is to manage the waste with the lowest possible expenditure. From this point of view, it was seen that the adaptation of any of recovery process adds economical return relative to the current process conditions.

The adaptability and feasibility of any process strongly depends on some parameters, such as composition and flowrate of WPL and marketability of the by-product. For different compositions, feasibility of each process alternative may differ. Also the flowrate of WPL strongly affect the feasibility of the recovery alternative.

Conversion of HCl to $FeCl_2$ process is the most economical process alternative, if the considerable quantity of $FeCl_2$ so produced can be marketed. Otherwise the process would not be the most economical way to handle the current situation.

Crystallization process requires purging to eliminate the accumulation of species coming from WPL. Moreover H_2, an explosive gas, should be used for the reduction of $FeCl_3$ to $FeCl_2$. Usage of hydrogen may not be desirable for plant safety. These negative points make the Conversion of HCl to $FeCl_2$ Process is more advantageous compared with crystallization process.

Crystallization process requires low energy compared to Evaporation Process but the process conditions are not easy to apply since the process requires temperature of –57°C for the crystallization, if very low $FeCl_2$ solubility is desired.

It seems the Conversion of HCl to $FeCl_2$ Process is the most economical process for the design basis. But any body who wants to have recovery process should think about the marketability of by product $FeCl_2$.

Based on design basis, feasibility of recovery processes decreases in the following order; Conversion of HCl to $FeCl_2$, Evaporative Recovery with Solid Formation, Evaporative Recovery without Solid Formation, Crystallization of $FeCl_2$ Process.

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APPENDIX A

DATA TAKEN FROM OPERATING PICKLING BATH

Data (HCl, Fe^{+2}, Fe^{+3} concentrations) from operating pickling bath was taken and it is tabulated in Table APP. 1. These data were used for the calculation of mass balance of pickling baths.

Table APP 1. Data Set from operating Pickling Bath

Data Set No	Date	Time	Main Pickling HCl (gr/lt)	Main Pickling Fe^{+2} (gr/lt)	Main Pickling Fe^{+3}(gr/lt)	Pre-Pickling HCl (gr/lt)	Pre-Pickling Fe^{+2} (gr/lt)	Pre-Pickling Fe^{+3}(gr/lt)
1	03.12.97	**17.00**	**185**	**33**	**2.5**	**130**	**81**	**5.4**
2		**21.00**	**192**	**38**		**134**	**85**	**5.4**
3	04.12.97	**01.00**	**190**	**35**		**131**	**93**	**5.5**
4		**05.00**	**180**	**36**	**2.8**	**120**	**84**	**5.5**
5		**09.00**	**185**	**36**		**117**	**85**	**5.3**
6		**13.00**	**190**	**38**		**123**	**89**	**5.3**
7		**16.30**	**183**	**38**	**2.8**	**129**	**88**	**5.2**
8		**20.30**	**184**	**38**		**127**	**89**	**5.2**
9	05.12.97	**01.00**	**177**	**39**		**126**	**85**	**5.1**
10		**05.00**	**175**	**40**	**3.2**	**124**	**84**	**5.1**
11		**09.00**	**174**	**41**		**124**	**89**	**5.1**
12		**13.00**	**180**	**44**	**3.1**	**131**	**84**	**5.1**
13		**16.30**	**188**	**36**	**2.2**	**131**	**83**	**4.8**
14		**20.30**	**180**	**38**		**125**	**79**	**4.8**
15	06.12.97	**01.00**	**171**	**42**		**130**	**79**	**4.9**
16		**05.00**	**166**	**45**	**3.1**	**124**	**83**	**4.9**
17		**09.00**	**182**	**47**		**134**	**88**	**4.9**
18		**13.00**	**177**	**49**		**128**	**84**	**5.0**

APPENDIX B

MASS BALANCE CALCULATIONS FOR THE PICKLING BATHS

Mass Balance Calculation is carried out to find out the WPL flowrate, FeO, Fe_2O_3 and fume flowrate of the pickling bath, flow diagram of the pickling bath is shown in Figure APP.1, based on the data taken from industry, tabulated in Table APP.1. It was assumed that FeO reacts with HCl to produce $FeCl_2$ and Fe_2O_3 reacts with HCl to produce $FeCl_3$.

Data for Fresh Acid (HCl fed to pickling bath)
Fresh acid HCl concentration, 204 g/l
Fresh acid volumetric flowrate, 81 l / h
Fresh acid density, 1091.3 g/l
HCl wt % of fresh acid, 18.7 %

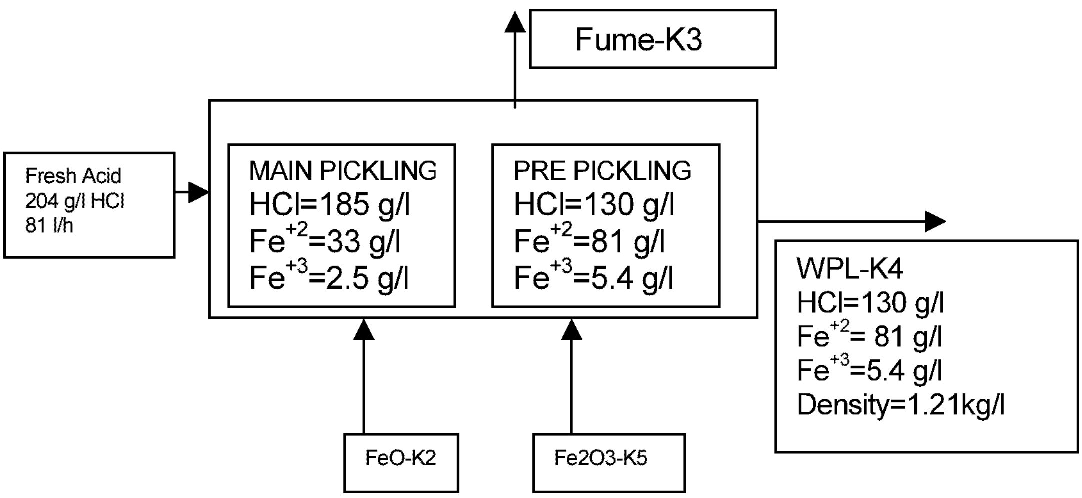

Figure APP.1. Concentration of Pickling Baths for First Data Set of Table APP.1

Pre-pickling composition from Data Set 1 of Table APP.1 is;

HCl 130 g/l

Fe^{+2} 81 g/l

Fe^{+3} 5.4 g/l

Pre-pickling mass fraction can be calculated by dividing the concentration of each component with density of WPL.

HCl (130 g /l)/(1209.7 g/l) =10.75 %

Fe^{+2} is 81 g/l $FeCl_2$ composition would be, % Fe^{+2} x Mw_{FeCl2}/Mw_{Fe+2}

where Mw is molecular weight.

$FeCl_2$ 81 g/l *(126.75/55.85)/1209.7=15.2 %

Fe^{+3} is 5.4 g/l $FeCl_3$ composition would be, % Fe^{+3} x Mw_{FeCl3}/Mw_{Fe+3}

where Mw is molecular weight.

$FeCl_3$ 5.4 g/l*(162.2/55.85)/1209.7=1.3%

Main Pickling Composition from the first data set 1 of Table APP.1 is;

HCl =185 g/l

Fe^{++} =33 g/l

Fe^{+++} =2.5 g/l

Density=1.14 kg/l

Main pickling mass fraction can be calculated by dividing the concentration of each component with density of bath.

HCl (185 g /l)/(1140 g/l) =16.22 %

Fe^{+2} 33 g/l $FeCl_2$ composition would be, % Fe^{+2} x Mw_{FeCl2}/Mw_{Fe+2}

where Mw is Molecular weight.

$FeCl_2$ 33 g/l *(126.75/55.85)/1140=6.57 %

Fe^{+3} 2.5 g/l $FeCl_3$ composition would be, % Fe^{+3} x Mw_{FeCl3}/Mw_{Fe+3}

$FeCl_3$ 2.5 g/l*(162.2/55.85)/1140=0.64%

The results of main pickling mass fraction calculations are tabulated in Table APP.2.

Table APP.2. Component Mass Fraction of Pre-pickling and Main Pickling Baths

Components	**Pre-pickling**	**Main Pickling**
% HCl	10.75	16.22
%$FeCl_2$	15.2	6.56
% $FeCl_3$	1.3	0.64
% H_2O	72.75	76.58

In order to find out the mass balance of pickling bath, component mass fraction of the fume (vapor leaving from pickling bath, containing HCl and H_2O) should be found out. Pickling baths have cover on them and baths are kept under negative pressure with fans (Stone, 1997). Vapor-Liquid equilibrium relation, shown in Equation 1, for the $FeCl_2$-HCl-H_2O system at 70 °C was found from Chen et. al. (1970). Mass fraction of HCl in the fume is required for mass balances. The ratio of mass of HCl to mass of H_2O can be found from equation 1, via the ratio of vapor pressures. For the present situation, $FeCl_3$ mole fraction is multiplied by 1.5 and added to $FeCl_2$ mole fraction, since vapor-liquid equilibrium model available from Chen et. al. (1970) does not include $FeCl_3$. Composition of Pre-Pickling in mass and mole fraction units is given in Table APP.3.

$$\log\left[\frac{p_{HCl}}{P_{H_2O}}\times\frac{X3(2X1+3X2+X3)}{X1(X1+2X2)}\right]=21.94\times(X1+3X2)^{4/3}-0.93 \qquad (1)$$

where

X1 is mol fraction of HCl

X2 is mol fraction of $FeCl_2$

X3 is mol fraction of H_2O

Table APP.3. Composition of Pre-Pickling Pickle Liquor in Mass and Mole Fraction Units

Comp.	Wt %	G. Mole	Mol Fraction
HCl	10.7	0.30	0.07
$FeCl_2$	15.2	0.12	0.03
$FeCl_3$	1.3	0.01	
H_2O	72.8	4.04	0.90

Vapor pressure of H_2O at different HCl composition of pickling bath, taken from Stone (1997) is tabulated in Tabble APP.4. Pre-pickling HCl composition is 10.7%. Water vapor pressure for the pre-pickling bath, containig 10.7 % HCl, can be found by means of interpolation between water vapor pressure of solution containing 10 % HCl and 12% HCl, the result for the interpolation is shown in Table APP.4.

Table APP.4. Vapor pressure of H_2O at different HCl compositions

Weight fraction of HCl	**P_{H2O} (mmHg)**
10	203.8
12	195.7
10.7	200.8

P_{HCl} can be calculated from Equation 1, the calculated P_{HCl} is,

$$P_{HCl} = 12.7 \text{ mmHg}$$

Same calculations can be done for main pickling bath. Composition of Main Pickling in mass and mole fraction units is given in Table APP.5.

Table APP.5. Composition of Main Pickling Pickle Liquor in Mass and Mole Fraction Units

Components	Wt%	Mol	Mol Fraction
HCl	16.2	0.45	0.09
$FeCl_2$	6.6	0.05	0.01
$FeCl_3$	0.6	0.007	
H_2O	76.6	4.25	0.9

Vapor pressure of H_2O data at 14 and 17 % HCl composition of main pickling bath, taken from Stone (1997), is tabulated in Tabble APP.6. Pre-pickling HCl composition is 16.22%. Water vapor pressure for main pickling bath can be found from the interpolation between water vapor pressure of solution containing 14 % HCl and 17% HCl, the result for the interpolation is shown in Table APP.6.

Table APP.6. Vapor pressure of H_2O at different HCl compositions

Weight fraction of HCl	**P_{H2O} (mmHg)**
14	189.1
17	175.6
16.2	179.1

After finding P_{H2O} , P_{HCl} for the main pickling bath can be calculated by the Equation 1.

Main Pickling

P_{H2O} =179.1 mmHg and P_{HCl} calculated from Equation 1 is 6.5 mmHg

Average vapor pressures for HCl and H_2O were taken to find out the mass fraction of total vapor that is the vapor exhausting from main and pre-pickling baths.

P_{H2O} = 189.9 mmHg

P_{HCl} =9.6 mmHg

Mass fraction of HCl in the fume can be found from relation, $n_a/n_T=P_a/P_T$

$$\frac{\text{Mass of HCl in Fume}}{\text{Total Mass of Fume}} = 9.6*36.46/(18*189.9+36.5*9.6)=0.0925$$

Mass Balances

1- Total Mass Balance

88.4+K5+K2=K3+K4

2- Fe^{+2} Balance

K2*55.85/(55.85+16)=X4*0.152/2.27

3- Fe^{+3} Balance

K5*55.85*2/(55.85*2+3*16)=1.3e-2/2.9*K4

4- Cl^- Balance

0.0925*K3+(0.1075+0.152/(126.75)*2*36.461+0.013/(162.2)*3*36.46
=88.4*0.1869

Results

K3- Fume =25.17 kg/h

K2- FeO=6.0 kg /h

K5- Fe_2O_3=0.45 kg/h

K4- Waste Pickling Liquor = 69.7 kg /h

These calculations were repeated for each data set in Table APP.1 by means of spreadsheet calculation and the results for each data set are tabulated in Table APP.7.

Table APP.7. Mass Balance for Each Data Set

PREPICK. HCL (g/lt)	Fe^{+2} (g/lt)	Fe^{+3} (g/lt)	FeO (kg/h)	Fume (kg/h)	WPL (kg/h)	Fe_2O_3 (kg/h)	Time Range (h)
130	**81**	**5.4**	**6.0**	**25.2**	**69.7**	**0.5**	**4.0**
134	**85**	**5.4**	**4.7**	**41.4**	**52.0**	**0.3**	**4.0**
131	**93**	**5.5**	**3.4**	**58.1**	**33.9**	**0.2**	**4.0**
120	**84**	**5.5**	**6.6**	**21.6**	**73.9**	**0.5**	**4.0**
117	**85**	**5.3**	**6.8**	**20. 9**	**74.7**	**0.5**	**4.0**
123	**89**	**5.3**	**5.8**	**33.5**	**61.0**	**0.4**	**3.5**
129	**88**	**5.2**	**5.5**	**35.4**	**58.9**	**0.4**	**4.0**
127	**89**	**5.2**	**5.6**	**35.4**	**58.9**	**0.4**	**4.5**
126	**85**	**5.1**	**6.2**	**26.6**	**68.4**	**0.4**	**4.0**
124	**84**	**5.1**	**6.4**	**23.7**	**71.5**	**0.4**	**4.0**
124	**89**	**5.1**	**6.0**	**31.0**	**63.8**	**0.4**	**4.0**
131	**84**	**5.1**	**5.4**	**33.6**	**60.5**	**0.4**	**3.25**
131	**83**	**4.8**	**5.8**	**28.6**	**66.0**	**0.4**	**4.25**
125	**79**	**4.8**	**6.5**	**18.4**	**76.9**	**0.4**	**4.5**
130	**79**	**4.9**	**6.2**	**21.6**	**73.4**	**0.4**	**4.0**
124	**83**	**4.9**	**6.4**	**22.0**	**73.3**	**0.4**	**4.0**
134	**88**	**4.9**	**3.9**	**50.5**	**42.1**	**0.3**	**4.0**
128	**84**	**5.0**	**5.6**	**32.0**	**62.4**	**0.4**	

Pickling baths are partially dumped and charged with fresh acid, this procedure is called as action. 600 liters of acid was added to the pickling baths, when data were taken. In order to find out the average flowrate of WPL from pickling bath WPL flowrate of all data set multiplied with time range and summed with amount of action. The summation gives the total flowrate of WPL from pickling bath during operation period. Data taking period was 68 h.

Total Waste Pickle Liquor =Time Range * Waste Pickle Liquor for each data set +Action

=5051 kg WPL taken from pickling bath during 68 h.

Average Flowrate of WPL would be 74.28 kg/h.

Table APP.8. Waste Pickle Liquor Composition

Components	Composition
HCl	**10.5**
$FeCl_2$	**15.85**
$FeCl_3$	**1.22**
H_2O	**72.43**
Mass Flowrate (kg/h)	**74.28**

There are three pickling lines with same densities. One is similar to this line on which the calculations was done, the other is fed 117 liters /hour where this line is fed 81 liters/hour.

Total waste flowrate would be

74.28*2+117/81*74.28=256 kg/h

APPENDIX C

CONVERSION HCl TO FECl2 PROCESS REACTOR ENERGY BALANCE

When iron is added to the WPL in the 'Conversion of HCl to $FeCl_2$ Process' conversion reaction of;

$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$

takes place. The energy balance is shown in this Appendix.

Reference Plane is:
T=25°C
P=1 atm
State: Liquid H_2O
Aqueous HCl, $FeCl_2$
Solid Fe
Gaseous H_2

ΔH rxn is -113.7 kcal /mole Fe reacted

If 0.37 kmol Fe/h reacts $\Delta H_{rxn} = -175.2$MJ/h

The general energy balance equation is;
$\Delta E = -\Delta[(H+P+K)\,m] + Q - W$
$Q = \Delta H$
$Q = \Delta H_{rxn,\,25°C} + (H_{products,\,70\,°C} - H_{products,\,25\,°C}) - (H_{reactants,\,70\,°C} - H_{reactants,\,25\,°C})$

Q= -175.2 +(-3068.8+3106.7) - (-3001.2+-3037.2)
Q= -177.1 MJ/h

Vapor Pressure of H_2O, P_{H2O} at 70°C is 234 mmHg, H_2O and H_2 vapor mixture is evolved from the reactor and $P_{H2} = P_T - P_{H2O}$

from the formula, $P_{H2}/P_T = n_{H2}/n_T$ n_T, total number of moles can be found

$(760-234)/760 = 0.37/\,n_T$

$n_T = 0.535$ where $n_T = n_{H2O} + n_{H2}$ and n_{H2} produced from the reaction is 0.37 kmol/h

$n_{H2O} = 0.165$ kmol /h =2.96 kg/h

Vapor (containing H_2O+H_2) = 15 m^3/h. Assuming the velocity of vapor leaving from the reactor as 5 meters/min

Calculation of exhaust hole diameter required for exhausting vapor leaving from the reactor:

15 m^3/h=5 m/min 60 min/1 h x Surface Area

Area=0.05 m^2=500 cm^2 D=26 cm where D is the diameter of the vapor exit hole.

Assuming Reactor Retention Time as 10 hour from Clair (1995).
Normal Reactor Capacity is multiplied by 2.5 to have space for vapor in the reactor.

Reactor Capacity =2.5*256 kg/h * 10 h /1200 kg/m^3 =5.4 m^3

Assuming the Diameter of reactor as 1 meter

Height of WPL in the reactor would be;

1.12 m^3 = (3.14 1^2/4) x L

L=1.43 meter

Since the reaction is exothermic, inside cooling is required.

Calculation of required cooling water:

$Q=UA\Delta T_{LMTD}$

Assuming cooling water inlet temperature as 25°C and outlet temperature as 40°C.

Water Contacting Surface Area =5.3 m^2

177.1x10^6 J/h 1h/3600 sec =U 5.3 37°C

U=251 W/m^2K

Cooling Water Flowrate is,

$Q=mCp\Delta T$

177.1x10^3 kJ/h= m 4.18kJ/kg K (15 °C)

m=2830 kg/h, where m is cooling water amount required to cool the reactor.

APPENDIX D

SIMULATION RESULTS FOR THE EVAPORATION PROCESS RECOVERY ALTERNATIVES

The simulation results for the Evaporation process is tabulated in this Appendix for each evaporative process recovery flowsheet alternative. The results are tabulated form Table APP.9 to APP.14.

Table APP.9. Simulation Results for Alternative -1 in Evaporation Process

P_f (atm)	T_f (°C)	V_f	P_d (atm)	T_d (°C)	Required Heat (For Flash Column)	Heat Duty (Watt)	Vapor/Feed	Solubility Limit Exceeded	Total %HCl Recovery
2	**127.2**	**0**	**0.6**	**93.3**	**0**	**5200**	**0.05**	**No**	**1.0**
4	**150.4**	**0**	**0.6**	**93.6**	**0**	**7100**	**0.07**	**No**	**2.0**
6	**165.4**	**0**	**0.6**	**93.8**	**0**	**8350**	**0.09**	**No**	**2.8**
10	**186.0**	**0**	**0.6**	**94.0**	**0**	**10100**	**0.12**	**No**	**4.2**
10	**186.0**	**0**	**0.4**	**84.0**	**0**	**10100**	**0.13**	**No**	**4.4**
10	**186.0**	**0**	**0.1**	**54.1**	**0**	**10100**	**0.17**	**No**	**4.5**
1	**106.5**	**0**	**0.1**	**52.8**	**0**	**3450**	**0.08**	**No**	**0.9**
10	**186.0**	**0**	**1**	**107**	**0**	**10100**	**0.10**	**No**	**3.9**

In the first case the process simulation was done, for the case of the waste acid being fed to the flash column as saturated solution.

As second process simulation, the process was simulated at different temperatures and pressures, and the results are presented in Table APP.10.

Table APP.10. Simulation Result of Alternative-2 in Evaporation Process

Run #	P_f (atm)	P_d (atm)	f	T_d (°C)	Fractional Recovery of % HCl
1	**1.00**	**0.10**	**0.30**	**55.4**	**13.0**
2	**1.00**	**0.10**	**0.45**	**57.3**	**39.8**
3	**1.00**	**0.10**	**0.60**	**59.7**	**75.9**
4	**1.00**	**0.30**	**0.30**	**79.1**	**17.3**
5	**1.00**	**0.30**	**0.45**	**80.9**	**44.9**
6	**1.00**	**0.30**	**0.60**	**83.7**	**78.6**
7	**1.00**	**0.50**	**0.30**	**91.4**	**19.0**
8	**1.00**	**0.50**	**0.45**	**93.2**	**46.4**
9	**1.00**	**0.50**	**0.60**	**96.0**	**78.8**
10	**2.00**	**0.10**	**0.30**	**55.4**	**13.0**
11	**2.00**	**0.10**	**0.45**	**57.3**	**39.8**
12	**2.00**	**0.10**	**0.60**	**59.7**	**75.9**
13	**2.00**	**0.30**	**0.30**	**79.1**	**17.3**
14	**2.00**	**0.30**	**0.45**	**80.9**	**44.9**
15	**2.00**	**0.30**	**0.60**	**83.7**	**78.6**
16	**2.00**	**0.50**	**0.30**	**91.4**	**19.1**
17	**2.00**	**0.50**	**0.45**	**93.2**	**46.4**
18	**2.00**	**0.50**	**0.60**	**96.0**	**78.8**
19	**3.00**	**0.10**	**0.30**	**55.4**	**13.0**
20	**3.00**	**0.10**	**0.45**	**57.3**	**39.8**
21	**3.00**	**0.10**	**0.60**	**59.7**	**75.9**
22	**3.00**	**0.30**	**0.30**	**79.1**	**17.3**
23	**3.00**	**0.30**	**0.45**	**80.9**	**44.9**
24	**3.00**	**0.30**	**0.60**	**83.7**	**78.6**
25	**3.00**	**0.50**	**0.30**	**91.4**	**19.1**

Table APP.10. Simulation Result of Alternative-2 in Evaporation Process (continued)

Run #	P_f (atm)	P_d (atm)	f	T_d (°C)	Fractional Recovery of % HCl
26	3.00	0.50	0.45	93.2	46.4
27	3.00	0.50	0.60	96.0	78.8
28	4.00	0.10	0.30	55.4	13
29	4.00	0.10	0.45	57.3	39.8
30	4.00	0.10	0.60	59.7	76
31	4.00	0.30	0.30	79.1	17.3
32	4.00	0.30	0.45	80.9	44.9
33	4.00	0.30	0.60	83.7	78.6
34	4.00	0.50	0.30	91.4	19.1
35	4.00	0.50	0.45	93.2	46.4
36	4.00	0.50	0.60	96.0	78.8
37	6.00	0.10	0.30	55.4	13
38	6.00	0.10	0.45	57.3	39.8
39	6.00	0.10	0.60	59.7	75.9
40	6.00	0.30	0.30	79.1	17.3
41	6.00	0.30	0.45	80.9	44.9
42	6.00	0.30	0.60	83.7	78.6
43	6.00	0.50	0.30	91.4	19.1
44	6.00	0.50	0.45	93.2	46.4
45	6.00	0.50	0.60	96.0	78.8
46	8.00	0.10	0.30	55.4	13
47	8.00	0.10	0.45	57.3	39.8
48	8.00	0.10	0.60	59.7	75.9
49	8.00	0.30	0.30	79.1	17.3
50	8.00	0.30	0.45	80.9	44.9
51	8.00	0.30	0.60	83.7	78.6
52	8.00	0.50	0.30	91.4	19.1
53	8.00	0.50	0.45	93.2	46.4

Table APP.10. Simulation Result of Alternative-2 in Evaporation Process (continued)

Run #	P_f (atm)	P_d (atm)	f	T_d (°C)	Fractional Recovery of % HCl
54	8.00	0.50	0.60	96.0	78.8
55	10.00	0.10	0.30	55.4	13
56	10.00	0.10	0.45	57.3	39.8
57	10.00	0.10	0.60	59.7	75.9
58	10.00	0.30	0.30	79.1	17.3
59	10.00	0.30	0.45	80.9	44.9
60	10.00	0.30	0.60	83.7	78.6
61	10.00	0.50	0.30	91.4	19.1
62	10.00	0.50	0.45	93.2	46.4
63	10.00	0.50	0.60	96.0	78.8

Table APP.11. Simulation Results for Alternative-3 in Evaporation Process

P_f (atm)	T_f (°C)	V_f	P_d (atm)	T_d (°C)	Required Heat	Heat Duty (Watt)	Vapor/Feed	Solubility Limit exceeded	Total % HCl Recovery
10.0	185	0.0	1.0	107.7	0	10000	0.10	No	3.8
10.0	189	0.50	1.0	113	0	36650	0.50	No	71.4
8.0	180	0.49	1.0	113	0	35600	0.49	No	67.8
4.0	155	0.49	1.0	113	0	36000	0.49	No	69.1
1.25	110	0.0	0.1	52.8	0	3750	0.08	No	1.0

In this case the process was simulated if the feed was fed to the flash column as vapor-liquid mixture and additional heat is supplied to the flash column

Table APP.12. Simulation Results for Alternative-4 in Evaporation Process

P_f (atm)	T_f (°C)	% Vapor formed in the 1st flash column	% HCl recovered the vapor phase from 1st flash column	P_d (atm)	Heat required (Watt)	Vapor/Feed (Liquid Phase)	% Recovery in the liquid phase	Solubility Limit exceeded	Total % HCl Recovery
10	**190**	**51.6**	**71.4**	**0.6**	41200	**0.08**	**7**	No	78.4

In this process simulation feed at high pressures firstly flashed in the flash column then the liquid phase was flashed in the second flash column under vacuum conditions.

Table APP.13. Simulation Results for Alternative-5 in Evaporation Process

P_f (atm)	T_f (°C)	Vapor Amount in the feed	Solubility Limit Exceeded	Recovery in the Vapor Phase	P_d (atm)	T_d (°C)	Vapor/Feed (liquid Phase)	HCl recovery in the liquid phase	Heat Required (Watt)	Solubility Limit exceeded	Total % HCl Recovery
1	**113**	**49.0**	**No**	**0.68**	**0.1**	**59.67**	**0.09**	**0.06**	**35700**	**No**	**74.7**
1	**120**	**64.0**	**Yes**	**0.95**	**0.1**	**68.86**	**0.09**	**0.04**	**46250**	**Yes**	**99.0**
1	**116**	**58.0**	**No**	**0.87**	**0.1**	**63.26**	**0.09**	**0.06**	**41900**	**Yes**	**92.9**
2	**130**	**27.0**	**No**	**0.24**	**0.1**	**56.44**	**0.10**	**0.05**	**22650**	**No**	**29.6**
2	**150**	**71.5**	**Yes**	**0.99**	**0.1**	**70.0**	**0.12**	**0.01**	**53520**	**Yes**	**99.9**
2	**135**	**55.6**	**No**	**0.81**	**0.1**	**62.4**	**0.11**	**0.01**	**41340**	**Yes**	**89.6**

In that process simulation, the simulation of feed under normal pressure as vapor-liquid mixture was separated in the vapor – liquid separator, then the liquid phase flashed under vacuum conditions.

Table APP.14. Simulation Results for Alternative-6 in Evaporation Process

P_f (atm)	T_f (°C)	Vapor phase	HCl in the vapor phase	Heat required (Watt)	% HCl Recovery	Solubility Limit Exceeded
1	**113**	**48.95**	**0.68**	**35678**	**68.26**	**No**
1	**117**	**59.91**	**0.9**	**43218**	**89.86**	**No**
1	**115**	**55.72**	**0.83**	**40275**	**82.56**	**No**

In this process simulation the simulation of process was done if only an exchanger and vapor –liquid separator were employed.

APPENDIX E

EVAPORATION PROCESS WITHOUT SOLID FORMATION PROCESS

REACTOR ENERGY BALANCE

When iron is added to the liquor from the evaporator, conversion reaction of;

$Fe+2\ HCl \longrightarrow FeCl_2+H_2$

takes place. The energy balance is shown in this Appendix.

Reference Plane
T=25°C
P=1 atm
State: Liquid H_2O
Aqueous HCl, $FeCl_2$
Solid Fe
Gaseous H_2

ΔH rxn is -113.7 kcal /mole Fe reacted

If 0.1 kmol Fe/h reacts $\Delta H_{rxn} = -45.57$ MJ/h

General Energy Balance
$\Delta E= -\Delta[(H+P+K)\ m]+Q-W$
$Q=\Delta H$
$Q= \Delta H_{rxn,\ 25°C} + (H_{products,\ 71\ °C} - H_{products,\ 25\ °C}) - (H_{reactants,\ 71\ °C} - H_{reactants,\ 25\ °C})$

Q= -45.57 +(-1848.2+1872)-(-1827.8+1855.5)
Q= -51.5 MJ/h

Vapor Pressure of water, P_{H2O}at 71°C is 245 mmHg, H_2O and H_2 vapor mixture is evolved from the reactor and $P_{H2} = P_T - P_{H2O}$

From the formula of $P_{H2}/P_T = n_{H2}/n_T$ n_T, total number of moles can be found

$(760-245)/760 = 0.1/\ n_T$

$n_T=0.148$ where $n_T=n_{H2O}+n_{H2}$

$n_{H2O}=0.048$ kmol /h =0.86 kg/h

Taking Reactor Retention Time as 10 hour from Clair (1995).
Normal Reactor Capacity is multiplied by 2.5 to have space for vapor.

Reactor Capacity =2.5*104 kg/h * 10 h /1200 kg/m^3 =2.2 m^3
Assuming the Diameter of reactor as 0.8 meter

Height of WPL in the reactor would be;

0.8 m^3 = (3.14 0.8^2/4) x L

L=1.5 meter

Since the reaction is exothermic, inside cooling is required.

Calculation of cooling water flowrate;

$Q=UA\Delta T_{LMTD}$

Assuming cooling water inlet temperature as 25°C and outlet temperature as 40°C.

Water Contacting Surface Area= 4.3 m^2

51.5x10^6 J/h 1h/3600 sec =U 4.3 38°C

U=88 W/m^2K

Cooling Water Flowrate is,

$Q=mCp\Delta T$

51.5x10^3 kJ/h= m 4.18kJ/kg K (15 °C)

m=820 kg/h, this is the cooling water amount required to cool the reactor.

APPENDIX F

PUMP DESIGN FOR THE PROCESS RECOVERY ALTERNATIVES

Pump Design for the Process Recovery Alternatives is shown in this Appendix.

Using Bernoulli Equation for the Pump design

$\eta W_p=(Pb/\rho+gZ_b+\alpha V_b^2/2)-(Pa/\rho+gZ_a+\alpha V_a^2/2)+\Sigma F$

$\eta W_p=g(Z_b-Z_a)+\Sigma F$

Mass flowrate of WPL=ρSV

$$256 = 1200\ kg/m^3\ 3.14(2,54\ x10^{-2})^2/4\ V$$

$$V = 421\ m/h = 0.117\ m/sec$$

Viscosity is 0.5 cP.

Assuming pipe diameter as 1”,

$Re=DV\rho/\mu=2.54e10^{-2}x0.117x1200/0.0005$

$=7140$ f=0.009, (fanning friction factor)

Assuming pump pumps through 5 meters of elevation and efficiency as 60 %.

$0.6\ W_p=9.81x5+2x0.009x0.117^2x500/2.54\ x10^{-2}$

Pump power required is; W_p=99 W

Select a pump of 1kW power. This design result was used for rating of all pumps.

APPENDIX G

KERN METHOD FOR HEAT EXCHANGER DESIGN

1. **Heat Balance**

Q preheat =

Q vaporization =

2. **ΔT weighted =**

(ΔT) LMTD vaporisation

(ΔT) LMTD pre-heating

Q pre heat/ (ΔT) LMTD pre heating $\boxed{1}$

Q vaporization / (ΔT) LMTD vap. $\boxed{2}$

Sum= 1+2

3. **Weighted ΔT=Q total/sum**

Tube Side

4. a`t = Flow area per tube
at =Nt a`t /144 n

where n is number of shell passes

5. Gt=W/at
where Gt is tube side mass velocity
6. At hot fluid temperature

μ=

7. Ret = DGt/μ tube side Reynolds Number
obtain Jh from Figure 28, Kern(1950)

8. hi = Jh k/D $(cp\mu/k)^{1/3}(\mu/\mu w)^{0.14}$

where Jh is factor for heat transfer

9. hio for condensation,

Shell Side

4`. as =ID C` B/144 Pt
ID= shell
C` = Clearance between tubes
B= Baffle Space
5`.Gs=W/as
where Gs is shell side mass velocity and as is shell side area
6`. At average T
μ=
where μ is the viscosity
De =
Res= DeGs/μ
7`. Jh (Figure 28, Kern(1950))
8`. $(cp\mu/k)^{1/3}k$=
9`. Outside heat transfer coeff., ho
= Jh k/De $(cp\mu/k)^{1/3}(\mu/\mu w)^{0.14}$

Clean overall heat transfer coefficient for preheating, Up hio= hi ID/OD

where,
ID, inside diameter of tube
OD, outside diameter of tube
hi, inside heat transfer coefficient

= hio *ho/(hio+ho)

Area for pre-heating, Ap
=Qp/Up (ΔT)p

Vaporization
6`. T= Tvap
μ=
Shell side Reynolds Number, Res
=DeGs/μ
7`. Jh from Fig 28, Kern (1950)
8`. $(cp\mu/k)^{1/3}k$=
9`. ho = Jh k/De $(cp\mu/k)^{1/3}$
Clean overall heat transfer coefficient for vaporization, Uv

= hio *ho/(hio+ho)

Area for vaporization , Av
=Qv/Uv (ΔT)v

Total Clean Area, Ac
=Av+Ap
Weighted Overall coefficient, Uc
=$\sum$UA/Ac

Design Overall Coefficient

Surface Area/ Linear ft for the tube
A (area) = Nt*tubelength*surface /lin ft
Ud=Qt/AΔT

Check for maximum flux
Av/At *Ad = ft2
Q/ … =…. (Satisfactory)
Should be greater than 2000 Btu/h ft2

Dirt Factor = Uc-Ud/(UcUd)

Pressure Drop Calculations

Tube Side

For Ret, obtain f From Figure 26, Kern(1950)

Specific gravity at T is s

Pressure Drop in the tube side is, ΔPt
$= 0.5f\ G^2 Ln/(5.22*10^{10}\ Ds\phi)$

Shell Side

Pre-Heating

For Res, obtain f From Figure 29, Kern(1950)
Length of pre-heat zone, Lp
= L Ap /Ac
Number of crosses, (N+1)
=12 Lp /B

Shell side preheating pressure drop, ΔPs_1
$= f\ Gs^2 Ds\ (N+1)/(5.22\ 10^{10}\ De\ s\ \phi)$
where f is friction factor and
ϕ is viscosity ratio, $(\mu/\mu w)^{0.14}$
Vaporization
For Res, obtain f From Figure 29, Kern (1950)

Length of Vaporization Zone, Lv

= Tube Length –Length of Pre-heat

Number of Crosses, (N+1)
=12 L/B

s outlet=
s inlet =
where s is the specific gravity

s mean= (s outlet + s inlet)/2

Shell side vaporization pressure drop, ΔPs_2
$= f\ Gs^2 Ds\ (N+1)/(5.22\ 10^{10}\ De\ s\ \phi)$
Total shell side pressure Drop, ΔPs

$=\Delta Ps_1+\Delta Ps_2$

APPENDIX H

MASS AND ENERGY BALANCE FOR THE CRYSTALLIZATION OF $FeCl_2$ RECOVERY PROCESS

Based on design basis HCl fed during 68 h working period would be with the 81 liters/h regular flowrate and 600 liters of action (addition of fresh acid to the pickling bath when the baths are partially dumped),

81 l/h *68 +600 l = 6108 l

Density of fresh acid is 1.1 kg /h

Fresh acid HCl composition is 18.7 %,

98 kg fresh acid / h is fed to the bath that is 18.3 kg HCl fed to the bath per hour.

The $FeCl_3$ content in the WPL would be reduced to $FeCl_2$, according the reduction reaction of $FeCl_3$

$FeCl_3 + 1/2H_2 \longrightarrow FeCl_2 + HCl$

From this reaction 0.7 kg $FeCl_2$/h and 0.2 kg HCl /h will be produced. The final composition of WPL after the reduction reaction would be

HCl =10.8%

$FeCl_2$=16.8%

H_2O =72.4%

Amount of make-up HCl required, that is the amount of HCl required to fed the bath as fresh acid after the recovery process is applied, can be found from the difference between current fresh acid amount and HCl that would be recovered from the crystallization process. This expression can be formulized as:

HCl required = fresh acid fed in the current situation- recoverable acid in the WPL

HCl req=337.7*0.187-0.1077*256=98.8 kg/h

As can be seen from Figure 5.13 there are two Crystallizers in the Crystallization Recovery Process.

The mass Balance for the 1 st Crystallizer:

Flowsheet of the process is shown in the Figure APP.2.

HCl required = fresh acid fed in the current situation- recoverable acid in the WPL

Fresh HCl Reqired=337.7*0.187-0.1077*256=98.8 kg/h

$FeCl_2$ solubility for the $FeCl_2$-HCl-H_2O system at –40 °C is 3.73 % when %HCl is 20.7 % from Figure 4.2.

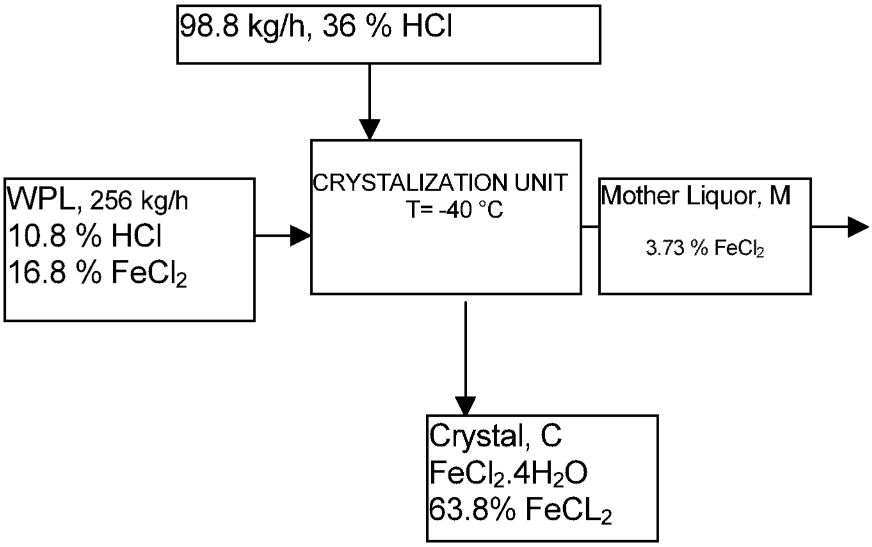

Figure APP.2. Mass Balance around the 1st Crystallizer

Assume %HCl in mother liquor would be 20.7%

Total Mass Balance

256+98.8 =C+M

$FeCl_2$ Balance

256*0.168=0.0373*M+C*0.638

Crystal = 49.6 kg /h

Mother Liq., M =305.1 kg/h

Check the assumption whether the % HCl is 20.7 % or not,

% HCl =337.7*0.187/305.1=20.7%

Energy Balance for the first crystallizer,

Heat of solution for $FeCl_2$ is 2.7 kcal / mole (Mullin, 1961)

$\Delta E = -\Delta[(H+P+K)\ m]+Q-W$
$Q=\Delta H$
$Q= H_{\text{final products}} - H_{\text{entering products}} + H_{\text{solution}}$

Q= 15.87 kmol/h x70690 J/kmole K x (-40- (-65)) +14.42 kmol/h x74721.6 (53.2- (-57)) –2.7 kcal/gmol x 10^3 gmol/kmol x 0.073 kmol/h x 10^3 cal/ kcal x 4.184 J/cal

Q= 0

The mass Balance for the 2 nd Crystallizer:

Flowsheet of the process is shown in the Figure APP.3. $FeCl_2$ solubility in the $FeCl_2$-HCl-H_2O system at –57 °C is 2.1 % when the HCl is 21.26% from Figure 4.2.

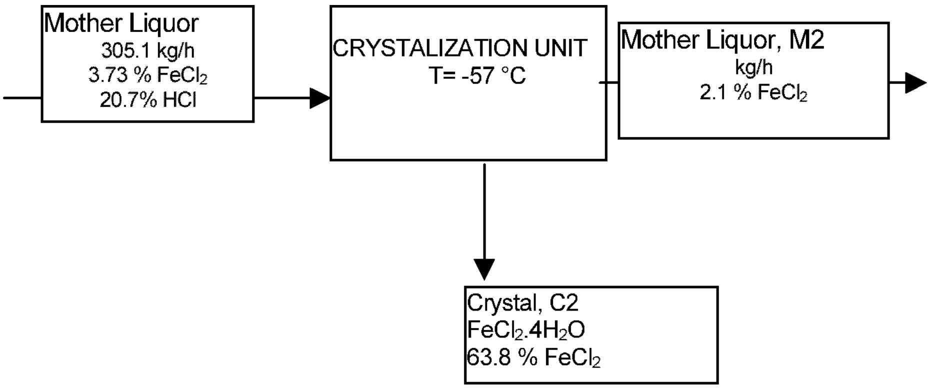

Figure APP.3. Mass Balance around the 2nd Crystallizer

Assume mother liquor HCl concentration is 21.26 % after the crystallization process.

Total Mass Balance

305.1=C2+M2

$FeCl_2$ Balance

0.373*305.1=C2*0.637+M2*0.021

C2=8.2 kg/h

M2=297kg/h

Check the assumption whether the % HCl is 21.26 % or not ,

% HCl =337.7*0.187/297=21.26%

Heat of solution for $FeCl_2$ is 2.7 kcal / mole (Mullin, 1961)

Energy Balance for the 2nd Crystallizer,

From General Energy Balance Equation;

$\Delta E = -\Delta[(H+P+K)\, m]+Q-W$
$Q=\Delta H$
$Q= H_{\text{final products}} - H_{\text{entering products}} + H_{\text{solution}}$

Q= 14.62 kmol/h x73308 J/kmole K x (-57- (-40)) –0.67 10^6 –2.7 kcal/gmol x 10^3 gmol/kmol x 0.04 kmol/h x 10^3 cal/ kcal x 4.184 J/cal
Q= -18 MJ/h
Assuming coefficient of performance as 4 for the compressor, the power required for the Refrigeration system would be;
18 MJ/h /4 x 1000 kJ/1 MJ x 1h / 3600 sec =1.25 kW