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RECLAIMING WASTE PICKLING ACID VIA BIPOLAR MEMBRANES AND AQUATECH SYSTEMS

K. N. Mani & C. H. Byszewski

Aquatech Systems

Allied-Signal Inc.

7 Powder Horn Drive

Mt. Bethel, NJ 07060

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Introduction

Water splitting using AQUATECH bipolar membrane technology offers an economic, environmentally sound alternative to dumping waste acids. With it, resource recovery is a practical solution. For example, in the production of stainless steel, the surface oxide film is removed via a chemical pickling (descaling) step that uses a mixed acid solution. Disposal of the spent acid from the pickling step is becoming increasingly difficult, expensive and environmentally constrained. AQUATECH bipolar membrane technology which converts salts into their constituent acids and bases at low energy consumption is the cost effective solution to this problem. The technology is presently being commercialized by the Aquatech Systems unit of Allied-Signal Inc. AQUATECH technology regenerates the liquor by recovering up to 95% of the hydrofluoric and nitric acid constituents. The once-thru pickling process is transformed into an essentially closed loop system with minimal chemical makeup and potentially no disposal cost.

In this paper we will provide some background on the technology and illustrate its utility in the recovery of mixed acids from stainless steel pickling. A review of pilot plant data will detail the process parameters specifically for waste acid reclamation, followed by highlights of future process improvements.

Technology Background

Neutralization is a well known exothermic chemical reaction. Efficiently reversing the reaction is not. Until recently, splitting of water was accomplished predominantly by electrolysis. However, this was very power intensive. With the development of a very specialized ion exchange membrane, the bipolar membrane, splitting water into hydrogen and hydroxyl ions efficiently has become possible.

Detailed descriptions of the membrane water splitting process can be found in references (1-3). Briefly, the process, which is electrically driven, uses ion exchange membranes to separate and concentrate the acid and base constituents from a salt stream. The key element in this electrodialytic process is the bipolar membrane, so called because it is composed of two distinctive layers which are selective to ions of opposite charges. An expanded view of this membrane and its operation is shown in Fig. 1. Under the influence of an applied direct current, water diffuses into the membrane interface where it dissociates to hydrogen and hydroxyl ions. The H^+ and OH^- ions are then transported across the cation and anion selective layers respectively to chambers on either side of the bipolar membrane. Acidification/basification of these chambers is the overall result.

Bipolar Membrane Construction and Operation

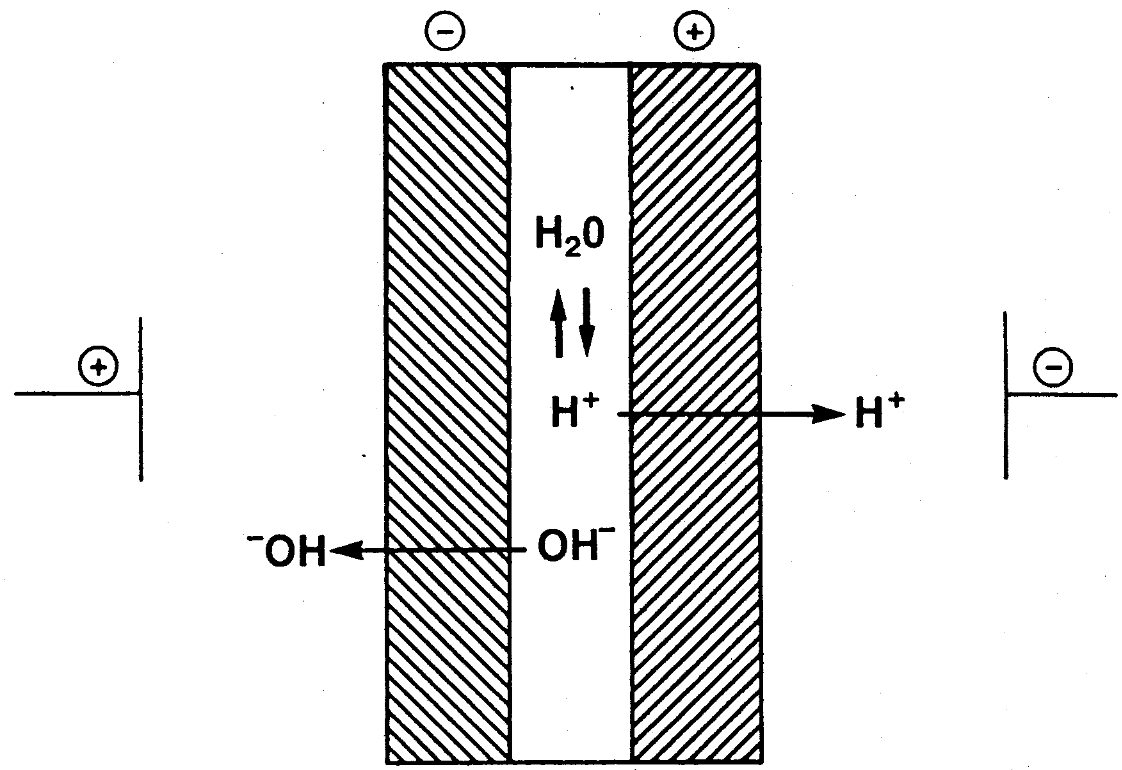
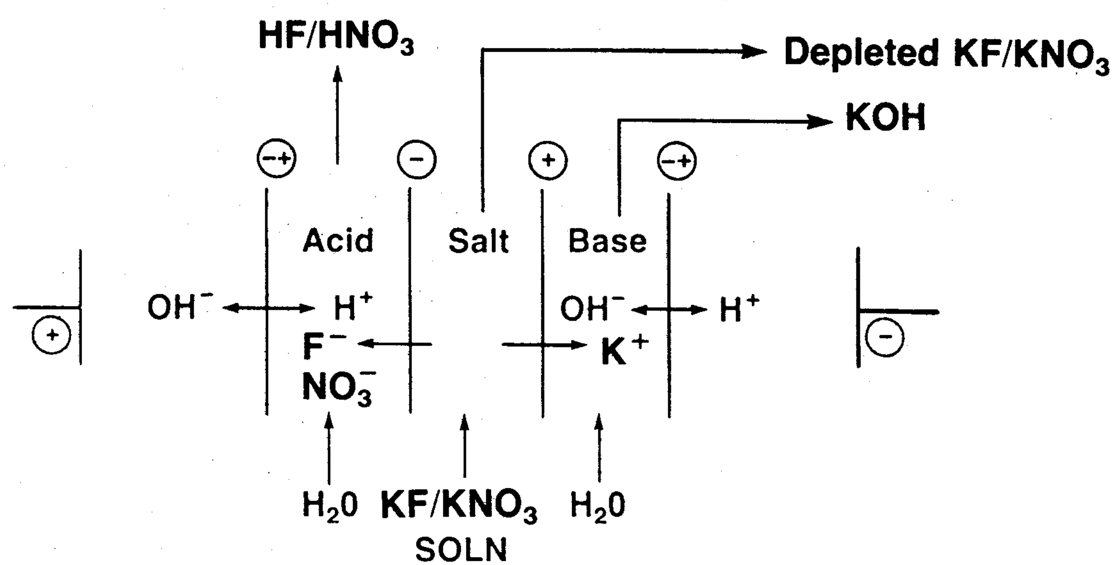


Figure 1

To achieve net production of acid and base, monopolar (i.e. cation and anion exchange) membranes are used in conjunction with the bipolar membrane. A schematic of a generalized three compartment cell unit is shown in Fig. 2. The salt (e.g. KF/KNO_3) is fed to a chamber between the cation and anion selective membranes. The cations (K^+) and anions (F^-/NO_3^-) move across the monopolar membranes and combine with the hydroxide and hydrogen ions, as shown, to form the base and acid. In a commercial operation, up to 200 of such cell units are assembled between a single set of electrodes to form a compact water splitting stack. Feed to the acid, base and salt chambers is achieved via internal manifolds built into the stack.

Key to the success of the water splitting operation is the development of highly efficient, long lasting, low energy consuming bipolar membranes by Allied-Signal. A typical potential drop behavior of the membrane in the standard solution of 0.5M Na_2SO_4 is shown in Fig. 3. The membrane shows a steeply rising voltage at low currents, followed by flattening-out at the higher current densities. In the commercially interesting range of 50-120 mA/cm^2, the membrane has a potential drop of 0.9-1.0V. The potential drop across the membrane is also dependent on the acid/base media on either side as shown in Fig. 4. The higher osmotic pressures result in slightly higher voltage drops. When contrasted with the minimum thermodynamic potential of 0.83V(1), the AQUATECH bipolars are highly energy efficient.

Waste Pickling Acid Application
Three Compartment Cell



Legend

(−+) Bipolar Membrane

(+) Cation Membrane

(−) Anion Membrane

Figure 2

Potential Drop Across Bipolar Membrane

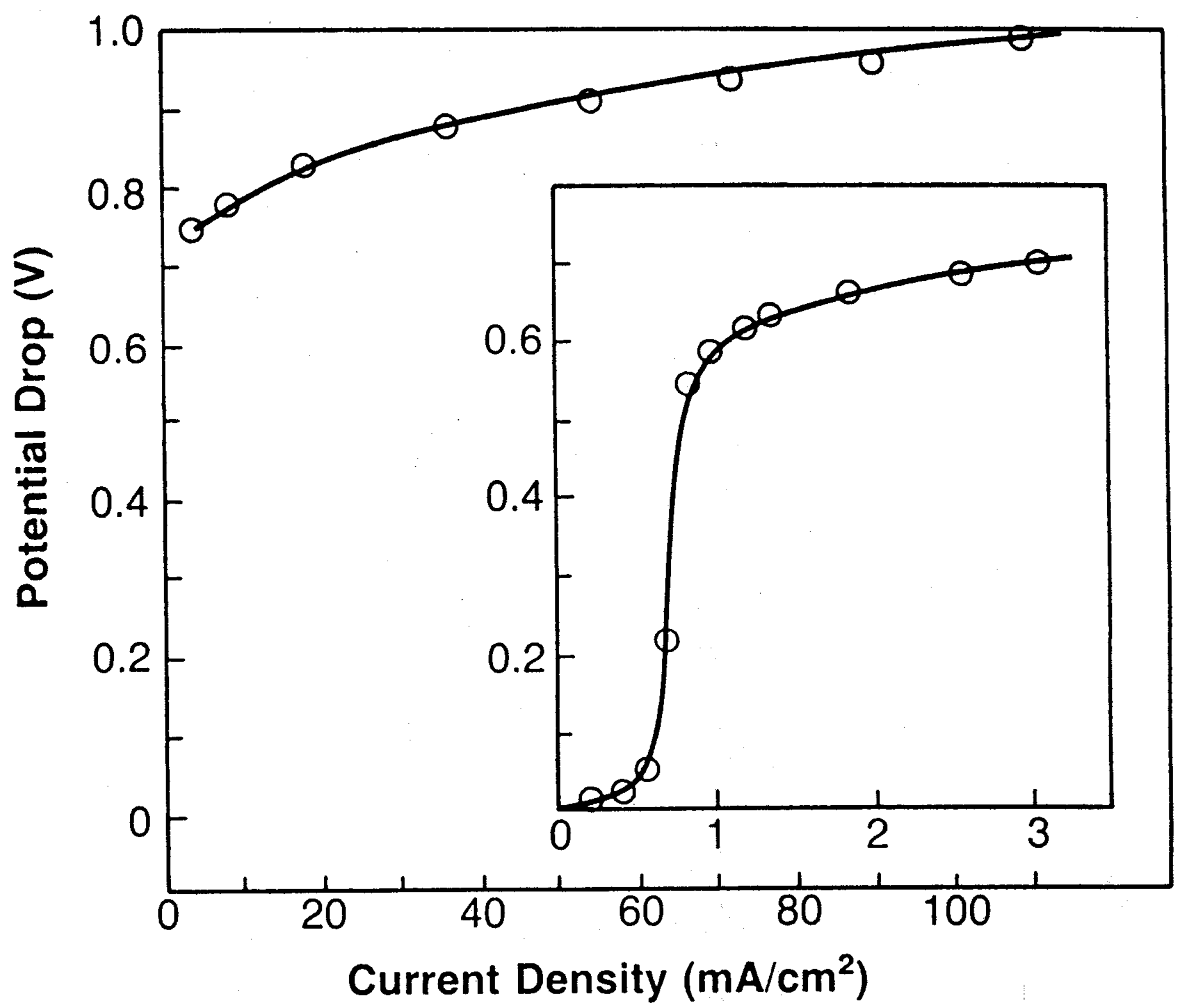


Figure 3

Potential Drop Across Bipolar Membrane In Various Media

	Acid	Base
○	7% Na_2SO_4	7% Na_2SO_4
□	Sat. NaCl	6.6% NaOH
△	Sat. NaCl	15.6% NaOH

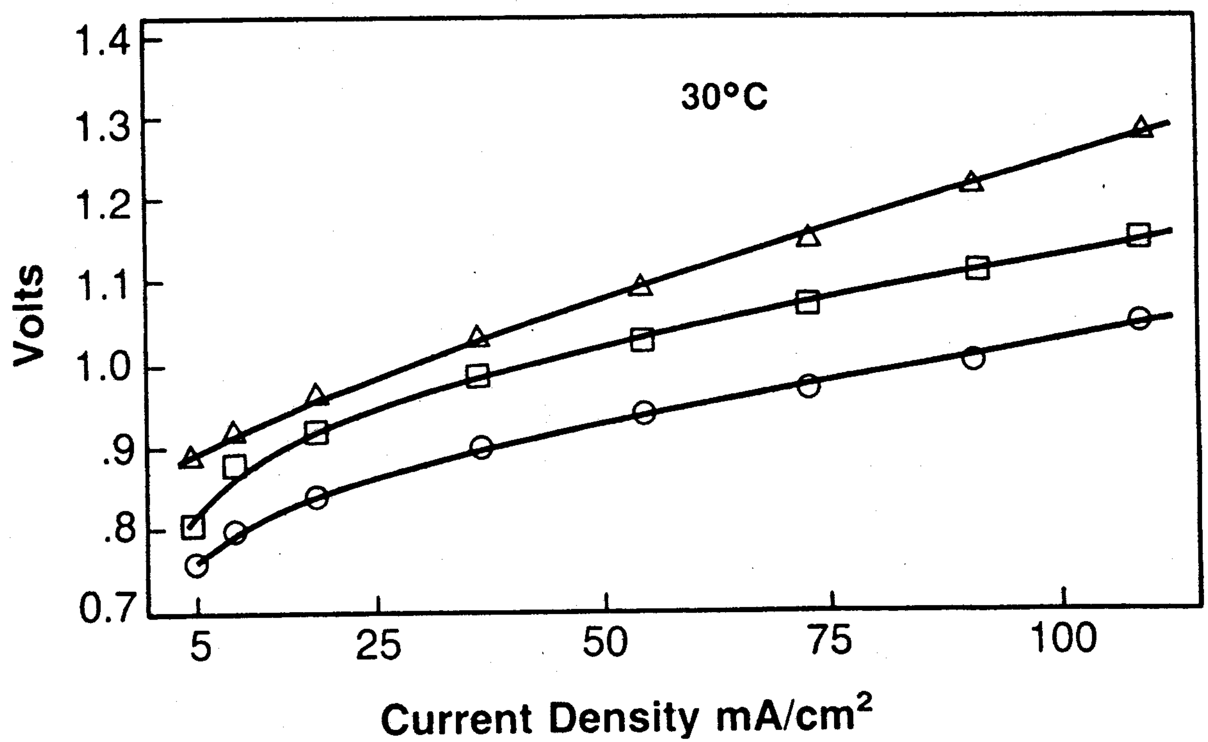


Figure 4

Allied-Signal's proprietary cation membranes were used in the pilot plant study. Nafion® perfluorinated cation membranes from DuPont were used at the two ends of the stack near the electrodes.

The anion membranes used in this pilot plant study were for the most part from commercial sources. RAI Corporation's R-4035 was used in the pickle liquor recovery process initially followed by Allied-Signal's own proprietary anion membranes.

Technology Applications

A large number of applications have been identified for the AQUATECH technology. A partial list of the applications is given in Tables 1 and 2 under the broad categories of pollution control/-resource recovery and chemical processing. Preliminary feasibility studies have been conducted on most of the applications. Applications marked with an asterisk in the Tables have been tested more extensively and are considered to be ready for immediate commercialization. The waste pickle acid application detailed below, fits the Resource Recovery category and serves to illustrate the capabilities of this general purpose unit operation.

Application: Waste Acid Recovery

Aquatech System's first commercial application is reclaiming waste pickling acid. The AQUATECH technology was successfully piloted at Washington Steel, a major stainless steel producer in Western Pennsylvania, and recovered the acids from waste pickle acid

TABLE 1

Technology Applications: Pollution Control/Resource Recovery

HF/Mixed Acid Recovery

- Stainless Steel Pickle Liquor Recovery*
- HF/NaOH Recovery from Spent Aluminum Potlinings*
- Fluosilicic Acid Conversion to HF, SiO_2
- Fluoride Emission Control in Chemical Processing

Sulfate Recovery

- Battery Acid Recovery*
- Waste Sodium Sulfate Conversion*
- Sodium Sulfate Conversion in Rayon Manufacture

Pulp & Paper

- Sodium Alkali Recycling in Pulping & Bleaching Operations

Flue Gas Desulfurization

- SOXAL Process SO_2 Recovery*
- Dry Sodium Scrubbing - Alkali Recovery

TABLE 2

Technology Applications: (Continued)
Chemical Processing

Organic Acid Production/Recovery

E.G., Acetic, Formic, Citric and Amino Acids

Ion Exchanger Regeneration*

Brine Acidification in Chlor-Alkali Industry*

Potassium and Sodium Mineral Processing

- KCl Conversion*
- Solution Mining of Trona and Subsequent Soldium Alkali Production
- Sodium Alkali Production from Natural Brines & Solid Trona

Ilmenite ($FeO.TiO_2$) Upgrading with Coproduction of KOH

- Upgrading to Synthetic Rutile
- Fluoride Route to TiO_2 Pigment

at the proper strength and purity for recycling back to the pickling operation. Figure 5 shows a simplified flow sheet of the process.

In the production of steel the metal surface is first annealed, forming an oxide film. A controlled chemical pickling step using a mixed acid solution of HF and HNO_3 descales the steel. These acid baths require periodic changing as they become inactive with rising metal contamination (50-60 g/l). The spent, bluegreen acid from the bath containing metal fluorides and nitrates is conventionally limed, filtered and discharged to landfills and waterways. Alternately, in the AQUATECH process, the spent pickle liquor is neutralized in a stirred tank to pH 10 with recycle KOH. The metal values form hydroxides precipitates, while the fluoride and nitrate values are retained in solution as soluble salts. The neutralization reaction is rapid, requiring only 10-20 minutes depending on metal content. The initial composition of the pickling liquor can vary over a wide range of HF (1-6 wt.%), HNO_3 (8-20 wt%), and metal (25-60 g/liter) content, with little effect on the neutralization step or AQUATECH process. A fluoride to nitrate ratio of greater than 1 does result in elevated current efficiencies as shown in Table 3.

Once the pH has stabilized between 9-11, the neutralized mixture is filtered in a conventional plate and frame filter press and washed with recycle water to recover substantially all of the

Aquatech Pickle Liquor Recovery Process

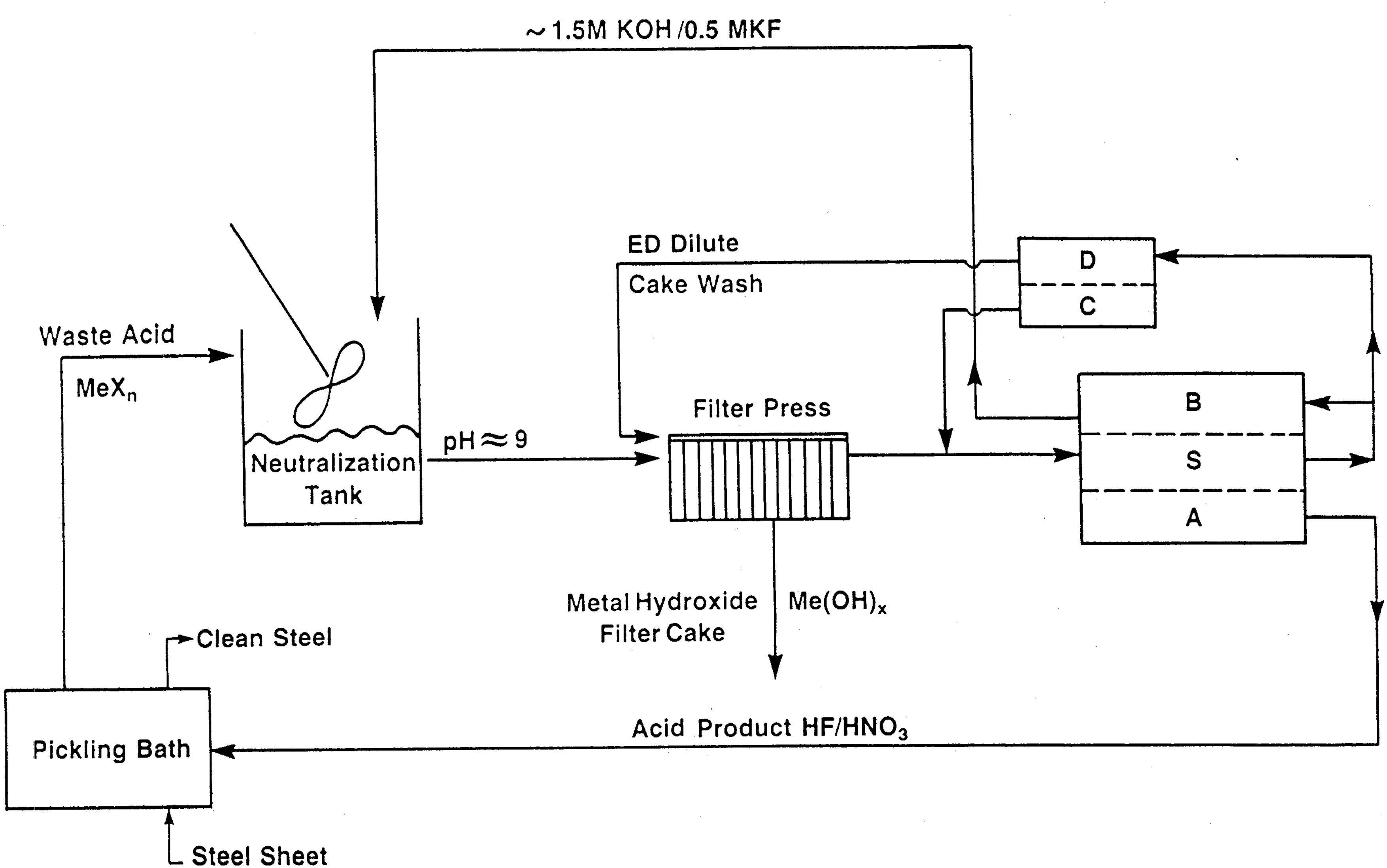


Figure 5

Table 3
Waste Pickling Acid Application
Trend Of F/NO_3 Ratio
On Current Density

Mole Ratio F/NO_3	Current Efficiency, %
0.50	60
0.75	65
1.00	70
1.50	75
2.00	80
2.50	85

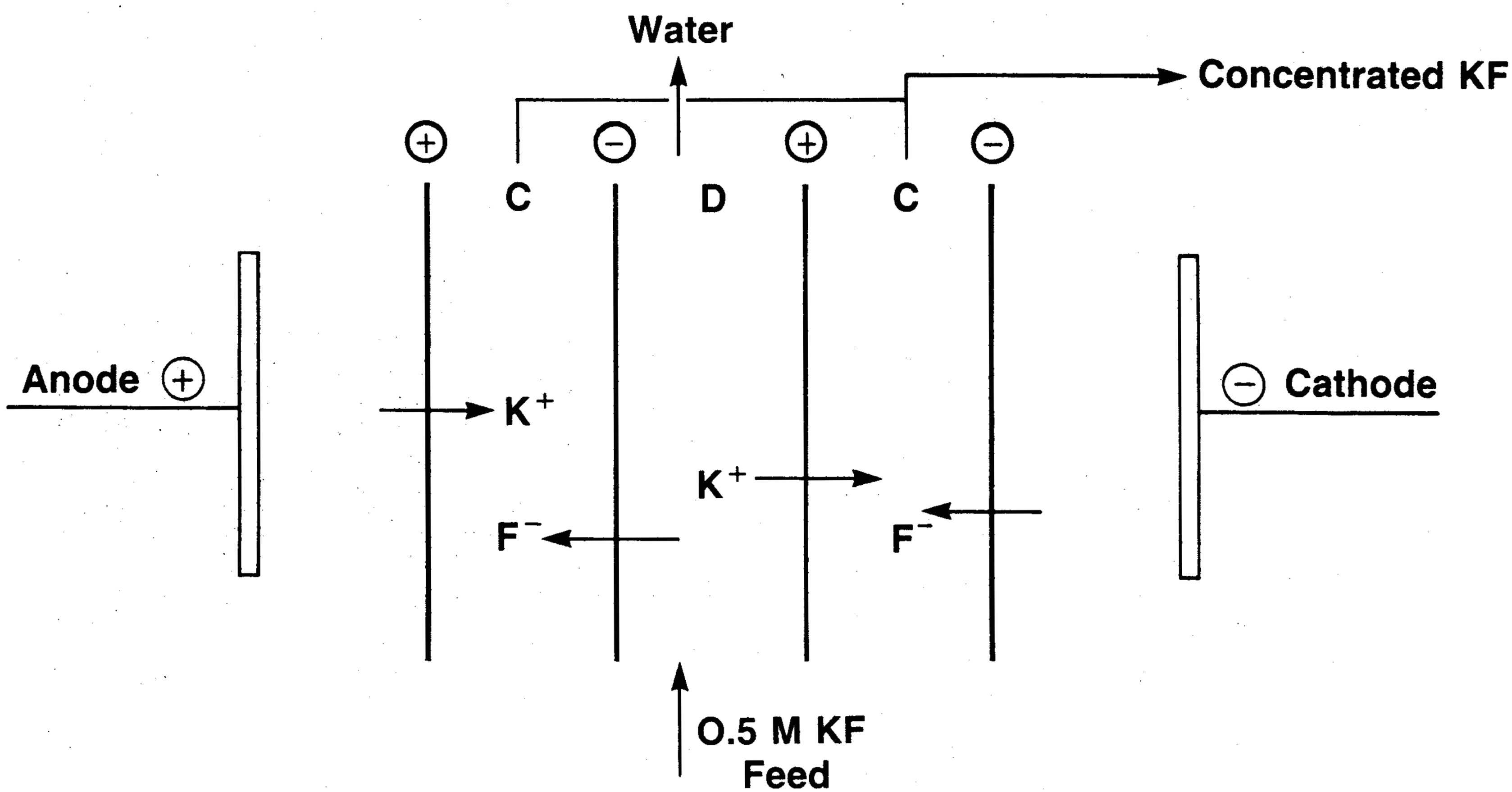
At 70 AMPS/FT2 And 80°F

F^-, NO_3^- values. Diatomateous earth is added as a body feed directly into the neutralization tank, to enhance the filtration rate and quality. The filtrate quality continually achieved is excellent, overall metals content being at the ppm level. The hydroxide cake from the filtration step, containing 38-45 wt% solids, can be dried and returned to the steel smelter. Typically 35 Ft^3 of cake are collected for every 1000 gallons of waste acid processed.

The clean, clear KF/KNO_3 solution from the filtration step is admitted to the salt loop of the three compartment AQUATECH cell. Here, through use of the direct current driving force, KOH is generated in the base loop while an HF/HNO_3 mixture is generated in the acid loop. During the water splitting step salt concentration decreases from 1.1-1.5N to 0.3-0.5N. A portion of the depleted salt solution is used to dilute the base generated, while the balance is forwarded to the water recovery step. An electrodialytic (or reverse osmosis) unit is employed to reject water as well as to concentrate the dilute salt up to 5 to 6 times the original concentration, to assist with fluoride recovery. The product from the base loop is typically 1.5N KOH/0.4N KF and is recycled to the waste acid neutralization step.

Water and KF recovery from the dilute salt solution from the AQUATECH unit is achieved using a conventional electrodialysis (ED) cell containing Allied's cation membranes and Asahi Glass' AMV anion membranes, as shown in Fig. 6. The concentrate from the electrodialysis process is returned to the AQUATECH salt loop while the dilute containing 0.02-0.04N salt is used for both internal makeup water stream and washing the filter cake.

Water Recovery
Electrodialysis For Concentrating KF



⊕ Allied Cation Membrane

⊖ AMV Anion Membrane by Asahi Glass

Figure 6

Pilot Plant Review

Details of the pilot operation are summarized in Figures 7-10 and Tables 4-8. An important factor that has ensured the success of the pilot run is the consistently high purity of the neutralized salt (KF/KNO_3) feed to the AQUATECH cell. Table 4 shows a typical analysis of the solution from the neutralization/filtration step. From the standpoint of cation membrane fouling, the troublesome impurities such as Ca, Mg are present at only 0.1-0.3 ppm levels while Fe, Cr, Ni are at acceptably low levels of 1-3 ppm. Fig. 7 shows the dramatic effect of total Cr on the cell stack's performance. It is reasonable to assume that the majority of the Cr is present as Cr^{+6} since Cr^{+3} is highly insoluable in hydroxide. Therefore, for waste acids where Cr^{+6} is normally present, a preliminary atomic adsorption analysis for total Cr level is recommended. Cr ppm levels exceeding 3 wppm require the addition of a reducing agent such as potassium sulfite.

The pilot plant was initially operated for 100 days to establish process reliability. Operating conditions are shown in Table 5. During this phase the plant successfully processed 204 L/day (54 gal/day) of waste pickle liquor. The AQUATECH cell had 25 cell units ($2.33M^2$ (25 Ft^2) total area) while the ED cell operated with 15 cell pairs ($1.4M^2$ (15 Ft^2) area). The effective area per cell was $0.093M^2$ (1 Ft^2). After this phase the run was extended an additional 70 days for the purpose of establishing long term membrane stability.

Table 6 shows an overall material balance for the 100 day run. Recovery of the key materials namely F^-, NO_3^- and K^+ was found to be quite high. Recovery levels of 93, 99 and 96 percent repectively

TABLE 4

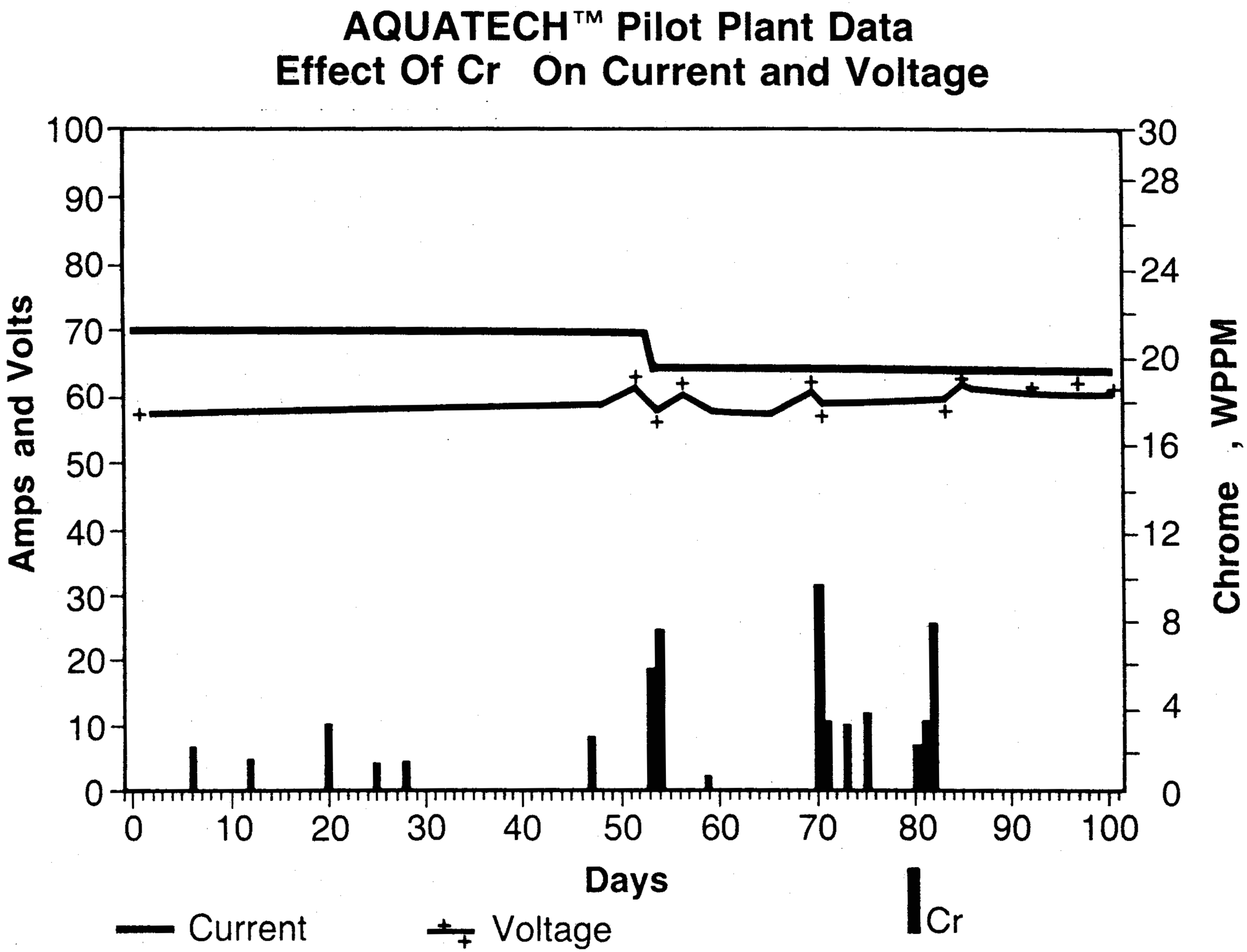
Pickle Liquor Neutralization

Typical Procedure: 100 Gallons of Spent Pickle Liquor Neutralized with 300 Gallons of Recycle KOH Solution to PH 9. 5 Kg of Filter Aid was Added and the Resultant Slurry Filtered.

Typical Filtrate Analysis: Total Salt Normality 1.2 Eq/L

Metals Analysis Using ICP, PPM.

Cr	1.0	Mn	0.02
Fe	0.79	V	0.09
Ni	0.50	Cu	1.1
Ca	0.20	Ti	0.2
Mg	0.01	Zr	0.08
W	0.4	Al	1.2
P	0.4	Ba	0.1
Cd	0.08	Mo	20.0
B	1.4	Zn	0.10
Si	2.9	Co	0.24


AQUATECH™ Pilot Plant Data
Effect Of Cr On Current and Voltage
Amps and Volts
Chrome , WPPM
Days
Current
Voltage
Cr
100
90
80
70
60
50
40
30
20
10
0
30
28
24
20
16
12
8
4
0
0
10
20
30
40
50
60
70
80
90
100

Figure

Table 5
Pilot Plant
Operating Parameters

Current, Amps/ft^2	67.6
Voltage, Volts	59.1
Volts/Cell	
Initial	2.0
100 Days	2.4
170 Days	2.6
Products	
Acid, Normality	2.6
Base, Normality	1.4
Salt, Normality	0.1
Acid Rate, gph	4.8
Base Rate, gph	10.0
Average Efficiency, %	80.8
Acid	75.0
Base	86.5
K^+ In Acid, %	0.3
Temperature, °F	81.5

TABLE 6

Washington Steel Corporation

100 Day Pilot Run – Overall Material Balance

#	Stream	Gallons	Lbs.	Material Handled, Lbs.		
				F^-	NO_3^-	K^+
1	Waste Acid	1000		520	800	
2	Recycle Base	2450		190		1750
3	Acid Product	1800		486	800	
4	Cake		2640	34	0	70

Overall Recovery	F^-	93%
	NO_3^-	99+%
	K^+	96%

were calculated. Obviously the neutralization step is effective in breaking the metal fluoride complexes in the waste pickle liquor.

Stream #4 - the metal hydroxide cake when be recycled to the electric arc furnace to fully eliminate any waste from this process. During pilot testing the cake was disposed of in landfills. However, technology to recycle the cake is presently being demonstrated. Roughly 2.5 lb (1.4 kilograms) of 40 wt% cake is collected for every gallon (3.78 liters) of waste acid processed. The pie chart Figure 8 illustrates the 40 wt% cake solids composition with thorough washing. The filter cake is predominantly iron hydroxide with fluoride and potassium levels reduced to 7% and 4.1% respectively.

Figure 9 shows the performance of the AQUATECH cell with time. The current density was maintained between 65-70 amps/Ft^2 (70-75 mA/cm^2) while the cell voltage (overall) remained within the range of 60-65V. The cell was operated at 86 $\pm$ 3.5^{o}F (30^{o}C $\pm$ 2^{o}C). A slight increase in stack voltage over time is normal and is an indication of the stack age. The step function increase in voltage at 100 days dramatically reflects the effect of high ppm levels of total Cr in the feed after resuming operations at 70 amp/Ft^2. The operations subsequent to the 100th day clearly illustrate the AQUATECH stacks ability to regain a stable operating voltage after an upset.

Figure 10 shows the average current efficiency for acid and base generation with time. The overall efficiency for the 100 day test is estimated at over 80%. A measure of the productivity of the AQUATECH cell is its current efficiency, i.e., the gram equivalents of acid and base produced per faraday (96,500 coulombs) of current input. In an actual cell the overall efficiency is less than 1.0

Detailed Filter Cake Analysis

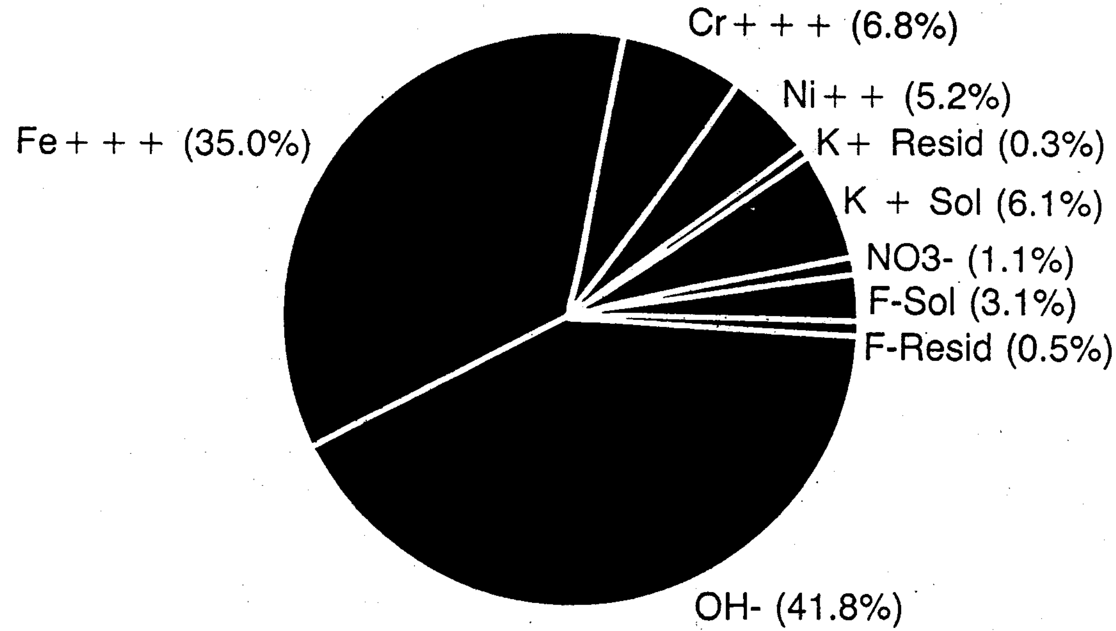
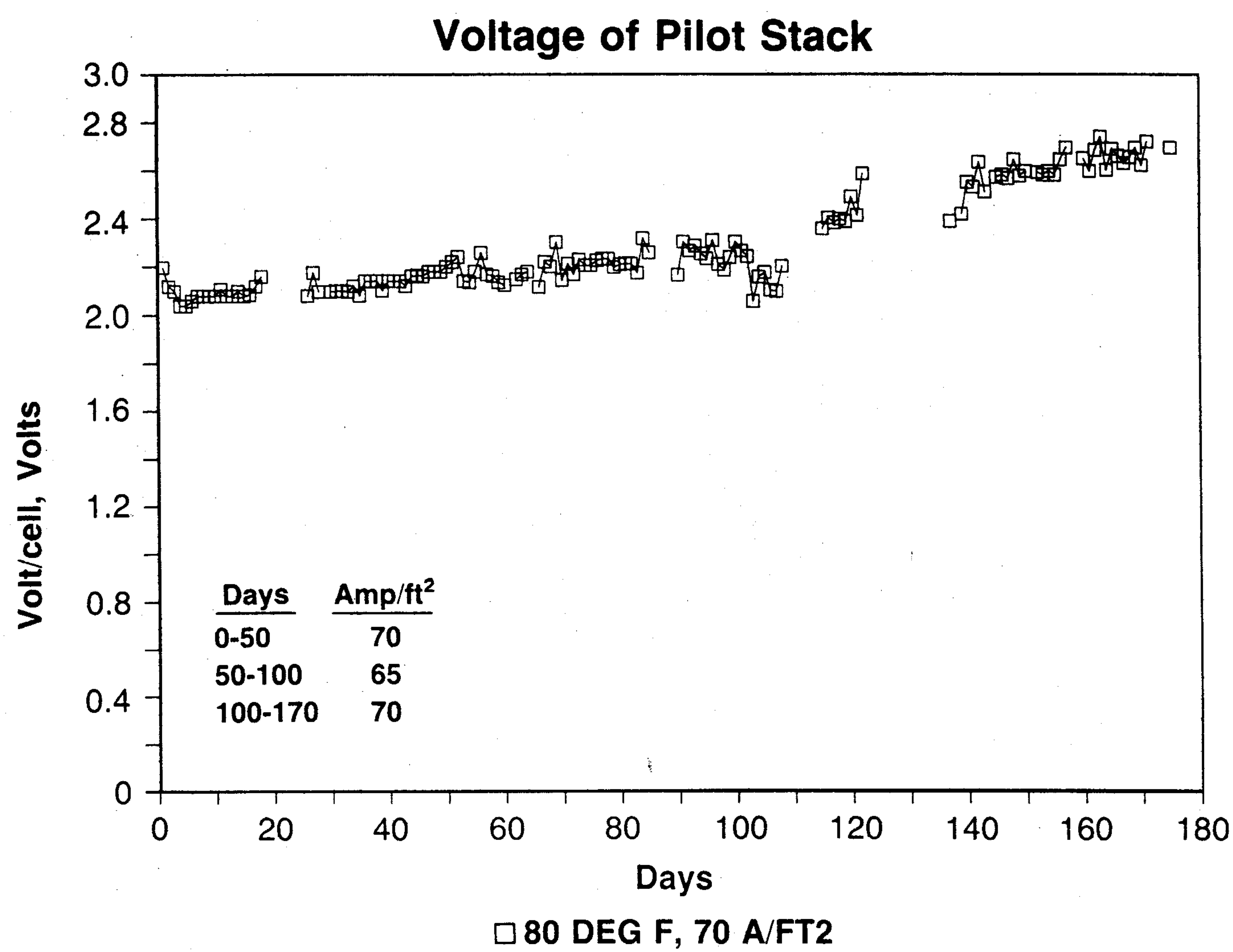


Figure 8



Voltage of Pilot Stack
3.0
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
Volt/cell, Volts
Days
Amp/ft2
0-50
70
50-100
65
100-170
70
0
20
40
60
80
100
120
140
160
180
Days
80 DEG F, 70 A/FT2

Figure 9

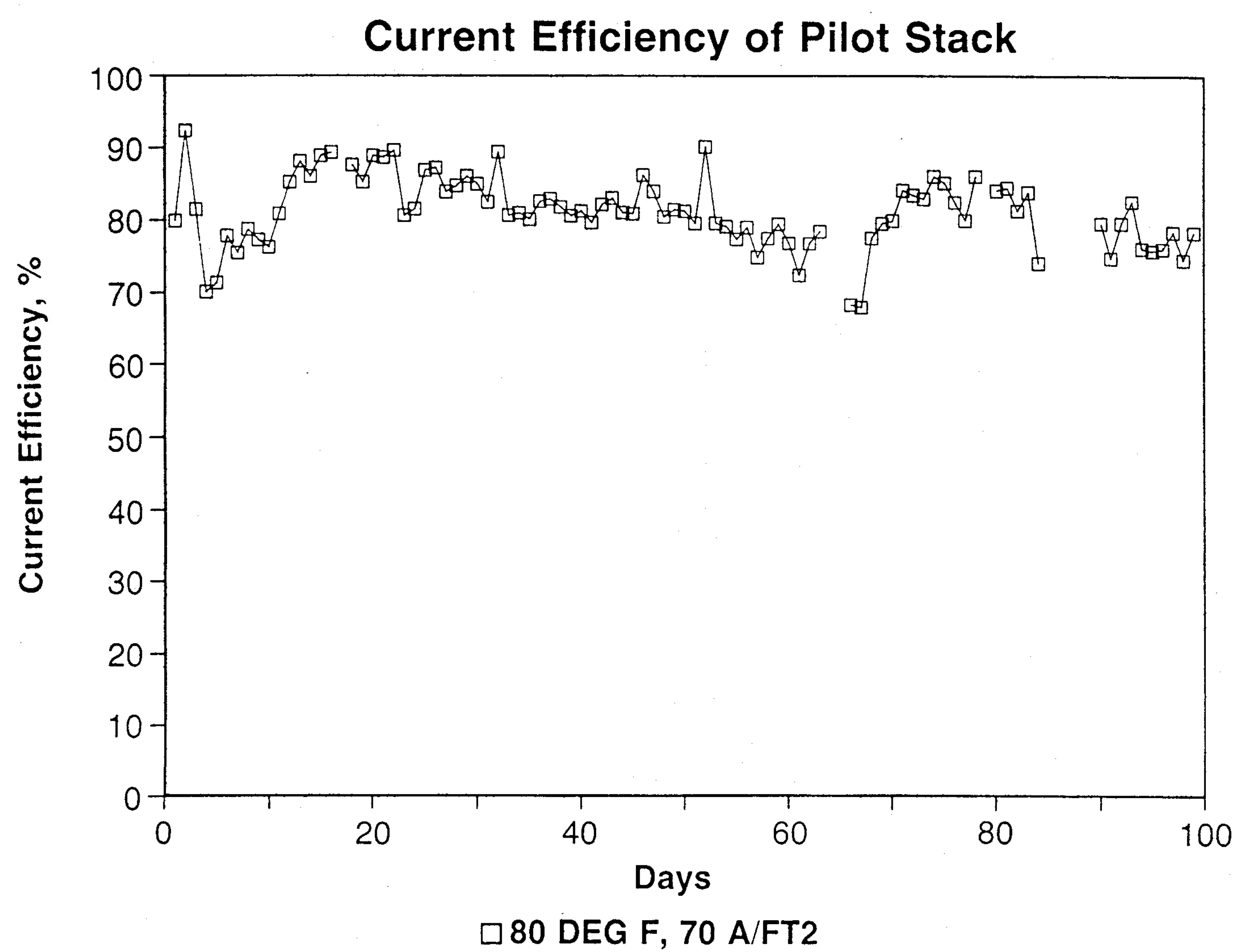

Current Efficiency of Pilot Stack
Current Efficiency, %
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
Days
□ 80 DEG F, 70 A/FT2

Figure 10

due to (a) the imperfect permselectivity of the bipolar and monopolar membranes and (b) diffusion of un-ionized species. In the pickle liquor recovery application for example, product HF can diffuse out of the acid compartment to the neighboring salt and base compartments.

The acid produced is 3N mixed acid suitable for pickling stainless steel while the base product strength is 1.5N or 8 wt percent. Producing a dilute base is adequate for the neutralization reaction and improves the cell stack performance by both elevating the acid purity (< 1% K^+ in acid) as well as boosting the current efficiency. The power required to regenerate the acid is estimated to be 1525 kwh/ton of 5% HF/8% HNO_3 on a 100% basis.

At the intermediate point and conclusion of the pilot run the membranes were recovered and analyzed individually. The results are summarized in Table 7. All of the membranes had retained their selectivity and mechanical properties and showed no evidence of fouling. The electrical resistance of the monopolar membranes was stable while the bipolar membranes had an acceptably low potential increase of <0.08V/month.

The pilot test has, therefore, successfully demonstrated the ability of the AQUATECH technology for pickle liquor recovery. On the basis of the pilot run the overall cell stack life is projected to be at least one year.

<u>Economics</u>

Table 8 shows an estimated capital and operating cost summary for a plant processing 6 x 10^6 liters/yr. (1.6 M gallon/yr) of spent pickle liquor. The battery limits investment covers the entire

TABLE 7

Washington Steel Corporation
Pilot Test Review
Membrane Analysis

Type	Manu-facturer	Units	Nominal (When New)	100 Days	170 Days
Bipolars	Allied	Volts @110mA/cm^2	1.1	1.29	1.4
Cation	Allied	ohm-cm^2	6.0	6.9	6.8
Anion	RAI 4035	ohm-cm^2	2.3	2.7	2.2

TABLE 8

Pickle Liquor Recovery
Capital and Operating Costs

Basis: 6×10^6 Liter/Yr. of Spent Pickle Liquor Containing
5 Wt% F^-, 10 Wt% NO_3^-
8000 Hrs./Yr.
One Year Life for Cell Assembly
Acids Recovered (Net): 320 Mt/Yr. of HF
675 Mt/Yr. of HNO_3

Total Battery Limits Capital for Plant $1.8 x 10^6
Jan. '86 Costs
All Costs in U.S. Dollars

Operating Cost Summary

Raw Materials	
Makeup KOH @ $600/Ton	36,000
Filter Aid @ $400	18,000
Cell Maintenance	300,000
Electricity @ 5¢/KWH	128,000
Other Maintenance	78,000
Labor & Supervision	40,000
Depreciation @ 10%	180,000
Taxes & Insurance @ 2%	36,000
Total Operating Costs	816,000
Product Credits	
HF @$1500/Ton	480,000
HNO_3 @ 225/Ton	152,000
Waste Disposal @ 8¢/L	480,000
Metals Credit	150,000
Total Credits	1,262,000
Savings	446,000
ROI	25%

plant including filtration, neutralization, tankage, AQUATECH system and ED water recovery unit. It should be pointed out that a considerable part of the total investment is for hardware and equipment other than the AQUATECH unit itself. If a steel manufacturer has some of the pretreatment and waste handling facilities already in place, the net capital requirements can be significantly lower.

Operating costs for the plant are more than offset by product credits. The waste disposal credit shown is typical for U.S. stainless steel producers. The cell maintenance cost is based on a one year life. Overall capital payback period is seen to be four years, which is quite attractive for a pollution control application. Studies also indicate that the AQUATECH technology is economically superior to other commercially available extraction or thermal processing techniques.

Advanced Application with EDX™ Free Acid Electrodialysis

Now, advanced pickle liquor regeneration combines current AQUATECH bipolar membrane technology with EDX™ state-of-the-art free acid electrodialysis. This is similar in concept to salt concentrating electrodialysis, the difference being acids are being concentrated. Because 90% of the free acids from the spent liquor is removed with EDX electrodialysis, recycle acid concentration is increased and the capacity requirement of the AQUATECH unit is decreased -- saving equipment and operating costs. Figure 11 depicts the improved process flow.

Free nitric and hydrofluoric acids present in the spent pickle liquor are isolated and concentrated by monopolar membranes in the

AQUATECH Systems
Advanced Stainless Steel Pickle Liquor Regeneration with EDX

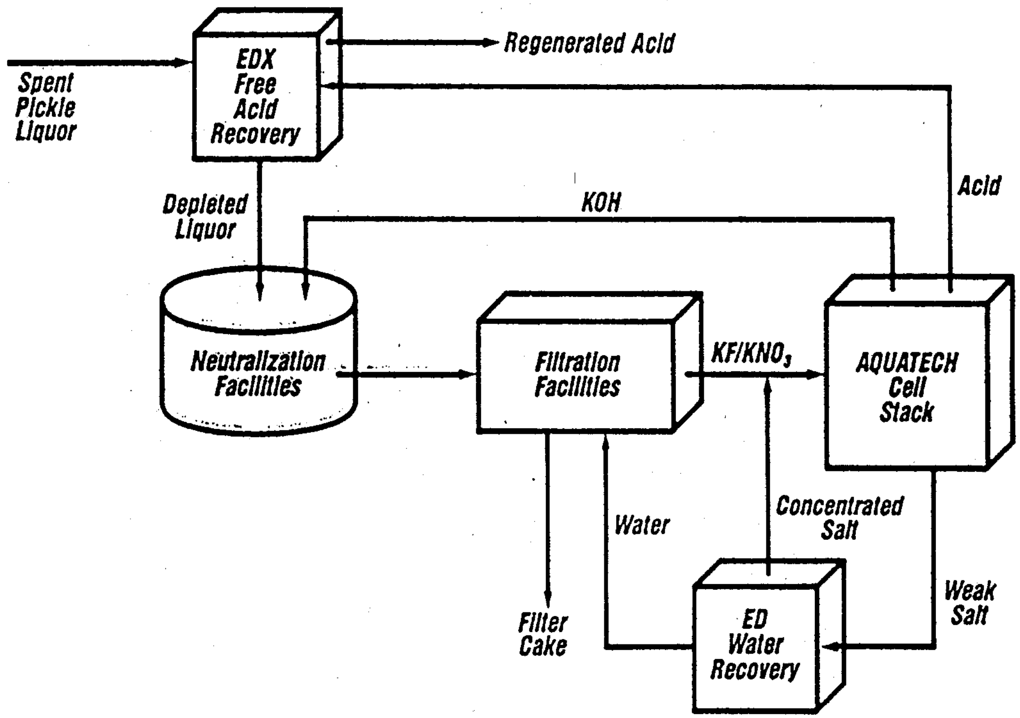


Figure 11

EDX unit. This allows the unreacted acid in the waste acid to be recycled before the complexed metal fluorides are neutralized. As before, potassium hydroxide neutralizes the remaining complexed-metal fluoride liquor to form a potassium fluoride/potassium nitrate solution and metal hydroxides precipitate. The KF/KNO_3 solution with suspended solids is sent to a plate and frame filter press which yields a clear, predominantly KF filtrate and a filter cake of iron, nickel, and chromium hydroxides. Processes are available and presently being demonstrated to dry and recycle this filter cake to the smelter. The salt solution enters the AQUATECH cell stack where hydrofluoric acid, nitric acid, and potassium hydroxide are regenerated. Low-voltage direct current drives the electrochemical reactions within the stack. The AQUATECH System returns the regenerated HF acid to the EDX unit to pick up free nitric acid and recycles the total to the pickling plant. Potassium hydroxide is returned to the neutralization facilities and depleted salt is routed to the water recovery unit. Water for washing the filter cake is recovered from the weakened salt by a secondary electrodialysis (ED) step, minimizing overall water consumption. Concentrated salt is recycled to the AQUATECH cell stack.

Conclusions

AQUATECH water splitting technology is a versatile unit operation which has a number of applications in the areas of pollution control/resource recovery and chemical processing. The technology enables closed loop processing of salts in an energy efficient manner and the consequent elimination/minimization of pollution control problems. The pilot study on the pickle liquor recovery process has demonstrated the long term stability of bipolar membranes, cell stack assembly and the ability to recover substantially all of the acid values in a cost effective manner.

It has been shown that AQUATECH technology is economically competitive with existing technologies, simple in concept, and beneficial to both the process and the environment. Exercising the option to recycle the cake, the AQUATECH system can result in a process giving acid, base and essentially pure water as products: "zero discharge". AQUATECH Systems believes AQUATECH technology is the electrochemistry for todays industrial needs.

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