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FINAL REPORT

Pilot Test of Pickliq® Process
to
Determine Energy and Environmental Benefits
&
Economic Feasibility

July 13, 1997

ENERGY RELATED INVENTIONS PROGRAM
Grant # DE-FG01-96EE15657

prepared for
US DEPARTMENT OF ENERGY
by
Douglas R. Olsen

GREEN TECHNOLOGY GROUP
58 North Quaker Hill Road
Pawling, NY 12564
Phone (914) 855-0331 • FAX (914) 855-5806

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1. EXECUTIVE SUMMARY

Green Technology Group (GTG) was awarded Grant # DE-FG01-96EE15657 in the amount of \$ 99,904 for a project to advance GTG's Pickliq® Process in the Copper and Steel Industries. The use of the Pickliq® Process can significantly reduce the production of waste acids containing metal salts. The Pickliq® Process can save energy and eliminate hazardous waste in a typical copper rod or wire mill or a typical steel wire mill.

The objective of this pilot project was to determine the magnitude of the economic, energy and environmental benefits of the Pickliq® Process in two applications within the metal processing industry. The effectiveness of the process has already been demonstrated at facilities cleaning iron and steel with sulfuric acid.

9207 companies are reported to use sulfuric and hydrochloric acid in the USA. The USEPA TRI statistics of acid not recycled in the US is 2.4×10^9 lbs (net) for Hydrochloric Acid and 2.0×10^9 lbs (net) for Sulfuric Acid. The energy cost of not reclaiming acid is 10.7×10^6 BTU/ton for Hydrochloric Acid and 21.6×10^6 BTU/Ton for Sulfuric Acid. This means that there is a very large market for the application of the Pickliq® Process and the widespread use of the process will bring significant world wide savings of energy to the environment.

A twenty foot utility trailer was assembled as a platform for the pilot equipment, to provide a field analytical laboratory and an on-site field office. This was brought to the Phelps Dodge rod mill in El Paso Texas in October 1996. The on-site experience at this site generated valuable information that was used to improve the design of this unit to be more useful for future site experimental work.

The results from this experimental work are translated into economic and quality benefits that will be meaningful to operators of metal processing plants. The first site visited was the Phelps Dodge facility at El Paso, Texas. This facility is an integrated copper rod mill. It produces electrolytically refined copper and feeds this pure copper to a furnace and rod mill that has the largest production capacity in the world.

The Phelps Dodge site uses a sulfuric acid - hydrogen peroxide based etch solution to clean the surface of copper rod produced by the rod mill. The experimental work at the site included experiments to demonstrate the decomposition of the hydrogen peroxide in the etch, crystallization of copper sulfate, and the recovery (recycle) of sulfuric acid and hydrogen peroxide. Continuous runs on the mobile lab provided the information necessary to design a full sized plant to accomplish the operations.

It was also determined that running the diffusion dialysis membranes on the etch with hydrogen peroxide enabled the hydrogen peroxide to be recycled. Subsequent

inspection revealed no apparent deterioration of the membranes from the run at 80° F. It is desirable to run the unit at 100° F on etch containing hydrogen peroxide. However, for this case, we have strongly recommended a long term test run with an on-line pilot that operates for approximately six months.

Cost benefits from using the Pickliq® Process are generated from:

- Acid cost savings by the recycling of sulfuric acid;
- Hydrogen peroxide cost savings by the recycling of hydrogen peroxide;
- Inhibitor savings by the recycling of inhibitor; and
- Manpower savings by the elimination of batch pump-outs and batch make-ups of the process pickling bath.

The capital and operating costs for a Pickliq® Process System with diffusion dialysis and copper sulfate crystallizer were estimated. Simple (before tax) paybacks of 6-7 months are estimated for this system. The controlling benefit was the sale of copper sulfate pentahydrate crystals. Prices used in the analysis were obtained from the Chemical Market Reporter, June 5, 1997.

For a system that used diffusion dialysis alone, payback periods under 2 years were determined at 100 ° F operation. The payback time for this option is sensitive to potential improvements in the reject rate due to a consistent strength and activity of the pickling bath.

The plan for the experiments at steel mills was to test the Pickliq® Process at plants using hydrochloric acid for pickling. Prior to beginning the studies, there was a realization that there may be a challenge since ferrous chloride is more soluble than ferrous sulfate. But the full extent of the problems was not realized until more study was done as the project progressed.

The plan for the experiments was to locate potential operating facilities using copper-sulfuric acid, steel-hydrochloric acid, and to pilot the Pickliq® unit operations of diffusion dialysis and crystallization. Some bench scale lab work would be done at the Pawling, NY facility, but most of the effort would be on-site with a portable mobile trailer pilot laboratory that would be constructed. From the data gathered at the test facility, economic cost templates would be developed that would be representative of the particular metal-acid combination in that subject industry.

The candidate site for hydrochloric acid was a small steel wire mill in a southeast state. This site pickled wire that came from an annealing furnace. However this site was discovered to be uncharacteristic of the rest of the industry. Other hydrochloric acid pickling sites were investigated. These were large continuous sheet steel mills in Pennsylvania and New York. (The names are confidential at this time.) Data from these mills indicate a substantial difference and difficulty for the Pickliq® process when

applied to continuous steel mills using hydrochloric acid. The controlling difference for our subject process is the terminal concentration of the acid is 2% or lower at the end of long pickling lines. In other words there is very little acid left to recover.

More effective waste minimization and hydrochloric acid recycling can be achieved with hydrochloric acid regeneration. A method of chemically regenerating the acid and recovering ferrous sulfate instead of ferrous chloride was investigated at the Pawling laboratory. This process has lead to interest by New York State Research and Development Authority in sponsoring a feasibility study for this process advancement.

This project has been extremely fruitful in advancing the art of the Pickliq® Process and pointing the direction for future work. There are sites that could benefit from the not only recycling the acid and hydrogen peroxide to the pickling operation, and not only recovering the copper sulfate as a crystal, but also to refine the copper sulfate into copper metal that could be used for furnace feed.

There is every indication that the use of the Pickliq® Process on selected copper processing sites would be an economically viable investment. There is a good possibility that future work will show an economically viable method for using the Pickliq® Process in conjunction with chemical reaction to regenerate hydrochloric acid and produce product ferrous sulfate crystal.

2. INTRODUCTION

Green Technology Group (GTG) was awarded a Financial Assistance Award, Grant # DE-FG01-96EE15657 in the amount of \$ 99,904 for a project period running from June 6, 1996 through December 6, 1997. The project was to advance GTG's Pickliq® Process in the Copper and Steel Industries.

The production, forming and treating of metals are typically energy intensive and present environmental risks. Green Technology Group developed the Pickliq® Process for this application in various industries. Specifically, the use of the Pickliq® Process can significantly reduce the production of waste acids containing metal salts.

The process combines new and proven technologies to substantially reduce or eliminate these problems. A pilot project was to be conducted to determine the effectiveness and economic feasibility of the Pickliq® Process to save energy and eliminate hazardous waste in a copper rod or wire mill or a typical steel wire mill. The results from this experimental work are translated into economic and quality benefits that will be meaningful to operators of these metal treating plants.

2.1. PROJECT OBJECTIVES

The study intended to establish whether the technology incorporated in the Pickliq® Process can be successfully applied both to the cleaning of copper with sulfuric acid and the cleaning of steel with hydrochloric acid.

These represent areas where substantial energy savings and environmental benefits can be accomplished. Specifically, Green Technology Group intends to conduct pilot tests using the Pickliq® Process at two existing metal processing operations; one where copper is processed; the other where steel is cleaned with hydrochloric acid. Results in both pilot applications will be monitored to determine:

- Efficiency of acid recovery;
- Economics of installing the equipment necessary for the process; and
- Energy savings with the use of the process.

2.2. POTENTIAL STUDY SITES

Four sites covering these examples were potential at the beginning of the project. These were investigated further as part of the project resulting in the following actions:

- Phelps Dodge, El Paso, Texas. This facility is an integrated copper rod mill. It produces electrolytically refined copper and feeds this pure copper to a furnace and rod mill that has the highest production capacity in the world. This site was chosen.

- Ansonia Copper and Brass, Ansonia, Connecticut. This facility was evaluated and though close to GTG's offices, it was not chosen for the initial pilot site. However, it is an ideal site for further work on a GTG process to recover refined copper from the etch used in copper mills. Work is under way to obtain other funds for a project on the site. Ansonia would receive copper sulfate etch and/or recovered copper sulfate and electrolytically produce copper to feed its copper furnace. the copper would be converted into copper alloy wire. The process would also recover sulfuric acid that would be reconstituted into etch for tolling back to other facilities.
- International General Superconductor, Waterbury, Connecticut. This small facility uses a hydrogen peroxide - sulfuric acid etch and is already recovering copper sulfate and recycling acid by using a cold crystallizer. They also have a process that uses nitric acid that produces copper nitrate that is waste treated. This facility was not ideal for the project. However, it would be an ideal supplier of copper sulfate should a project be initiated with Ansonia Copper and Brass.
- Gilbert & Bennett, Toccoa, Georgia. Initially it was believed that this facility would be ideal for a study of recovering hydrochloric acid from pickle used on steel wire. The concentration of the acid recycled was fairly high, and the facility was small enough so that it would be manageable for GTG. A however, when we visited the facility it was discovered that the process they were using was so atypical that data from the site would be useless. The etch was saturated with Sodium Chloride. This resulted from the practice of decanting the resulting liquid from the waste treatment facility and recycling it back to the pickling tank. No other producer does this to our knowledge, as it results in producing a sludge with a high water content that is difficult to handle. Additionally, there is also probably an inefficiency with the amount of ferrous chloride that can be handled by the etch solution due to the common ion effect, making the pickling operation inefficient.

3. U.S. ACID USE STATISTICS

The relevance of this project is clearly demonstrated by the widespread production of waste acid by the metals processing industries and the monetary and life cycle energy cost of producing new acid compared to recovering and recycling acid.

3.1. ENERGY COST OF WASTE ACID

There is a substantial cost to the environment for not recovering acid. The following energy costs per net ton have been made for typical pickling operations:

TABLE 3-1 ENERGY CONSUMPTION OF WASTE ACIDS BTU/NET TON¹

ACTIVITY	SULFURIC ACID	HYDROCHLORIC ACID
Mining & manufacture	0.83×10^6	9.25×10^6
Delivery 300 miles	0.78×10^6	2.25×10^6
Waste return ship	13.0×10^6	3.60×10^6
Lime Neutralization	4.85×10^6	6.51×10^6
TOTAL	10.73×10^6	21.6×10^6

3.2. TARGET INDUSTRY SITE DEMOGRAPHICS

To provide some marketing focus, several Standard Industrial Classification (SIC) codes were chosen to illustrate the acid user population. This was done both to provide an insight into the size of the precise targeted market segments for the Pickliq® System and to break out portions of the potential system user database into these targeted segments. The targeted segments, based on past experience and confirmed by both past studies and current literature searches, are:

- SIC 33XX: Primary Metal Industries
- SIC 34XX: Fabricated Metal Products
- SIC 3672: Printed Circuit Board Manufactures
- SIC 3674: Semiconductor Manufacturers

For each of the major (2 Digit) SIC code user industry segments, an analysis was performed to determine the total number of large manufacturing plants in each segment. The analysis was based on data compiled in the acid user database. Table 3-2 shows the quantitative results from the analysis, and Figure 3 shows the market segmentation graphically.

¹ Calculated from data obtained from *Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing*, Battelle Columbus Laboratories, June 1975.

Table 3-2 Primary SIC Code Breakdown of U.S. Companies Using Selected Acid

Acid	SIC 33XX Primary Metals	SIC 34XX Fabricated Metal Prods	SIC 3672/76 Printed Circuit Boards and Semiconductors	Total - Targeted Codes	Total - Other SIC Codes	Total - All SIC Codes
Hydrochloric	251	837	165	1,253	2,047	4,302
Nitric	185	475	130	790	1,037	2,432
Phosphoric	145	243	35	423	2,237	2,938
Sulfuric	371	765	245	1,381	2,514	4,905
Total	952	2320	575	3,847	7,835	14,577

Figure 3-1 Distribution of U.S. Acid Using Companies by Targeted SIC Codes

3.3. ACID TREATMENT AND RECYCLING STATISTICS

For each of the acids under consideration, an analysis was made of the reported amounts released, treated, transferred, used in energy recovery processes, and recycled. This analysis was performed for all SIC codes and the specific SIC codes targeted for the Pickliq® System. Table 3-3 presents the full results of the analysis, and Figure 3-1 graphically illustrates the relative relationship between amounts released/transferred/treated and the amounts recovered/recycled. As can be seen from Figure 3-1, the targeted SIC codes represent industries where recovery and recycling are mature technologies, in that the amounts are fairly close in magnitude to the amounts still "wasted."

Table 3-3 U.S. Acid Releases, Treatment, Transfers, Energy Recovery, Recycling Summary²

U.S. Total Acid Releases, Treatment, Transfers, Energy Recovery, Recycling Summary						
	Units	Hydrochloric	Nitric	Phosphoric	Sulfuric	Total
Acid Releases - Total	1000 lbs	214,952	21,365	78,766	26,208	341,292
Acid Treatment - Total	1000 lbs	2,008,282	277,733	392,605	1,746,498	4,425,119
Acid Transfers - Total	1000 lbs	141,872	20,694	18,175	236,931	417,671
Total Releases, Treatment, Transfers		2,365,106	319,792	489,546	2,009,637	5,184,082
Acid Energy Recovery - Total	1000 lbs	8,752	23	57	162	8,994
Acid Recycling - Total	1000 lbs	320,008	38,705	218,448	1,506,657	2,083,818
Total Energy Recovery, Recycling		328,760	38,728	218,505	1,506,819	2,092,812
U.S. Target SIC Codes - Acid Releases, Treatment, Transfers, Energy Recovery, Recycling Summary						
	Units	Hydrochloric	Nitric	Phos-phoric	Sulfuric	Total
Acid Releases - Target SIC Sectors	1000 lbs	21,820	1,448	515	3,130	26,913
Acid Treatment - Target SIC Sectors	1000 lbs	313,751	116,973	34,879	336,694	802,296
Acid Transfers - Target SIC Sectors	1000 lbs	87,904	11,163	10,638	75,577	185,282
Total Releases, Treatment, Transfers		423,475	129,584	46,032	415,401	1,014,492
Acid Energy Recovery - Target SIC Sectors	1000 lbs	8,665	0	5	4	8,674
Acid Recycling - Target SIC Sectors	1000 lbs	201,677	7,420	22,862	576,399	808,358
Total Energy Recovery, Recycling		210,342	7,420	22,866	576,403	817,032

² A Review of Market Potential for The Green Technology Group Pickliq® Process and Resulting Ferrous Sulfate By-Product, Infactix, May 12, 1997.

4. TECHNOLOGY AND OBJECTIVES OF STUDY

Sulfuric and hydrochloric acid are top ranking wastes in the Toxic Release Inventory, (See Table 3-3). Pickling liquors in the primary metals and metal finishing industries supply much of this waste, (See Table 3-2). The Pickliq® Process is a method for recovering and recycling purified acids from the pickling liquors at the point of use. It also recovers the metals salts as commercial products. The process is a novel combination of the new technology of membrane diffusion dialysis with the older processes of crystallization of the pickling liquors and dewatering of the metal salt crystals. A particular advantage of this process is the ability to ship the product crystal as a non-hazardous material. Use of the process results in energy savings in the production of acid, the lime or caustic that would be needed for waste treatment, and the fuel in transportation, (See Table 3.1). Savings in fuel, man-hours, and material are also realized from the use of higher acid strengths resulting in faster pickling times. A constant acid level also results in savings of fuel and man-hours by eliminating the cause of rejected work from insufficient pickling.

A simple representation of the process is shown in Figure 4-1.

Figure 4-1 Pickliq® Process Block Diagram

Previous engineering studies indicated the process effective and economic. The project was to confirm the physical chemistry of the process solutions, construct a mobile pilot laboratory, and to perform tests of the various technologies or unit operations required at copper and steel processing mills. Data from the operation of the pilot and lab would

be used to create cost and economic templates typical for the industry to demonstrate the benefits of installing the process at prospective customers.

The unit operations planned were:

- Diffusion dialysis;
- Heat interchange;
- Crystallization, (cold and evaporative);
- Electrodialysis;
- Energy conservation; and
- Other operations as appropriate for site.

4.1. DIFFUSION DIALYSIS

Diffusion dialysis is a process that uses semi-permeable anionic membranes to transfer acid from the metal rich acid stream to a recycling acid stream free from the majority of the metals. The source of this equipment is Pure Cycle Environmental Technology, Inc. A 5 gallon per day capacity pilot unit was purchased and installed in the pilot lab.

The testing would demonstrate the efficiency of separating the metal salts in the acid stream feed from the acids that would migrate through the membranes. Also, the efficiency of blocking the metal salts from following the acid into the reclaim stream.

4.2. HEAT EXCHANGE

Heat exchange is a key part of the process. Considerable energy efficiency is obtained by the choice and placement of specially design heat exchangers. Because of process considerations, these heat exchangers need to be highly corrosion resistant, have high heat transfer efficiency and have a low residence time.

The type of heat exchange units used is key because there is the chance of the crystallization taking place in the heat exchangers and could result in plugging up the equipment. The units used by GTG in many processes have demonstrated the superiority of the GTG design.

The heat exchange would not be tested in the program. This unit operation is well known and does not need testing. Further, only demonstration at the prototype scale has any relevance.

4.3. CRYSTALLIZATION

Crystallization by cooling the solutions down to a temperature at which the crystals of the metal salts will form is the preferred method of operating the system. There are metal salt solutions, however, that at the concentrations found in the industry, are too soluble to be obtained by simple cold crystallization. Recognizing this, it is realized that in some applications, water will need to be removed before the salts are crystallized. Evaporative crystallization and diffusion dialysis are candidate processes for these situations.

The testing program will test the solution concentrations that are required to make cold crystallization. The important consideration are the saturation temperatures of various salt solutions at various acid concentrations at selected temperatures. Important results would be the size and dewatering characteristics and composition of the crystals formed.

The crystallizers that were part of the mobile lab were:

- 15 Gallon continuous crystallizer;
- 2 liter batch crystallizer; and
- 250 ml testing flasks utilize the constant temperature bath.

4.4. ELECTRODIALYSIS

An alternative to evaporation for reducing the water content of metal salt solutions is a process called Electrodialysis. In some situations, electrodialysis can be more energy efficient than evaporation. Electrodialysis has been used to make potable water from seawater, thus concentrating the residual salt solutions. It has also been used by the author to concentrate nickel salts in nickel plating rinse waters to reconstitute nickel solutions for recycle to nickel plating process baths.

However, severe corrosion problems occur involving hydrochloric acid applications that require the use of special anodes. An electrodialysis unit was planned for the original pilot study. However, delays were experienced in obtaining the anodes and constructing the unit in time for shipment to the Phelps Dodge, location.

By the time the anode was ready for the hydrochloric acid application, an alternative technology had surfaced that would not require solution concentration, and so this technology was not applied.

4.5. REFRIGERATION AND ENERGY CONSERVATION

In cold crystallization, refrigeration is used. Refrigeration is the major energy consumer in the Pickliq® process that is used with sulfuric acid and steel. The Pickliq® Process saves significant energy by the use of high efficiency, low residence time heat interchange equipment. The input streams from the acid tanks are generally heated to 140-160 °F. The stream first has to be reduced to 100 °F prior to diffusion dialysis, then to 32 °F for the cold crystallization process. The stream from the crystallizer has to be raised back to 100 °F and then to 140-160 °F. Interchanging the heat between these streams saves up to 50% of the power required for refrigeration.

Evaporation and evaporative crystallization can require approximately 1000 BTU per pound of water removed from the stream. (This is why electrodialysis was considered in the original proposal.) However, when two stage evaporative crystallization is done with vapor recompression, significant energy is saved. The energy consumption reduces to approximately 570 BTU/lb of water removed.

A controlled refrigeration system was an important part of the pilot testing lab. There were two crystallizers that were used in the testing plus equilibration crystallization test that were made in a controlled temperature bath.

4.6. NEW TECHNOLOGY APPLICATION

As the project began to unfold in practice, it became apparent that a large amount of acid applications using hydrochloric acid produced very soluble metal salt solutions that could not be economically crystallized by simple cold crystallization. Additional technology would be needed.

Three types of technology were evaluated:

- Evaporative Crystallization;
- Electrodialysis; and
- Chemical Transformation.

Of these, the most innovative and promising for energy and capital cost efficiency is Chemical Transformation. Specifically, the sulfate salt of most of the interesting metals is less soluble than the chlorides or the nitrates of the materials coming from the pickling baths. If 96% sulfuric acid is added stoichiometrically to the spent pickling liquors, and then depending on the application the resultant solution is treated with a selected arrangement of Pickliq® Process operations, the sulfate salt may be recovered. The nitric or hydrochloric acid would be regenerated and returned to the pickling operation. See Figure 10-2.

5. PROGRAM PERSONNEL AND PLAN PARTICIPATION

The original plan was to locate potential operating facilities using copper-sulfuric acid, steel-hydrochloric acid, and possibly nitric to pilot the Pickliq® unit operations of diffusion dialysis and crystallization.

Some bench scale lab work would be done at the Pawling, NY facility, but most of the effort would be on-site with the portable mobile trailer pilot laboratory that would be constructed.

From the data gathered at the test facility, economic cost templates would be developed that would be representative of the particular metal-acid combination in that subject industry.

5.1. PERSONNEL AND PARTICIPATION

Biographies of the key people working on the project are given in the appendix.

Douglas Olsen, President of GTG had overall project responsibility. Doug also was responsible for data analysis and report writing. After the initial work at the Phelps Dodge site by King and McLaughlin, Olsen completed the test runs and the analytical work to obtain the data that were used to develop the cost profiles for the copper rod mill. Olsen completed the drawings and prepared the drawing and the final report.

Olsen delivered the lab to the El Paso site with the GTG Bronco. When the work was completed, he hauled the lab back to Pawling with the Bronco.

Hugh McLaughlin designed the initial pilot plant. This included the interior safety features of emergency lights, a sprinkler system, and the fume hood ventilation system for the lab bench. He designed and built the crystallizer, lab bench, storage racks, wall desk, hydrogen peroxide decomposition tank and column. Most of the construction of the pilot was done in Massachusetts by Hugh McLaughlin, who was aided in the last weeks by David King. A diagram of the initial set-up of the laboratory is shown in Figure 6-1.

McLaughlin also completed the installation of the crystallizer and the hydrogen peroxide decomposer after the lab was in place at the El Paso site. He adapted the Pure Cycle diffusion dialysis unit to operate at an elevated (80 °F) temperature. He also supervised the initial experimental work of David King on:

- Decomposition of hydrogen peroxide solutions in recirculating batch mode;
- Crystallization of water-copper sulfate solutions; and
- Diffusion dialysis of diluted plant pickling solutions that had been treated with sodium meta bisulfite to decompose peroxide.

Mr. McLaughlin expressed objections to operating the diffusion dialysis system on pickling solutions that contained hydrogen peroxide. He believed that the membranes would fail and GTG's reputation would be irreparably damaged. He recommended that the experimental work at El Paso be terminated immediately and the equipment returned to GTG facilities for redesign. (This recommendation was not accepted and the work at El Paso was completed by Doug Olsen.)

***David King** performed much of the technical work on the project. This included the diffusion dialysis experiments on the altered plant solutions, the hydrogen peroxide decomposition experiments, and the crystallization experiments.*

He was involved in the construction of the lab in its final stages in Massachusetts; he did the initial experimental and analytical work, (under the direction of Hugh McLaughlin) in El Paso Texas, and he began the reorganization and reconstruction of the laboratory when it returned to Pawling. He also performed the experimental work to obtain the steel hydrochloric acid data. This work was done at the GTG Pawling facilities.

Mr. King's attention to detail in his experimental work and his ability to conduct the experimental work as directed and make repairs and modifications as needed to the pilot equipment was invaluable to the project's success.

6. MOBILE PILOT LAB

Laboratory work was carried out in the mobile lab and at the GTG headquarters located in Pawling, New York.

6.1. CONSTRUCTION OF MOBILE PILOT LAB

A twenty foot Utility trailer was proposed for the platform for the pilot equipment, to provide a field analytical laboratory, and a field on-site office. The arrangement as originally built is shown in Figure 6-1.

The mobile pilot lab was designed and constructed at Manchester, Massachusetts by Hugh McLaughlin, assisted by Dave King. A plan of the operating features of the lab is shown in Figure 6-1. A photo of the Lab as pulled by the GTG Bronco is shown in Figure 6-2.

FIGURE 6-1 ORIGINAL PILOT LAB ARRANGEMENT

FIGURE 6-2 PILOT LAB AS PULLED BY GTG BRONCO

FIGURE 6-3 REVISED DESIGN OF PILOT LAB

6.2. MODIFICATIONS REQUIRED

Experience at the Phelps Dodge facility in El Paso, Texas resulted in a better concept of an optimum design for the Pilot Lab. When the Lab returned to Pawling, work was begun on the modifications to prepare the Lab for its next assignment. The plans for the revised lab are discussed below.

6.2.1. Lighting and air conditioning

The design, as built, had some drawbacks. These became apparent when the lab was put into operation in El Paso Texas. The original GTG plan was to have Air conditioning units mounted in the roof and supplied with the trailer. Roof skylights were also intended. However, the trailer as finally specified and supplied omitted these features. A window was installed in the trailer at Manchester to provide light and also to provide a mounting for a 7000 BTU/hr commercial air conditioner. This choice requires the air conditioner to be added or removed every time the unit is moved. It also eliminates any natural outside light when the air conditioner is in place.

6.2.2. Fume handling

The preliminary work at El Paso used feed solutions that contained sodium metabisulfite. This presented a serious problem, since there had been no provision for venting the pilot unit. While the lab bench had a complete hood and ventilation system, there was no provision to vent fumes from the diffusion dialysis unit. Dave King made field modifications that provided sufficient ventilation by constructing a fume hood for the diffusion dialysis, and leading the fumes to the exhaust fan in the lab bench hood.

The fume hood over the lab bench was not necessary, since all analytical work was done on diluted solutions.

Fume handling accessories must be provided for the pilot equipment when working on potential fuming acids such as, nitric, nitric-HF, and hydrochloric.

6.2.3. Laboratory bench

As shown in Figure 6-3, the laboratory bench was relocated on the "East" wall of the lab. This is better location is a better location and a better utilization of trailer space. More room is needed when equipment is located on the "west" wall of the trailer. The lab bench top was also set at an elevation of 32 inches with a hood panel that required the analyst to either squat or sit to work. When the lab returned to Pawling from El Paso, the lab bench was moved to the "north" wall and set at an elevation of 31 inches. No hood will be provided over the entire lab bench. However a vent connection will be available should a local area need venting. This arrangement will permit the technician to work standing or seated on a stool.

6.2.4. Floor finish

The floor initially had a finish of spar varnish. This did not hold up well to the corrosive nature of the acids used. Upon return, the floor and wall to 24 inches high were sanded and painted with a corrosion resistant Urethane compounded paint. Grit was incorporated into the paint used on the floor for skid resistance.

6.2.5. Secondary containment

Secondary containment in the initial lab was within the cabinets that were around equipment for heat insulation. With this arrangement, there was no visible indication of any leaks that may have developed. Upon return, the heat cabinets were removed. It is planned that all equipment for the lab will be modular and self contained, including any necessary heat insulation. A common secondary containment will be installed on the west wall for several units and a containment will be installed on the east wall for container storage. Construction of the containment will be as shown in Figure 6-4.

FIGURE 6-4 TYPICAL SECONDARY CONTAINMENT

6.3. FUTURE USE OF MOBILE PILOT LAB

The mobile pilot lab will be a very essential tool in demonstrating the performance and efficiency of the Pickliq® Process at large steel and copper facilities. At these locations, although laboratory assistance is sometimes available, it is not always convenient or flexible for other than routine production missions. Additionally, these facilities are extremely large and the distance from the analytical laboratory to where it is convenient to run a pilot system on the plant solutions is usually very far. There is also the problem of environmental control and convenience of a private and secure work space for operators of the pilot lab.

The next assignments for the lab are seen to be a large scale test of the regeneration method of hydrochloric - steel pickle as shown in Figure 10-2 and the Recovery of copper metal from tolled etching solutions and copper sulfate as shown in Figure 10-1.

Replications of pilot work will be required at other potential "Big Steel" or "Big Copper" clients in the rod and wire industry at geographic areas in the Midwest, West Coast, Gulf Coast, and Southwest. The mobile pilot lab will be essential for these tests and demonstrations.

7. COPPER MILL EXPERIMENTS

7.1. HYDROGEN PEROXIDE DECOMPOSITION

Figure 7-1 shows the demonstration of decomposing a test solution composed of 1 liter of 50% hydrogen peroxide to 5 gallons of reverse osmosis (RO) water. The 15 gallons were pumped up through the column (estimated at approximately 3 GPM and then flowed back to the feed container for recirculation. No measurement was taken of the weight or volume of carbon or the flow rate of solution. Therefore, while the experiment qualitatively demonstrated the effectiveness of the carbon of decomposition, and indicated that the decomposition was a first order reaction, no quantitative design data can be gleaned from the work.

FIGURE 7-1 DECOMPOSITION OF TEST SOLUTION OF H_2O_2 IN 2"Dx24" COLUMN @ 75° F

The system would not be very practical for use as a pretreatment for solutions that would be tested in the diffusion dialysis stacks. This is essentially a batch operation. Each batch of etch would have to be separately treated as a unit prior to feeding it to the membrane stacks to feed essentially "zero" hydrogen peroxide.

At 7.25 hours, the concentration of peroxide was 0.27 grams/liter. A rough estimation of 10-30 hours for a 5 gallon batch would be required to eliminate the hydrogen peroxide. This would significantly complicate the operation and make a serious delay between taking a sample of the etch and testing the sample in the diffusion dialysis.

FIGURE 7-2 DECOMPOSITION OF ETCH IN STIRRED BEAKER @ 75°F

Dave King demonstrated the decomposition rate of hydrogen peroxide solution in a beaker stirred continuously at room temperature. Figure 7-2 shows the decomposition results. When these results are examined, it is seen that this is an exponential curve indicating that this is a first order reaction proportional to the concentration of the hydrogen peroxide. At 3.0 hours, the concentration of peroxide was 0.32 grams/liter.

It is apparent that a single pass column ahead of the diffusion dialysis stacks with a residence time of 30 hours would remove the hydrogen peroxide to almost undetectable limits. Such an apparatus would certainly protect the membranes from any hydrogen peroxide attack should that be necessary. Although there would be a 30 hour delay between the entry of material into the column and entry into the diffusion dialysis stacks, there would be the ability to immediately change the feed entering the system without a delay for batch treatment to decompose the peroxide.

Because there was not sufficient time to rebuild the column system in the field, and make a system that could maintain the temperature required to keep copper sulfate in solution during the time the solution was in the decomposing column, the decision was made by Doug Olsen to decompose the samples from the etch line using sodium metabisulfite prior to placing the solutions into the feed tanks of the PCET diffusion dialysis system. (After an initial baseline was made in the early work that showed that the system was indeed recycling acid and rejecting copper sulfate, the etch was fed to the diffusion dialysis as it came from the etch process line without decomposing the hydrogen peroxide.)

7.2. DIFFUSION DIALYSIS

The rod mill facility in El Paso Texas is an integrated with an electrolytic copper refining plant. The refining plant electrolytically purifies raw copper anodes from a smelter and produces pure copper feedstock to for the furnace that feeds the rod mill.

The saturated etch solution from the rod mill pickling operation, (Dr. Otto machine) is returned to the electrolytic refining plant and fed to an existing copper sulfate crystallizer. Commercial copper sulfate crystals are produced and marketed from this operation. A flow sheet of this arrangement is shown in Figure 7-3.

FIGURE 7-3 PHELPS DODGE ROD MILL, EL PASO, TEXAS

This existing operation may be out-dated from a process economics point of view. The following analysis is based on using a Pickliq® diffusion dialysis system to recover sulfuric acid, hydrogen peroxide and inhibitor from the etch, and send deacidified copper sulfate solution to the crystallizing section of the plant.

7.3. EARLY SHAKE-DOWN EXPERIMENTS

Beginning November 2nd early runs were made on the diffusion dialysis system with low strength test solutions to test the initial performance of the system. Full strength solutions were not tried until November 6th.

To begin the diffusion dialysis experiments, a 55 gallon sample of etch was taken from the pickling tank. The solution was hot and contained high copper concentrations. By the time the solution was ready to be used, the solution had cooled and substantial copper sulfate had crystallized in the drum. Fumes from the residual sodium metabisulfite were a problem that eventually required a field modification to the exhaust system to vent the fumes directly from the diffusion dialysis system.

Most of the time during the period prior to November 15th was utilized for crystallizer experiments. The diffusion dialysis experiments were all run at a low copper concentrations due to copper crystallizing out of the solution in the 55 gallon drum that was stored outside the trailer. Sufficient data was accumulated to assure that the acid was being reclaimed at a good recovery rate and that there was a satisfactory rejection rate of the copper.

7.4. TEMPERATURE OF OPERATION

The temperature of operation is important to the capacity of diffusion dialysis. The experiments at the Phelps Dodge Facility were all conducted at 80° F. this is the highest temperature that could be uniformly obtained with the equipment as modified at the site. The preferred temperature of operation on the basis of the membranes and mass transfer is 100° F. The current GTG pilot unit is designed to operate at this temperature but was not available for the Phelps Dodge experiments.

Prior experimental work at O.W. Hubbell and Sons, Inc. indicates that the capacity of the diffusion dialysis unit operating at 100° F is 2.5 times the capacity at 80° F. This ratio was used in predicting the performance of the unit at the higher temperature for the economic analysis.

However, there is a caution that needs to be observed. At the present time we do not know the effect of the higher temperature on the membranes. A long term run of a pilot unit at a 100° F operating temperature is recommended to assure that there is no long term deterioration of the membranes.

7.5. 200 HOUR DIFFUSION DIALYSIS PILOT RUN

Doug Olsen performed a continuous 200 hour diffusion dialysis test run at 80° F. The purpose of this run was to:

- Demonstrate the recovery efficiency for acid at various flow rates;
- Demonstrate that the membranes could be run on solutions containing hydrogen peroxide without loss of recovery efficiency;
- Demonstrate the recovery efficiency of hydrogen peroxide;
- Demonstrate the rejection efficiency of the system to copper ions; and
- Perform all operations on etch solutions taken from the plant pickling tank without decomposition of the hydrogen peroxide.

The initial feed to the diffusion dialysis was made with a pickling solution that was treated with sodium metabisulfite. the first 49.5 hrs of the test run was run with treated solution to establish an efficiency baseline so that the efficiency without hydrogen peroxide could be compared to the efficiency after several hours running with hydrogen peroxide.

FIGURE 7-4 SULFURIC ACID CONCENTRATIONS 200 HOUR RUN

FIGURE 7-5 ACID RECOVERY EFFICIENCY 80°F

Figure 7-5 shows the sulfuric acid recovery efficiencies. At 49.5 hours a baseline of recovery efficiency had been established, and the system was fed with pickling liquor containing hydrogen peroxide. It is clear from the figure above that the recovery efficiency varies between 80-100% and does not seem to be effected, (in the short term) by the oxidizing effect of hydrogen peroxide.

Examination of the membranes by Dan Bailey, of Pure Cycle Environmental Technologies and manufacturer of the membrane stacks, showed no visible deterioration of the membranes, reinforcing the hypothesis that they will not be effected negatively by the solution.

Note: numbers on the plots indicate ml/min feed.

Figure 7-6 shows the concentrations of hydrogen peroxide in the streams.

FIGURE 7-6 HYDROGEN PEROXIDE CONCENTRATIONS

There is a variation in the acid recovery efficiency during the run. The flow rates of reclaim and reject were kept approximately 1:1 during the run. It would be expected that the efficiency of recovery would be higher at lower throughput rates and lower at higher flow rates.

Figure 7-7 shows recovery efficiency plotted against the reclaim flow rate. As expected, the lower the flow rate, the higher the efficiency.

FIGURE 7-7 ACID RECOVERY VS FLOW RATE (80°F)

FIGURE 7-8 EFFICIENCY OF RECLAIMING HYDROGEN PEROXIDE

Figure 7-8 shows that hydrogen peroxide will be recycled by the system. Since hydrogen peroxide is a significantly costly ingredient of the etch, this substantially improves the saving that are obtained by use of the Pickliq® process.

7.7. CRYSTALLIZATION

Figure 7-8 shows the solubility of copper sulfate (as copper) in water and sulfuric acid solutions.

TABLE 7-8 SOLUBILITY OF COPPER SULFATE IN SULFURIC ACID

8. COPPER MILL ECONOMICS DEVELOPED

The economics for a copper mill using the Pickliq® Process in various arrangements and operating temperatures are developed. The two temperatures considered are 80° F and 100° F. the significance of the temperatures are discussed in Paragraph 7-4. The most economic temperature of operation is 100° F if the membranes will tolerate long term exposure to that temperature in the presence of the hydrogen peroxide.

There are two potential arrangements that are possible for the application of the Pickliq® Process in a copper rod or wire mill such as the Phelps Dodge facility at El Paso, Texas. Either the complete system using diffusion dialysis, (See Figure 8-1) could be installed or a system using diffusion dialysis and crystallization (See Figure 8-2) could be installed.

8.1. COPPER MILL WITH DIFFUSION DIALYSIS ONLY

A flow sheet of the system using diffusion dialysis alone is shown in Figure 8-1.

FIGURE 8-1 COPPER ROD MILL WITH DIFFUSION DIALYSIS

With diffusion dialysis on this system, the pickling acid can be maintained at a concentration of 300-360 gpl sulfuric acid, 35 gpl copper, 10 gpl hydrogen peroxide and 90 gpl propylene glycol with the combination of recycling the acid continuously through the diffusion dialysis and periodic additions of acid, hydrogen peroxide and propylene glycol.

The capacity of the system is designed to remove the average copper that is dissolved into the system from the etching operation. The costs of sulfuric acid, hydrogen peroxide and inhibitor were obtained from a confidential client source.

TABLE 8-1 GALLONS OF ETCH AND POUNDS OF COPPER AND ACID DISCHARGED - PHELPS DODGE, EL PASO, TX - MAY 1996 - APRIL 1997

ANNUAL			
TOTALS	GALLONS	ACID LBS	CU LBS
JAN	174,682	364004	75091
FEB	134497	279675	58175
MAR	115535	218804	42815
APR	193889	413946	83692
MAY	171199	365666	71634
JUN	173165	376040	74447
JUL	123420	261513	51623
AUG	117207	255677	50101
SEP	176323	372583	75211
OCT	206388	420649	90768
NOV	128048	260348	54077
DEC	114119	239800	47082
TOTAL	1828472	3828705	774716
DAY AVG	5010	10490	2123

The system design basis is to recycle hydrogen peroxide, inhibitor, and sulfuric acid and send copper sulfate solution to the existing copper sulfate crystallizer.

Cost of a diffusion dialysis modular Pickliq® System to accomplish this is given below in Table 8-2 for operation at 100 °F and Table 8-3 for operation at 80 °F.

TABLE 8-2 PICKLIQ® MODEL 2415-1 7500 GPD (100 °F)

COST ESTIMATE		
TEMPERATURE OF OPERATION	100	
CAPACITY GALLONS/DAY	7500	STACKS
FLOW/STACK GALLONS/DAY	500	15
TOTAL PRICE		
		\$899,745

TABLE 8-3 PICKLIQ® MODEL 4480-1 7500 GPD (80 °F)

COST ESTIMATE PICKLIQ		
TEMPERATURE OF OPERATION	80	
CAPACITY GALLONS/DAY	7500	STACKS
FLOW/STACK GALLONS/DAY	200	38
TOTAL PRICE		
		\$2,186,940

Detailed data for economic justification from the minimization of rejected work is also shown in Tables 8-4 to 8.7. The cost benefits of the system are discussed below in Section 8-2

8.2. COST BENEFIT DISCUSSION

Cost benefits from using the Pickliq® Process come from:

- Acid cost savings by recycling sulfuric acid;
- Hydrogen peroxide cost savings by recycling hydrogen peroxide;
- Inhibitor savings by recycling inhibitor;
- Manpower savings in eliminated batch pump-outs and batch make-ups of the pickling tank; and
- Minimizing lost production time from remanufacturing work rejected due to inadequate or improper pickling.

Quality control is a very important factor in the operation of the pickling line. The prime function of the pickling operation is to completely clean the surface of the rod (or wire) for the subsequent operations by the mill or its customers. In the case of the El Paso mill, many of their customers will be wire producers and will manufacture electrical conductors. The quality of the wire surface is extremely important to the performance of their products and the quality of the surface is directly related to the performance of the pickling operation.

A very sensitive test of the quality of the surface of the rod or wire is the appearance of the surface of the mill product. Any visual imperfections are taken as an indication that the surface has not been properly conditioned by the pickling operation, i.e. all of the scale has not been removed and there may be spots of higher surface resistance that would make the product perform poorly. Poor visual appearance can be a cause for product rejection, and the only cost effective way to deal with a rejection is to melt down the rod and remanufacture the product.

There is a significant loss of productivity and profit when this must be done. A major cost benefit of the use of the Pickliq® Process is that the pickling bath is easily kept as a uniform and predictable level of performance. It does not approach the extremes of a "new" bath that could etch the surface of the rod, or an "old" bath that might not remove all of the scale or leave visual imperfections on the surface.

The visual imperfections from the extremes of old and new baths can cause product rejections from time to time. While there may be no official records of how often this happens, we have estimated the effect of the elimination of rejects from this cause in our economic analysis tables. The first case shows no benefit from any improvement in the reject rate. The succeeding tables show an improvement that would occur if a reject rate of 1% of production were eliminated as a result of stable pickling bath operation. The succeeding tables reflect similar 1% incremental improvements in the reject rate as a function of the production rate and a cost of rod mill down time of \$2,200/hour.

TABLE 8-4 DIFFUSION DIALYSIS (NO REJECT IMPROVEMENT

TABLE 4 - DIFFUSION DIAPHRAGM (NO REJECT RATE IMPROVEMENT)			
OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT			
	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
	0.00%		
Average production hours saved/day			
	0		
average savings /day			
	0	\$0	\$0
LABOR			
	(No net change expected)		
MAINTENANCE			
		\$27,000	(\$27,000)
NET SAVINGS			
			\$890,579
@100 F OPERATION			
GTG PLANT COST			
			\$900,000
SIMPLE PAYOUT - MONTHS			
			12
@80 F OPERATION			
GTG PLANT COST			
			\$2,200,000
SIMPLE PAYOUT - MONTHS			
			29.6

TABLE 8-5 DIFFUSION DIALYSIS WITH 1% REJECT IMPROVEMENT

OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
1.00%			
Average production hours saved/day			
0.24			
average savings /day			
528	\$192,720		\$192,720
LABOR	(No net change expected)		
MAINTENANCE		\$27,000	(\$27,000)
NET SAVINGS			\$1,083,299
@100 F OPERATION			
GTG PLANT COST			\$900,000
SIMPLE PAYOUT - MONTHS			10
@80 F OPERATION			
GTG PLANT COST			\$2,200,000
SIMPLE PAYOUT - MONTHS			24.4

TABLE 8-6 DIFFUSION DIALYSIS WITH 2% REJECT REDUCTION

OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT			
	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
2.00%			
Average production hours saved/day			
0.48			
average savings /day			
1056	\$385,440		\$385,440
LABOR			
	(No net change expected)		
MAINTENANCE			
		\$27,000	(\$27,000)
NET SAVINGS			
			\$1,276,019
@100 F OPERATION			
GTG PLANT COST			
			\$900,000
SIMPLE PAYOUT - MONTHS			8
@80 F OPERATION			
GTG PLANT COST			
			\$2,200,000
SIMPLE PAYOUT - MONTHS			20.7

TABLE 8-7 DIFFUSION DIALYSIS WITH 3% REJECT IMPROVEMENT

OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT			
	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
3.00%			
Average production hours saved/day			
0.72			
average savings /day			
1584	\$578,160		\$578,160
LABOR			
	(No net change expected)		
MAINTENANCE			
		\$27,000	(\$27,000)
NET SAVINGS			
			\$1,468,739
@100 F OPERATION			
GTG PLANT COST			
			\$900,000
SIMPLE PAYOUT - MONTHS			7.4
@80 F OPERATION			
GTG PLANT COST			
			\$2,100,000
SIMPLE PAYOUT - MONTHS			17

8.3. COPPER MILL WITH DIFFUSION DIALYSIS AND CRYSTALLIZATION

The Pickliq® Process, including diffusion dialysis and crystallization, applied to a copper mill without facilities is shown in Figure 8-2. This system will recover and recycle acid, hydrogen peroxide and inhibitor from a pickling etch and produce copper sulfate pentahydrate crystals.

The value of the crystals offered for sale as a product of the operation is taken from the Chemical Market Reporter, June 5, 1997. The costs of sulfuric acid, hydrogen peroxide and inhibitor were obtained from a confidential client source.

FIGURE 8-2 COPPER MILL WITH DIFFUSION DIALYSIS AND CRYSTALLIZATION

There is an economic benefit for a crystallizer in mills that have the opportunity to market copper sulfate pentahydrate crystal. In this case the major return is from sales of the crystal. Tables 8-8 - 8-11 show the operating and capital cost estimates for a plant of the same capacity as described in Section 8.1.

The crystallizer for this case is a two stage evaporative crystallizer with vapor recompression. Crystal dewatering is by centrifuge and an allowance has been made for product packing.

TABLE 8-8 DIFFUSION DIALYSIS & CRYSTALLIZER (NO CREDIT FOR REJECT IMPROVEMENT)

OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT			
	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
0.00%			
Average production hours saved/day			
0			
average savings /day			
0	\$0		\$0
LABOR			
		\$75,000	(\$75,000)
MAINTENANCE			
		\$65,000	(\$65,000)
ENERGY (Steam and Electric)			
		\$163,000	(\$163,000)
NET SAVINGS			
			\$614,579
SALES INCOME (CuSO₄*5H₂O)			
2456 Tons/yr			\$2,871,583
NET INCOME			
			\$3,486,162
@100 F OPERATION			
GTG PLANT COST			\$2,175,000
SIMPLE PAYOUT - MONTHS			7

TABLE 8-9 DIFFUSION DIALYSIS & CRYSTALLIZER WITH 1% REJECT IMPROVEMENT

OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT			
	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
1.00%			
Average production hours saved/day			
0.24			
average savings /day			
528	\$192,720		\$192,720
LABOR			
		\$75,000	(\$75,000)
MAINTENANCE			
		\$65,000	(\$65,000)
ENERGY (Steam and Electric)			
		\$163,000	(\$163,000)
NET SAVINGS			
			\$807,299
SALES INCOME (CuSO₄*5H₂O)			
2456 Tons/yr			\$2,871,583
NET INCOME			
			\$3,678,882
@100 F OPERATION			
GTG PLANT COST			\$2,175,000
SIMPLE PAYOUT - MONTHS			7

TABLE 8-10 DIFFUSION DIALYSIS & CRYSTALLIZER WITH 2% REJECT IMPROVEMENT

OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT			
	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
2.00%			
Average production hours saved/day			
0.48			
average savings /day			
1056	\$385,440		\$385,440
LABOR			
		\$75,000	(\$75,000)
MAINTENANCE			
		\$65,000	(\$65,000)
ENERGY (Steam and Electric)			
		\$163,000	(\$163,000)
NET SAVINGS			
			\$1,000,019
SALES INCOME (CuSO₄*5H₂O)			
2456 Tons/yr			\$2,871,583
NET INCOME			
			\$3,871,602
@100 F OPERATION			
GTG PLANT COST			
			\$2,175,000
SIMPLE PAYOUT - MONTHS			
			7

TABLE 8-11 DIFFUSION DIALYSIS & CRYSTALLIZER WITH 3% REJECT IMPROVEMENT

OPERATING COST SAVINGS			
	CURRENT	NEW	SAVINGS
ITEM	COST	COST	
RAW MATERIALS			
Sulfuric Acid	\$78,202	\$26,588	\$51,614
Hydrogen Peroxide	\$826,500	\$281,010	\$545,490
Inhibitor	\$191,250	\$62,025	\$129,225
			\$0
Sub Total	\$1,095,952	\$369,623	\$726,329
WASTE TREATMENT			
	\$191,250	\$0	\$191,250
OPERATING COST			
Improvement in reject rate @ \$2200/hr			
3.00%			
Average production hours saved/day			
0.72			
average savings /day			
1584	\$578,160		\$578,160
LABOR			
		\$75,000	(\$75,000)
MAINTENANCE			
		\$65,000	(\$65,000)
ENERGY (Steam and Electric)			
		\$163,000	(\$163,000)
NET SAVINGS			
			\$1,192,739
SALES INCOME (CuSO₄*5H₂O)			
2456 Tons/yr			\$2,871,583
NET INCOME			
			\$4,064,322
@100 F OPERATION			
GTG PLANT COST			\$2,175,000
SIMPLE PAYOUT - MONTHS			6

9. STEEL MILL EXPERIMENTS

The plan of the experiments at steel mills was to test the Pickliq® Process on plants using hydrochloric acid for pickling. Prior to beginning the studies, there was some realization that there may be a challenge since ferrous sulfate was more soluble than ferrous sulfide. But the full extent of the problems was not realized.

The candidate site was a small wire mill in a southeast state. This site pickled wire that came from an annealing furnace. However, when this site was visited, we discovered that the mill used an atypical method of waste treatment. Data from this site would be uncharacteristic of the rest of the industry. Since the objective was to develop an industry template, this site was rejected for the study.

Other hydrochloric acid pickling sites were investigated. These were large continuous sheet steel mills in Pennsylvania and New York. The names are maintained confidential. Data from these mills indicated a substantial difference and difficulty for the Pickliq® Process when applied to continuous steel mills using hydrochloric acid.

9.1. DIFFERENCES BETWEEN HYDROCHLORIC AND SULFURIC ACID PICKLING

There are several differences between sulfuric and hydrochloric acid pickling. A good discussion of some of these differences is available in a paper presented to the American Hot Dip Galvanizers Association, Mineral Acids as used in the Pickling of Steel, R. W. Ockershausen and C. L. Alderuccio, September 22, 1965.

The controlling difference for our subject process is the terminal concentration of the acid in large continuous pickling operations. Typically, sulfuric acid exits from pickling operations at 5-6 weight percent. Hydrochloric acid enters at 13% or higher and exits 2% or lower at the end of long pickling lines. In other words there is very little acid left to recover.

This is not always the case in small batch operations in the galvanizing or metal finishing industry. There are some applications where sufficient acid is left to recover by diffusion dialysis, but then the problem of the increased solubility of the ferrous chloride comes into effect.

Ferrous sulfate benefits from the energy efficient method of cold crystallization to separate the salt from the deacidified stream that comes from diffusion dialysis. Because of the higher solubility of the ferrous chloride, the solution must be concentrated and water must be removed to crystallize the ferrous chloride. Methods to remove water from the ferrous chloride solution include evaporative crystallization and electrodialysis.

10. CONTINUING EXPERIMENTAL WORK

This project has been extremely fruitful in advancing the art of the Pickliq® Process and pointing the direction for future work. In the area of copper, the studies have shown that there are sites that have existing crystallizing equipment as well as furnaces that use metallic copper as a feed. These sites could benefit from the not only recycling the acid and hydrogen peroxide to the pickling operation, and not only recovering the copper sulfate as a crystal, but also to refine the copper sulfate into copper metal that could be used for furnace feed. (See Section 10.1)

For steel plants that are using hydrochloric acid and consuming the acid down to as little as 2-3% free acid, "acid recovery" may not be an economic plan. In these situations, almost all of the acid values have been converted to ferrous chloride.

What is needed is a means to regenerate the acid from the ferrous chloride salt. This is accomplished by the Reuthner and Lurgi processes. However, GTG has begun experiments on chemically treating the ferrous chloride rich liquor with sulfuric acid. This treatment is then followed by cold crystallization that will precipitate ferrous sulfate crystals and regenerate hydrochloric acid for recycle to the pickling bath. (See Section 10.2)

10.1. PROCESS FOR COPPER MILLS WITH A FURNACE

The Pickliq® Process can be integrated with electrolytic refining to recover copper metal feed to an on-site mill furnace. Figure 10-1 is a flowsheet that shows this process.

The energy saving of this procedure would be substantial. The published energy cost of obtaining electrolytically refined copper cathodes for furnace feed, including energy from mine to furnace is 112.29×10^6 Btu /net ton of copper. In contrast, the energy cost for producing copper cathode feed from copper sulfate from the Pickliq® extended process on site as shown by Figure 11.1 is approximately 7.57×10^6 .

GTG is developing a plan for a research feasibility study for this process at a copper mill site using the Mobil Pilot Lab. The proposed project would confirm the feasibility, the energy savings and the economical benefits that would result from its adoption.

FIGURE 10-1 COPPER RECOVERY FROM COPPER ETCH WITH PICKLIQ® PROCESS

10.2. PROCESS FOR STEEL MILLS USING HYDROCHLORIC ACID

As discussed above, GTG has begun investigations on a chemical process to regenerate hydrochloric acid etch for steel mills by reacting the spent etch with sulfuric acid and then crystallizing ferrous sulfate. Figure 10.2 shows a flowsheet of the proposed process.

FIGURE 10-2 REGENERATION OF HYDROCHLORIC ACID PICKLE WITH SULFURIC ACID

10.3. SOLUBILITY IRON IN HCL AND H₂SO₄

A comparison of the solubility of ferrous chloride (as iron) in hydrochloric acid and ferrous sulfate (as Fe) in sulfuric acid is given in Figures 10-3 and 10-4. The charts are arranged to show the percentage of iron ad equivalent acid strengths. The weight percentages of the acids are also plotted.

FIGURE 10-3 SOLUBILITY FeSO_4 IN H_2SO_4 (as Fe^{++})¹

FIGURE 10-4 SOLUBILITY FeCl_2 IN HCl (as Fe^{++})¹

As shown by Figure 10-4 ferrous chloride is soluble in water at 32 F to over 14% iron while ferrous sulfate is soluble only to 5% iron. At an equal acid equivalent percentage (0.5 equivalents/1000 grams of solution) ferrous chloride is soluble in hydrochloric acid to over 13% iron. This is approximately the exit concentrations of the pickling acid from large continuous pickling lines using hydrochloric acid.

The comparable sulfuric acid case shown by Figure 10-4, ferrous sulfate is soluble only to 5% iron or 0.5 equivalents of acid per 1000 grams of solution. This is equal to approximately 2.5% sulfuric acid.

Cold crystallization could not remove enough ferrous chloride to have an economical process. Also, the amount of acid that could be recycled at 2% would make the capital investment for diffusion dialysis economically unattractive.

¹ Figures 10-2 and 10-3 plotted from data from Solubilities of Inorganic and Metal Compounds, Linke, William, (Originated by Seidel, Atherton), 4th. Ed. Vol. I. pp1015 - 1047, American Chemical Society, 1958.

An alternative to cold crystallization to recover the ferrous chloride would be evaporative crystallization. However, the difficulty here is the materials of construction that would be required for the evaporative crystallizer in the presence of chloride ions and hydrochloric acid. Either plastics or very expensive alloys would be necessary.

Plastics could be possible at small sizes, but would not have sufficient strength for the large flows that would be encountered at the large steel sheet and wire mills.

10.4. NEW PROCESS REQUIRED

There are sheet and wire mills that use sulfuric acid for pickling and there are sheet and wire mills that use hydrochloric acid. There are some advantages for hydrochloric acid that make some mills tolerate the increased fume and corrosion problems that come with the use of this acid.

There are other problems when the disposal of ferrous chloride and the recycling of waste acid are considered. First, ferrous sulfate is considered a hazardous material by Department of Transportation regulations. Ferrous sulfate is not. The method that is most used to recover hydrochloric acid from the waste pickle is a roasting process. This is embodied in the Reuthner Process and the Lurgi Process.

These are both complete regeneration processes where the ferrous chloride is roasted regenerating hydrochloric acid and forming ferric oxide, Fe_2O_3 . Ruethner generates a powdered oxide while Lurgi generates a pelletized oxide.

10.5. MODIFIED PLAN FOR EXPERIMENTAL PROGRAM

One alternative for consideration for the Pickliq® Process for hydrochloric acid pickling is the use of diffusion dialysis with evaporative crystallization. However, the typical sheet mill uses the acid down to 2-3% hydrochloric acid. Under these conditions, there is little economic hydrochloric acid to recover. This is a good reason why acid regeneration processes, like the Reuthner or Lurgi process have been used.

The effect of these considerations is that the best use of the Pickliq® process would be to work on ferrous sulfate that was formed from the action of sulfuric acid on ferrous chloride from a hydrochloric acid pickling bath. This in effect regenerates the hydrochloric acid by precipitating the sulfate as the less soluble ferrous sulfate. The second advantage of making ferrous sulfate from ferrous chloride is that ferrous sulfate is not a hazardous DOT material while ferrous chloride is. Finally, there is a glut of ferrous chloride in the USA while there is a serious shortage of ferrous sulfate. Much of the ferrous sulfate used is imported from Finland and Germany.

The simple solubility experiments that GTG performed show that there is promise for the process. However there is much that needs to be proved that would require a feasibility study conducted on-site of an operating plant.

We need to determine the composition of the regenerated acid:

- What is the ratio of Cl^- and SO_4^{2-} ?
- What is the rate of pickling of the resultant acid on typical metal stock used at the facility?
- What is the condition of the surface pickled?
- What is the concentration of returning iron in the mother liquor?
- What are the economic temperatures for crystallization?

This work is planned to be accomplished using the refitted trailer lab that was funded by this grant. The work is planned to be accomplished by a NYSERDA grant at a New York State Steel Mill that uses Hydrochloric Acid.

11. CERTIFICATION OF NO INVENTIONS

Green Technology Group hereby certifies that there were no discoveries or inventions made by employees or subcontractors of GTG in connection with the work performed on this grant.

Certifying for Green Technology Group

Douglas R. Olsen

Date 2/23/97

Douglas R. Olsen, President

12. CONCLUSIONS, PLANS & RECOMMENDATIONS

12.1. MOBILE LABORATORY

The mobile laboratory was conceived as necessary equipment to both test and promote the use of Pickliq® technology at a specific site where it might be used. The design was intended to bring the complex combination of unit processes to a facility along with a self contained analytical laboratory. We believed that in this way we could demonstrate the effectiveness of the process, allow site personnel to participate in a "hands on" demonstration, and be assured that the experiments were being conducted on real process streams from the prospect site.

The experimental work at Phelps Dodge, El Paso, Texas demonstrated that this approach was indeed was an effective tool for this approach. Additionally, for the particular unit operations that are needed for our process, certain modifications were needed for the lab, in keeping with its mission. These modifications were planned and partially accomplished as a part of this grant.

12.2. COPPER INDUSTRY

The experimental work at the Phelps Dodge Rod mill in El Paso Texas was extremely useful in learning the special requirements of the copper rod and wire industry for the application of the Pickliq® Process. While we were confident that the diffusion dialysis technology would be an effective process for the separation and recycling of sulfuric acid from copper sulfate, we did not have experience in processing etch containing hydrogen peroxide.

Work with the mobile laboratory was able to demonstrate:

- Diffusion dialysis will recover 80-99% sulfuric acid from H_2SO_4 - H_2O_2 etch solutions;
- Diffusion dialysis will recover 80-99% hydrogen peroxide from H_2SO_4 - H_2O_2 etch solutions;
- The percentage recovery of acid in diffusion dialysis is inversely proportional to the flow rate;
- Mobile pilot lab crystallizer design can effectively crystallize copper sulfate from water solutions; and
- Hydrogen peroxide can be effectively decomposed to low levels by activated carbon treatment. this could be an effective processing technique to feed a diffusion dialysis system where the presence of hydrogen peroxide was undesirable.

Copper sulfate may be crystallized from sulfuric acid etch solutions using cold crystallization. However, where diffusion dialysis is utilized to deacidify the copper sulfate and recycle the hydrogen peroxide prior to crystallization, the high solubility of

copper sulfate in water requires that the crystallization be accomplished by evaporative crystallization.

The results from the experimental work were translated into capital and operating cost estimates for a facility that utilized diffusion dialysis alone and for a facility that utilizes both diffusion dialysis and crystallization. The economic benefits that were evaluated for these systems were for a facility that recovers acid, hydrogen peroxide, inhibitor and copper sulfate from etch containing an average of 2,123 lbs/day of copper as Cu^{++} .

In addition to the benefits accruing from the recovery of the process materials there should be benefits from maintaining the pickling bath at a constant copper and acid concentration. These could include a decrease in product reject rate due to surface imperfections caused by operation of the pickling bath at extreme ends of the range. Cost estimates of the benefits possible by eliminating the production time for rework of off-spec product were also made.

There appears to be a very definite economic benefit for constructing a Pickliq® Process that recovers acid, hydrogen peroxide, inhibitor and copper sulfate from etch containing an average of 2,123 lbs/day of copper as Cu^{++} . Simple (before tax) paybacks of 6-7 months were estimated for this system. The controlling benefit was from the sales of copper sulfate pentahydrate crystals. Prices used in the analysis were obtained from the Chemical Market Reporter of June 5, 1997.

For plants that can accept the deacidified product of a water solution of copper sulfate, the incremental benefit of diffusion dialysis alone was estimated with the benefit of improvement of reduced the product reject rate. For operation of the diffusion dialysis stacks at an optimum 100° F plant payback periods of 7-12 months are projected.

If it is necessary to operate the diffusion dialysis unit at a temperature of 80° F, more diffusion capacity would be required and the payback period would be increased to 17-30 months, depending on the improvement in the reject rate.

Clearly there is a strong advantage to industry for installing a Pickliq® Process. What is needed to assure the most economic installation is the demonstration of a system that is able to operate at 100° F for extended periods of time with no deterioration of the membranes. An experimental program utilizing a pilot unit continuously operating on a real plant etch solution is strongly recommended. GTG will begin immediately to obtain the cooperation of a copper mill where such a test can be made. GTG has two possible sites that would be good candidates for this work.

12.3. STEEL INDUSTRY

The Pickliq® Process has been shown to be a very beneficial addition to those steel facilities that pickle steel with sulfuric acid. This work was done as part of the Prototype

Plant built at O.W. Hubbell and Sons, Inc., New York Mills, NY, sponsored by the New York State Energy Research and Development Authority. Paybacks of less than two years can be expected for appropriate installations.

For hydrochloric acid operations, work during this grant indicated that cold crystallization was not a viable process. This is due to the high solubility of ferrous chloride in water. Evaporative crystallization could recover ferrous chloride, however, there was so little acid remaining from the typical continuous hydrochloric acid pickling operation, that recovery of the acid would not be economically attractive.

The fundamental conclusion was that a process that regenerates hydrochloric acid is the appropriate technology for hydrochloric acid operations. The ferrous chloride roasting process by Reuthner or Lurgi accomplishes this, however, GTG studies indicate that by chemically transforming the ferrous chloride in the exiting pickle liquor with sulfuric acid, ferrous sulfate is formed and hydrochloric acid is generated. This is not a novel process, being predicable from long published solubility data. However, GTG has begun studies into the best conditions for industrial application.

12.4. FUTURE WORK

A modular design for all components of the Pickliq® Process equipment has been completed. This very economical design will be the standard design for all sizes of Pickliq® Process installations. This design work was done outside scope of this grant. However, for very large installation, the immediate installation of two modules, the "Utility" module and the "Stack" module can give technical and cost data that is easily scaleable to make a proposal for a complete installation. Such a "Modular Test" has been proposed for a major steel facility with potential for more than 10,000 gallons per day of sulfuric pickling acid.

12.4.1. Mobile Laboratory

The mobile laboratory has been redesigned for its next assignment. This will either be the copper metal recovery or hydrochloric acid regeneration project. The work to adapt it to one of these new assignments could be accomplished in as little as one week at as minimal cost.

12.4.2. Copper Metal Recovery

The Copper Development Association and the New York State Research and Development Authority have expressed strong interest in assisting with obtaining a site and sponsoring the research on the continuing development of the Pickliq® Process. Work on this feasibility study would be conducted with the mobile laboratory. There are three prospective sites now for this work, one of which has expressed strong interest. In this work a copper mill that uses large quantities of sulfuric acid etch for cleaning

copper and has an on-site furnace for wire or rod manufacture would be able to recover copper metal for furnace feed.

12.4.3. Hydrochloric Acid - Chemical Regeneration

The New York State Research and Development Authority has expressed strong interest in sponsoring a feasibility study for regenerating hydrochloric acid from ferrous chloride exiting a continuous steel pickling line using hydrochloric acid. This would be accomplished with the Mobile Lab at a New York State Steel Mill. GTG is in the process of obtaining the permission of a New York State site to conduct this work.