ENVIRO-CHEM SYSTEMS
A Monsanto Company

CORROSION RESISTANT ALLOYS IN SULFURIC ACID
Combining Corrosion Technology With Design

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AICHE CLEARWATER CONVENTION
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Abstract

With the advent of corrosion resistant stainless steels, the sulfuric acid industry has witnessed a gradual but consistent shift, away from traditional materials of construction such as cast iron and brick lined carbon steel to these newer materials. Monsanto Enviro-Chem Systems Inc. (MEC) has been a pioneer in this field. One of the most widely accepted such alloys, Sandvik SX Sulfuric Acid Stainless Steel™ (SX) was first introduced to the US industry by MEC almost a decade ago. Since then, MEC has gone on to provide many components of sulfuric acid plants fabricated from SX. Indeed today, there are several sulfuric acid plants in the US and abroad where the majority of the components are fabricated from corrosion resistant alloys. SX has become the standard for applications in the 93%-98% concentration range.

Since the introduction of SX, MEC has extended its portfolio to include numerous other corrosion resistant alloys for a wide range of applications within the sulfuric acid process. Each sulfuric acid plant offers a unique set of challenges based on operating parameters. Every such variable must be carefully studied to determine the best alloy for use in that particular application. The ability to provide the right alloy for the application is critical to ensuring long, trouble free service life, typically for 20 years or more.

The focus of this paper is to share some of the operational experience of SX in various applications over the past 10 years and to discuss the important advantages of combining corrosion technology with design. Several issues regarding the use of SX compared to the traditional and conventional materials of construction will be addressed.

Installations of Alloy Systems

MEC Offers various components of an acid plant, fabricated from SX. These include:

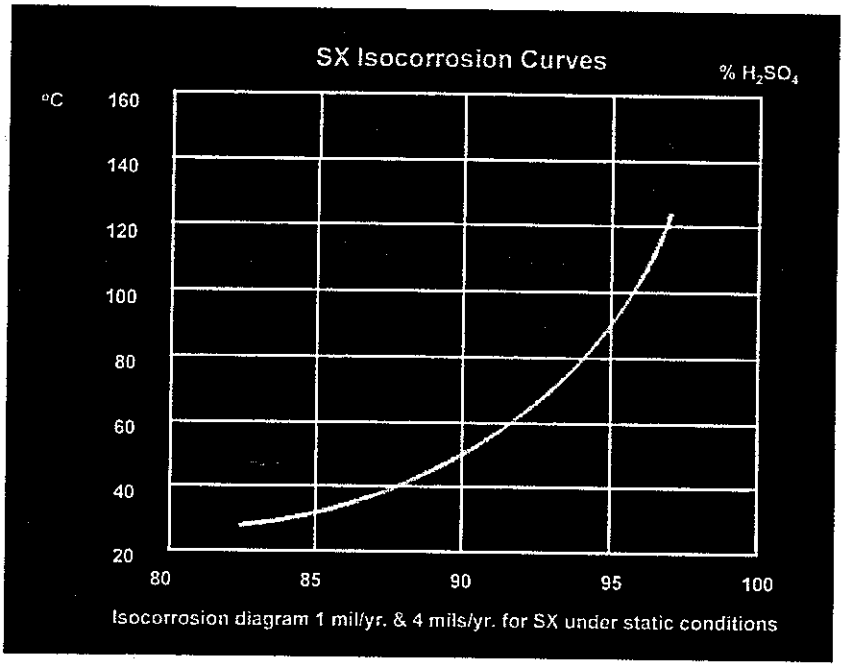
- Acid Distributors
- Drying & Absorbing Towers
- Pump Tanks
- Piping Systems
- Acid Coolers
- Orifice Plates
- Strainers
- Nozzle Sleeves
- Nozzle Assemblies

To date MEC has installed over 160 alloy trough distributors and 25 alloy towers worldwide. In addition there are numerous alloy piping systems being used to circulate sulfuric acid. In fact, alloy piping systems are offered as the standard for most new MEC plants today.

The unique advantage of SX is its inherent resistance to corrosion in concentrated sulfuric acid. SX, an austenetic stainless steel was developed exclusively for sulfuric acid applications. SX has been conclusively demonstrated to show extremely low rates of

corrosion in the range of 1 mpy or less in concentrations of 93%-98% sulfuric acid (Figure 1).

Figure 1.



Isocorrosion diagram 1 mil/yr. & 4 mils/yr. for SX under static conditions

MEC systematically monitored one of the original installations of SX towers in the US in 1988. SX coupons were strategically located in various areas within the towers to study the effects of temperature, acid irrigation and other factors on corrosion rates. These coupons were then measured on a scheduled basis for the next four years to chart and study the performance of SX. The results are shown below in Figure 2.

Figure 2.

Time between measurements are as follows:

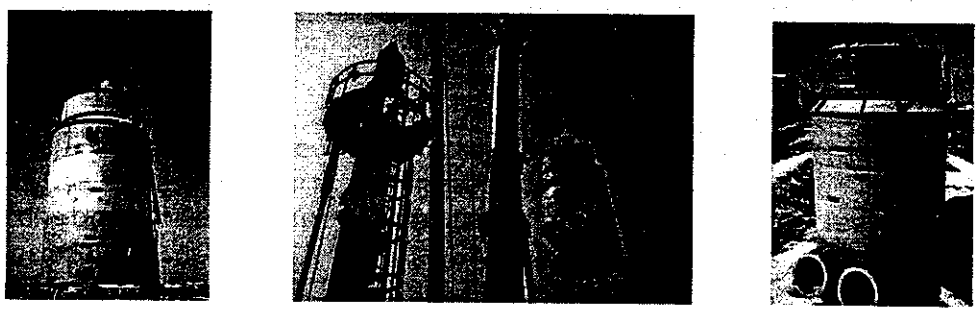
1st	**Measurement**	**3,336 Hrs**
2nd	**Measurement**	**2,328 Hrs**
3 rd	**Measurement**	**11,160 Hrs**
4th	**Measurement**	**14,112 Hrs**
Total duration monitored.		**30,936 Hrs**

Tower	1st Period	2nd Period	3rd Period	4th Period
Drying Tower	<0.1	<0.1	1.7	<0.1
IPA Tower	<0.1	0.1	0.1	0.7
Final Tower	<0.1	<0.1	<0.1	<0.1

Using nominal 1/4" plate for fabrication of these towers, the service life of the equipment was calculated to be well in excess of 20 years. During the period covered, no significant maintenance was required. The last set of measurements was taken in 1992. Since then, the towers have been visually inspected each year. No visible change or deterioration has been reported.

There are also numerous practical advantages to using SX for fabrication of vessels such as towers and pump tanks. In addition to the low corrosion rates, SX vessels weigh considerably less than the traditional brick lined carbon steel vessels. As a result, installation costs are less. The SX vessel can in most instances be completely shop fabricated and shipped to the site in one piece. During a shutdown, the existing vessel can be demolished and the new SX vessel simply lifted into place. This reduces the downtime involved in the replacement of such vessels and can have a significant impact on the overall cost of the project. Because there is no brick to contend with, the possibility of acid seeping behind the brickwork and causing continuous maintenance is eliminated. The elimination of brickwork also reduces the risk of damaging the pumps or coolers downstream. SX will not be subject to sulfate buildup that tends to clog the packing in towers leading to higher pressure drop and increased mist generation. The quality of acid is far superior to that produced using brick lined vessels and cast iron piping systems.

An example of the quick installation of an SX tower is shown below (Figure 3).



Replacement Alloy Tower

- **20' diameter**
- **Built off to side in one piece**
- **Lifted onto foundation in one piece with distributors installed**
- **Quick turnaround**

Demolition of existing bricklined tower
Field assembly of alloy tower
Erection and installation on foundation
All in 10 Days

This tower was installed in 1988 as a turnkey project. Recently a complete inspection of the tower was performed. The area of highest corrosion was observed to be around the inlet gas nozzle. Based on the original plate thickness of 3/8" (nominal), the average corrosion rate was calculated to be 4.3 mpy. A 20+ year service life span is expected to be easily maintained.

Another key component of a sulfuric acid plant is the acid distributor. Good acid distribution in any tower is extremely critical to ensure optimum tower performance and maximum service life of downstream equipment. In this age of heightened environmental awareness and fiscal responsibility, the choice of acid distribution systems must be made very carefully. Current technology available for acid distribution includes cast iron troughs, pipe type and alloy trough distributors. Acid distributors are a very good example of how important process and design technology is to the overall performance of the plant.

Cast Iron Trough Distributors

Most people tend to associate the term "Trough Style Distributors" with cast iron troughs. Cast iron trough distributors are still used in applications today. However, cast iron is prone to corrosion rates up to 100mpy. High corrosion rates in turn lead to problems with sulfating leading to poor acid quality, increased mist generation and high pressure drop, due to plugging of the packing. Coupled with the high corrosion rates, one must deal with the limited availability of replacement parts. Due to casting limitations, cast iron trough distributors cannot provide adequate distribution (> 1.3 pts/ft^2) for high efficiency towers that use packing depths of less than 12-14 feet.

Pipe Distributors

Pipe distributors have long suffered from the same problems as have the cast iron trough distributors. Until recently, pipe distributors had also been fabricated from cast iron. In addition to the problems listed above, pipe distributors are very prone to pluggage. This can lead to some very serious and expensive operating problems in the operation of acid plants. More recently, pipe distributors have become available in "High silica stainless" and other such alloys. Although these alloys demonstrate higher resistance to corrosion, they are still subject to plugging of the orifices by packing chips and other debris. In addition, pipe distributors generate excessive mist due to the high velocities that occur in the restricted area between the lateral branches.

Hybrid distributors attempt to combine some of the features of the pipe and trough distributors. Although this is an improvement over the two systems discussed, the hybrid does not provide a complete solution to acid distribution.

Alloy Trough Distributors

Acid distributors have undergone radical improvements over the years in both design and performance. Newer corrosion resistant materials have added a dimension never before possible; long life with virtually no maintenance. The alloy trough distributor designed by Monsanto Enviro-Chem Systems Inc. combines the best in process and materials technology. In order to fully appreciate the advantages of this design, it is necessary to understand what factors affect the overall performance of the tower and then review the benefits and advantages of the alloy trough distributor.

The primary purpose of any acid distribution system is to ensure that the acid and gas come in thorough contact throughout the tower. This is key to good drying and absorption. Theory would suggest that acid distribution can be modeled in very general terms. This is true to some extent. However, practical experience has demonstrated that each application is unique in that the process conditions contain variables that affect the design and performance of the distributor.

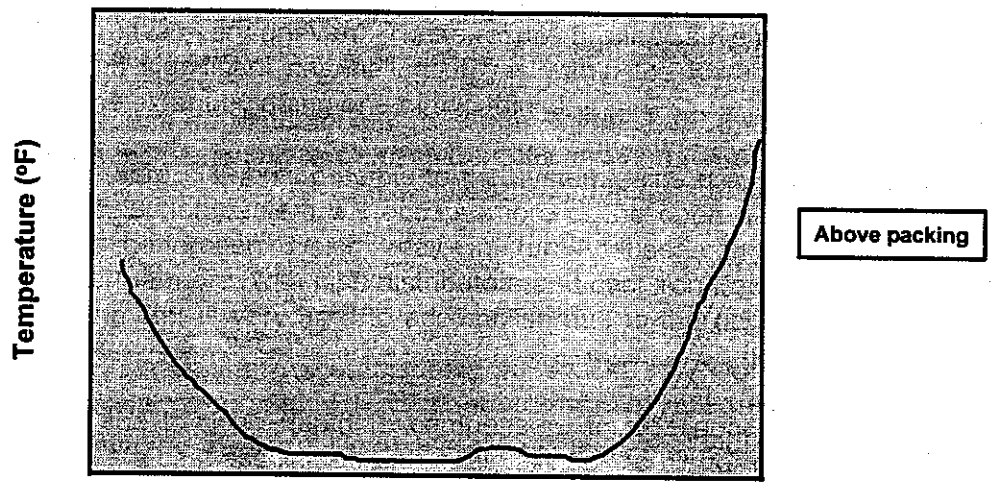
In order to study the relationship between acid distribution and gas absorption, MEC conducted the following: Thermocouples were placed along the cross section of a tower above an acid **pipe distributor** to chart the gas temperature. The resulting temperature profile (see Fig. 4) was very uneven. These results are indicative of poor distribution along the perimeter and significant channeling of gas within the tower. This problem can be alleviated to some extent by doing one of two things;

(a) - introducing more distribution points to the system. The drawback of this approach is that the pipe distribution system will occupy more of the open area in the tower thereby increasing mist generation which may in turn cause corrosion problems further downstream. Furthermore, with pipe distributors and cast iron troughs, obtaining coverage on the tower perimeter is very hard to accomplish due to the geometry of the distribution system.

(b) - increasing the packing depth to compensate for the poor distribution. Increased packing depth has a cost associated with it, usually tied to higher pressure drop and larger tower sizes.

Figure 4

Gas Temperature Profile in Tower Using Pipe Distributor



The hybrid distribution system incorporating a pipe delivery system with Teflon downcomers is an improvement over cast iron troughs and pipe type designs but, is still subject to most of the same drawbacks. The only way to get additional distribution points with this system results in smaller metering orifices that in turn are very prone to plugging. Increasing packing depth results leads to the same concerns as described above. In addition, the material of construction for the main header is subject to high corrosion rates compared to the higher alloys.

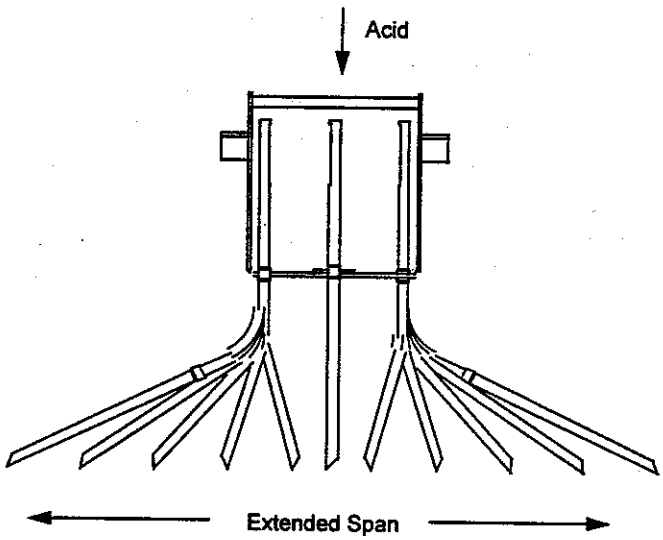
The Monsanto Enviro-Chem alloy trough distributor was first offered on the market in 1987 after extensive lab and pilot plant tests. This distributor was designed with the following key criteria.

- Continuous and uniform distribution
- Resistant to plugging
- Must limit mist generation
- Low pressure drop
- Long life with minimum maintenance
- Must be fabricated from corrosion resistant materials
- Ease of installation
- Ease of inspection
- Must be cost effective
- Easy to clean

The alloy trough distributor consists of downcomer tubes extending through the bottom of a trough and directed to the desired location in the tower (Fig 5).

Figure 5

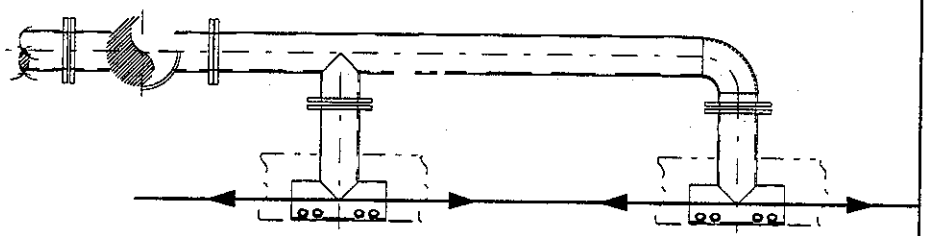
MEC Alloy Trough Distributor



The top of the tubes are slotted in a weir to ensure uniform and correct acid flow down each tube based on particular flow conditions. The weir ensures accurate and uniform delivery of the acid and virtually eliminates any chance of pluggage. The dimensions of the weir slot are chosen based on extensive pilot plant data and verified by field data. The downcomer tubes are typically 3/4" to 1 1/4" OD and provide gentle low velocity delivery of acid on the packing. An added benefit of this design is that the acid is discharged outside of the acid/gas contact area. This design also occupies the least amount of cross sectional area of the tower. As a result, there is no splashing, gas velocities are kept low and mist generation is significantly reduced. Acid is supplied to the troughs by an alloy header system with branches into each trough, discharging through specially designed tees (Fig 6).

Figure 6:

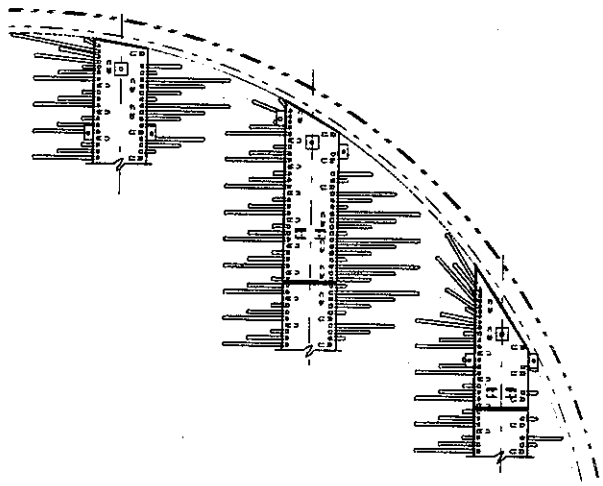
MEC Alloy Trough Distributor Header System



The benefits of the design is that it ensures uniform distribution to each tube. Each trough is subjected to a "water test" prior to shipment to verify the distribution from tube to tube. By design, all packing chips, brick, sulfates and other loose debris will collect in the bottom of the trough and not restrict the distribution and flow of acid. The MEC alloy trough distributor is the only distributor that can provide complete coverage over the entire packing surface. By design, the geometry and location of each downcomer tube is calculated to deliver a specific amount of acid over a certain area in the tower. The advantage of this design is in the ability to cover the perimeter of the tower (Fig. 7)

Figure 7

Alloy Trough Provides Optimum Coverage of Tower



and to provide uniform coverage thus eliminating any channeling of gas and providing complete drying or absorption coverage. In contrast, cast iron troughs , pipe distributors or hybrids of the two cannot provide this level of total coverage due to the physical limitation on the number and/or location of distribution points.

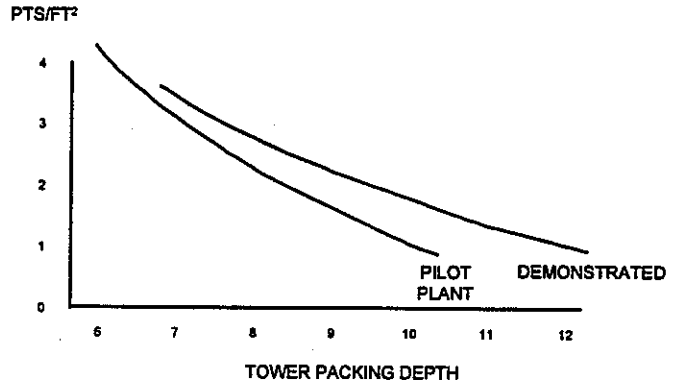
The unique advantage of the trough design is that it allows for significantly less packing depth which in turn provides a lower pressure drop across the packing. By increasing the number of distribution points (up to 4 pts/ft2), we can reduce the packing height as much as 8 feet in some cases. Pressure drop is reduced in proportion. This is possible only because the distributor can provide very thorough acid distribution over the packing. Other designs including the hybrid design cannot achieve this distribution efficiency. It has been claimed by others that the advantage of going from 1 pt/ft2 to 4 pts/ft2 is limited to about 6" in packing depth reduction. This is true for the cast iron trough, pipe and hybrid distributors for the simple reason that these systems cannot provide high quality, efficient distribution. The MEC alloy trough distributor is the only system that can deliver this reduction in packing depth. MEC has demonstrated both in pilot plant tests and also in actual plant installations that the savings in packing depth and pressure drop are real (Fig. 8).

PCS Phosphates and Cargill in the United States are just two examples of applications where packing depth (and resulting pressure drop) has been reduced significantly utilizing the MEC distributor.

FIGURE 8

TOWER PACKING HEIGHT VS. ACID DISTRIBUTION

MEC ALLOY TROUGH DISTRIBUTOR



The materials of construction for the MEC alloy distributor consist of highly corrosion resistant stainless steels with established corrosion rates of less than 1mpy. Expected service life of these distributors is 20+ years. Each trough is fully assembled in the shop and shipped to the plant site for easy installation through a 30" manway. Complete video and written instructions are provided for the customers' benefit. Due to the few numbers of rows of troughs, there is plenty of room in the tower to walk around with ease. Most operators of these distributors seldom need to actually enter the tower for inspection purposes. The flow of acid is easily viewed through the manway. Maintenance of these distributors is typically little or none at all.

It is important to point out that for any given distribution density, the MEC distributor will have fewer rows than any other system currently available (Fig 9). This advantage in turn benefits the customer by providing:

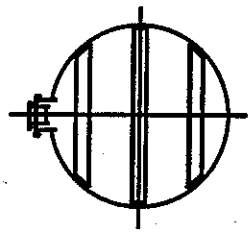
- More open area in tower
- Lower gas velocity = less mist generation
- Ease of installation and maintenance

FIGURE 9

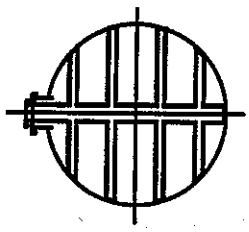
COMPARATIVE LAYOUT OF ACID DISTRIBUTORS

21'-0" I.D. TOWER

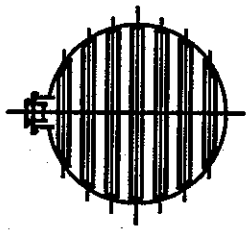
APPROXIMATELY 600 FEED POINTS



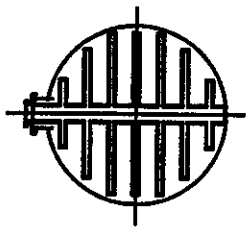
TYPICAL MEC ALLOY TROUGH DISTRIBUTOR
3 ROWS.



TYPICAL PIPE HYBRID DISTRIBUTOR
4 ROWS.



TYPICAL CAST IRON TROUGH DISTRIBUTOR
7 ROWS.



TYPICAL PIPE DISTRIBUTOR
7 ROWS.

The MEC alloy trough distributor can be retrofitted into any tower without the need for any modification to the tower. MEC has installed these systems in both brick lined and alloy towers. Many customers have replaced existing cast iron troughs and pipe type distributors with the MEC system to realize the benefits discussed above.

Piping Systems

Acid piping is a serious concern for every plant operator. The issues facing us each day deal with safety, the environment, reliability, maintenance and cost of operation. The two most obvious choices for materials of construction are cast iron and alloy systems. For years cast iron has been the choice of many primarily because it was the most inexpensive option. With the development of new alloys and the practical appreciation of the cost of safety and quality, alloy piping systems are becoming an industry standard.

The question most often posed when considering strong acid piping systems for replacement is always "What should we replace it with and why?". When making your final determination, many factors must be taken into account to make the right choice for you.

The most important factors are:

- Safety and the Environment
- Reliability
- Maintenance
- Total Cost - Capital Cost + Installation Cost + Replacement Cost

Safety and the Environment

Piping systems are especially important when one considers personnel safety and the environment. The Emergency Response Notification System (ERNS) database shows that there have been more than 34,500 accidents in the US during the period 1988-1992 involving toxic chemicals. This translates to approximately one accident each hour. An average of 2 people/day were injured as a result. The following table (Table 1.) chart shows the chemicals and accident rates that were reported during this period. As you can see, H_2SO_4 is one of the leading chemicals that make up these statistics.

TABLE 1.

TOP 15 CHEMICALS RELEASED FROM CHEMICAL ACCIDENTS IN THE U.S. RANKED BY NUMBER OF ACCIDENTS, 1988- 1992

CHEMICAL	NUMBER OF ACCIDENTS	ACCIDENTS W/INJURIES, EVACUATIONS OR DEATHS*	QUANTITY IN POUNDS
POLYCHLORINATED REFINYLS	3,586	34	19,022,604.50
AMMONIA, ANHYDROUS	3,333	389	20,746,742.40
SULFURIC ACID	*2,387*	*130*	*39,846,080.86*
CHLORINE	2,099	409	84,857,536.10
HYDROCHLORIC ACID	1,504	143	9,078,589.20
ETHYLENE GLYCOL	1,470	18	4,437,716.98
SULFUR DIOXIDE	1,310	86	2,460,527.00
RADIOACTIVE MATERIAL	1,073	30	129,416,251.65
BENZENE	1,048	14	9,140,482.40
HYDROGEN SULFIDE	939	49	1,496,056.00
SODIUM HYDROXIDE	867	47	56,200,314.52
VINYL CHLORIDE	621	11	119,939.00
TOLUENE	579	49	3,453,829.80
MERCURY	567	13	3,756,944.48
ETYLENE OXIDE	535	27	541,945.20
TOTAL	21,918	1,449	384,575,560.09

Source: ERNS database 1988 - 1992, compiled by MELC.
Note: Many accident notifications do not indicate quantity.
Many notifications do not properly identify all chemicals.
*Only includes accidents with immediate injuries known at the time of notification and assumes chronic health and environmental effects.

Conventional cast iron piping systems require numerous flange connections. The potential for leaks and accidents is in direct proportion to the number of flanges. Cast iron systems also corrode at rates of 30-100 mpy depending on the acid concentration and temperature. Although we, as an industry have spent considerable time and money in developing responsible responses to accidents, we tend to concentrate more on the response than prevention, at every stage of production, use and handling. The value of safety is an intangible component in any evaluation of piping systems or other equipment. Alloy piping systems answer most of these concerns by significantly reducing the number of flanges. Typical corrosion rates of the alloys we use in strong acid provide corrosion rates of less than 1 mpy.

****It is interesting to note that legislation in several European countries has been adopted mandating the use of alloy systems over cast iron strictly based on safety and the impact to the environment.**

Reliability and Maintenance

Alloy piping systems offer a virtual maintenance free component in the acid plant. The low corrosion rates of these alloys result in the following:

- 15-20 year life without replacement. Virtually no maintenance required.
- No sulfate contamination of the acid or tower packing.
- Significant reduction in number of "leak points" due to fewer flange connections.
- Light weight construction - easier to handle when required.
- Pipe sizes are typically smaller than cast iron since velocity erosion is not a concern.

Summary

The advantages of using corrosion resistant alloys such as SX are significant when combined with process and design technology to provide the optimum system. MEC continues to work in the area of corrosion resistant alloys for all applications within the sulfuric acid industry.