

**SULFURIC ACID STORAGE TANK CORROSION**

**1993 A.I.Ch.E. CLEARWATER CONVENTION  
CLEARWATER BEACH, FLORIDA**

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## **Summary**

The serious consequences of sulfuric acid storage tank corrosion may not be fully appreciated, due in part to the excellent safety record in recent years. In today's modern plants, the opportunity for storage tank corrosion is more severe than ever. The concentration of dissolved iron is lower due to the conversion to lower maintenance stainless steel acid handling equipment. Plants are being pushed to capacities higher than design , with hotter product acid being placed into storage. Anodic protection of storage tanks has proved a safe and effective method for extending tank life and reducing the risk of a catastrophic loss.

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## SULFURIC ACID STORAGE TANK CORROSION

### Background

The first A.I.Ch.E. meeting at Clearwater Beach was held in 1977. The technical presentation at that meeting included a paper by Mr. John Futers of IMC, Port Maitland, Ontario (1). Mr. Futer recounted the sudden and catastrophic failure of a 3,000 ton sulfuric acid storage tank two years previously. He reported that after fourteen years of service, this tank suffered a vertical parting of the side wall, dumping sulfuric acid with such force that a nearby tank under construction was moved 75 feet off its foundation. A number of other physical damages occurred, causing the total plant to be shut down for six weeks of cleanup and equipment restoration.

IMC had exercised the normal inspection procedures of scheduled ultrasonic thickness testing and internal visual inspections over the years of operation. This particular tank had been inspected ten months before the accident, without detecting any sign of potential failure.

An immediate detailed inspection of the ruined tank was undertaken. The examination revealed that the side wall failure occurred due to a grooving corrosion of such narrow magnitude that the normal inspection procedures were not adequate to identify the localized metal loss. The grooving was located on the wall adjacent to the inlet nozzle and the upper half of horizontal manways. Inspection of the other three sulfuric acid storage tanks on site revealed the same grooving phenomena, though not as advanced.

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Canadian Industries Limited, at the time the world's leading producer and distributor of metallurgical sulphuric acid (2), was understandably concerned about this previously unrecognized hazard. C-I-L commissioned a study by Chemetics International Company, with the objective to investigate the types of corrosion occurring in sulphuric acid tanks, and to determine the effectiveness of anodic protection toward these mechanisms (3).

At the time of C-I-L's heightened concern for the safety of their storage tanks, Chemetics clearly was the most knowledgeable in understanding the theory and practical application of anodic protection of metals containing sulfuric acid. They were the natural choice to adapt this technology to storage tank protection. After the first adaptation of anodic protection to stainless steel heat exchangers at C-I-L's Copper Cliff plant, Chemetics continued the development of this technology for numerous process combinations of acid concentration and temperature. In 1993 the number of acid coolers supplied to producers around the world is approaching 900.

One alternative solution was to place an impermeable barrier between acid and metal. Tank linings had been used for smaller tanks, but were not economic for the tank sizes in service for a major sulfuric acid distributor. Aside from economic considerations, the contraction and expansion of these large tanks put a severe stress on the durability of plastic linings. Even in the small tanks, linings have a limited life.

An understanding of anodic protection brings the realization that it is just another type of impermeable barrier. The basic features of anodic protection seemed to indicate that this technology offered a good solution to some types of corrosion if properly developed.

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## Types of Corrosion

The most common corrosion is the uniform general metal loss acting completely over the interface between sulfuric acid and metal. The rate of metal disappearance is a function of the acid temperature, concentration, and velocity, and has been characterized as 5-30 mpy. This corrosion is well recognized and documented in the literature. The references used for this presentation list several general discussions of the subject.

To minimize this general corrosion, one important aspect is to minimize acid storage temperature. This includes product acid cooling before storage, and using heat reflective paint on the tank shell. The storage tank is a type of solar heater, with a maximum heat absorption, in some locations, approaching 350 Btu/ft<sup>2</sup>-hr. Figure 1 illustrates the relationship between corrosion rate and acid temperature for 93.5% acid in an agitated vessel.

The concentration of product acid is fairly well controlled as a plant variable. However a weak acid layer can form on the surface by rain leakage, or dessication of the air layer above the acid. A local corrosion problem can occur in a relatively dormant tank, allowing the acid to remain layered and attack the metal circumferentially. In this case the corrosion indications appear as horizontally etched lines around the tank circumference.

A relatively small, highly utilized tank with relatively large flow rates in and out is subject to continual wiping away of the protective ferrous sulfate layer, and exposes fresh metal to the corrosive acid. Some careful attention to proper tank sizing and adequate corrosion allowance should minimize general corrosion.

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The technology of today's sulfuric acid plant has increased the corrosivity of product acid. Where older plants made extensive use of cast iron for handling sulfuric acid, the modern plant utilizes stainless steel for piping, pump tanks, tower distributors, and cooling. Even tower design has succumbed to the new materials available; Chemetics has supplied three towers constructed of SARAMET® plate. Stainless steel converters and hot heat exchangers are standard specifications in the modern plant.

The application and usage of stainless steel has reduced the iron content of sulfuric acid from above 40 ppm, to a typical 5-10 ppm. At this low iron level, sulfuric acid exhibits a strong affinity for dissolving available iron. Figure 2 shows the relationship between corrosion rate and iron content in 93.5% acid at 77°F in an agitated vessel.

These results were previously published by Chemetics (4) some years ago, and the results indicated significantly higher corrosion rates than previous studies. Since this testing program was conducted in a stirred tank, and previous studies were thought to be in stagnant acid, these results are more applicable to the turbulent condition found with an active storage tank.

It has also been reported (4) that the amount of tramp copper showing up in steel plate has greatly declined due to better scrap sorting. Small amounts of copper in steel significantly reduce the rate of corrosion of carbon steel in sulfuric acid. One reference in this article cited a halving of the corrosion rate by the addition of 0.25% copper.

"Grooving" corrosion, identified as the failure mechanism in the IMC tank, was later identified in a number of locations and applications. This small etched line is very difficult to spot

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applications. This small etched line is very difficult to spot without knowing exactly what to look for. The grooves are typically 1/16" or less, wide and usually obscured by rust and scale. Ultrasonic testing will not normally pick up these slight flaws. A proper inspection must include the vigorous wire brushing of the inside wall, adjacent to the acid inlet and above manways or other discontinuities.

Grooving is caused by hydrogen bubbles evolving from the reaction of iron and sulfuric acid. Multitudes of very small bubbles migrate upward from the point of reaction. The large differential in relative specific gravities imparts a high velocity to the escaping bubbles. As they rise up the wall, they continually erode the soft ferrous sulfate layer protecting the wall. This exposes a thin vertical strip of fresh, clean metal to corrosion, and a perpetual etching cycle is instituted with sustained hydrogen release within the groove.

Since the area under the acid inlet is the most turbulent with the hottest acid, this is the most active point of corrosion. Before this phenomena was identified, the acid inlet was usually close to the side wall, to give good access to inlet valves and piping without having to climb on the tank. This area of the wall requires the closest scrutiny. Since this corrosion mechanism has been publicized, tank inlets have been moved well away from side walls, which has minimized but not totally eliminated the potential hazard.

In many tanks "blistering" has been identified as a problem. These blisters are also a product of hydrogen release from steel corrosion. The first reaction product is atomic hydrogen, which forms the gaseous molecule. However some of the atoms diffuse into the metal, and if a lamination is present these atoms pocket, and form gaseous hydrogen at this point. The gas is trapped within the

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plate, and tremendous pressures build up slowly over time until the blister ruptures.

These blisters are easily identified by frequent visual inspection, and can be repaired before the blister bursts. Care must be exercised not to spark the pure hydrogen gas during repair.

There are other forms of corrosion, such as galvanic, crevice, and end grain attack, which can occur under very specific circumstances. A comprehensive treatment of all the types of corrosion has been published (5). This cited paper is recommended reading for every one with any responsibility for sulfuric acid storage.

### Anodic Protection Theory

When a metal contacts a chemical solution, it develops an electrical potential relative to a reference electrode. The reference electrode has a constant potential which does not change even though the solution in contact may change composition or physical properties. This relative electrical potential is defined as the free corroding potential, and is dependent on the metal alloy and the chemical solution in contact.

The free corroding potential may be changed and controlled by passing a DC current through the metal into the solution. This is referred to as "polarizing" the metal. If the current density applied is graphed versus the resulting potential achieved, the plot is called a polarization curve. Figure 3 shows a typical polarization curve.

As the potential is increased above the free corroding potential, there is a corresponding increase in current density. During this



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period, a thin film begins forming on the metal surface. This film is a result of metal oxidation as it changes valence state due to the supply of electrons. The film is an inertial barrier between acid and the metal surface, and the electrical current flow. As the film builds to a point where the metal surface is completely covered, the current density falls off to a very low level, and the metal is passivated.

The metal will remain in this passive state while the anodic potential is maintained. The amount and range of potentials over which passivity can be maintained is a function of the acid concentration and temperature, and type of metal.

Not all metals can achieve this passive state. Some metals give up the electrons to ionize to a state which is soluble in the acid (e.g.,  $\text{Fe} \rightarrow \text{Fe}^{+2}$ ). The continued loss of iron is in proportion to the impressed current, offering no corrosion protection. This condition is represented by the dashed line on Figure 3.

There is a transpassive region of high potential where the passive film goes into solution, and the current density increases rapidly. This can occur when dissimilar metals with differing polarization curves are being passivated by the same cathode. For example stainless steel valves on a storage tank drain nozzle can possibly be driven transpassive by the tank cathode, resulting in quick deterioration of the valve. Improper location of cathodes and reference electrodes can also lead to situations where transpassive areas exist in a vessel which seems to be quite passive. There is a great deal of knowhow and experience involved in the correct setup of anodically protected vessels.

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## Tank Protection System Development

The mechanics of anodic protection are quite simple in principal, as shown in Figure 4. An anode, a cathode, and a reference electrode are attached to the vessel to be protected. A current flow is applied from a power supply, and the reference electrode signals the increase in potential to a controller. The control circuit compares this value with the preselected set point, and signals the power stage to increase or decrease current flow to the cathode.

The earliest anodic protection systems for sulfuric acid storage tanks featured controllers with massive rectifier systems. The first units were three phase, air cooled systems. Later the rectifier systems were modified to oil cooling. These operated much like an HVAC thermostat, switching on a large power supply when the signal potential dropped below the set point, and shutting off when the set point was achieved. On a few large tanks two 750 amp power supplies were mounted.

The early units also featured reference electrodes entering through the side wall. The packing gland assembly was always a concern in this arrangement, with a serious potential for large acid losses to the environment. A level sensing device was also required to shut down the system when the tank was drained. The first system improvement was to locate all reference electrodes to roof entry locations.

Proportional control circuits for the controllers in sulfuric acid cooler duty were adopted about the time storage tank protection systems were being commercially developed. This new development was quickly phased into storage tank systems, which made a tremendous improvement in system control stability. These systems were

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installed up to 1986, and are still working well for dozens of tanks in service.

Microprocessor technology was introduced in 1986, which was a major improvement in many respects. Chemetics made the new system high or low amperage switchable, and can team several units in parallel for larger tanks requiring greater power supply. The largest system to date connects three Controller/Power Stage (C/PS) units to provide 300 amps, in place of the old style, multiple 750 amp supply units.

The microprocessor design allows for monitoring multiple systems, up to twelve, at distances in excess of one half mile. These systems can be any combination of anodically protected acid coolers, storage tanks, or stainless steel piping. Relatively inexpensive shielded conductor wire is the only connection to the remotely located C/PS units. Recently a communication board has become available for the Remote Display Unit (RDU), which relays all operating parameters to a Distributed Control System monitor. The operating cost of tank protection systems is considerably lower now than it was ten years ago. The installed cost has also declined, thanks to the improvements in hardware and installation design. Knowledge gained from start up experience and service call responses by our Technical Service Department has been implemented into our design standards.

Level sensing circuitry is no longer required with the installation of a "seal pot" for the cathode on the floor of the vessel. This has simplified control circuitry and eliminated one source of low level nuisance alarms. The price of reference electrodes has also been reduced with this improvement. The revised system keeps the tank passive, even with changes in level. The passive layer remains intact on the walls as the tank is drained, and is quickly reinforced when it is refilled.

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Chemetics has continued to determine the correct operating parameters for passivating storage tanks with weaker acid concentrations. Last summer a storage tank containing 77% sulfuric acid was successfully passivated for a plant in the U.K., and another is in the initial stages of operation in the southeast. Alky waste acid storage tanks have also been successfully passivated.

Since this technology was introduced to the industry in 1976, 123 tanks have been equipped with anodic protection by Chemetics. We estimate that 86% of these units are still in operation. The tank systems no longer in service were a victim of plant site economic viability, not a failure of the anodic protection system to protect the tank.

In preparation for this paper, some of the operators who have had tank protection systems in continuous service for more than ten years were contacted. All who were contacted avow the continued reliability of their systems. One Central Florida plant installed tank protection systems back in the late 1970's after having to replace some wall plate on existing storage tanks. Since the installation they have continued timely inspections and monitored plate thickness. They have found only minor metal loss from general corrosion in thirteen years, and no occurrence of grooving or localized attack.

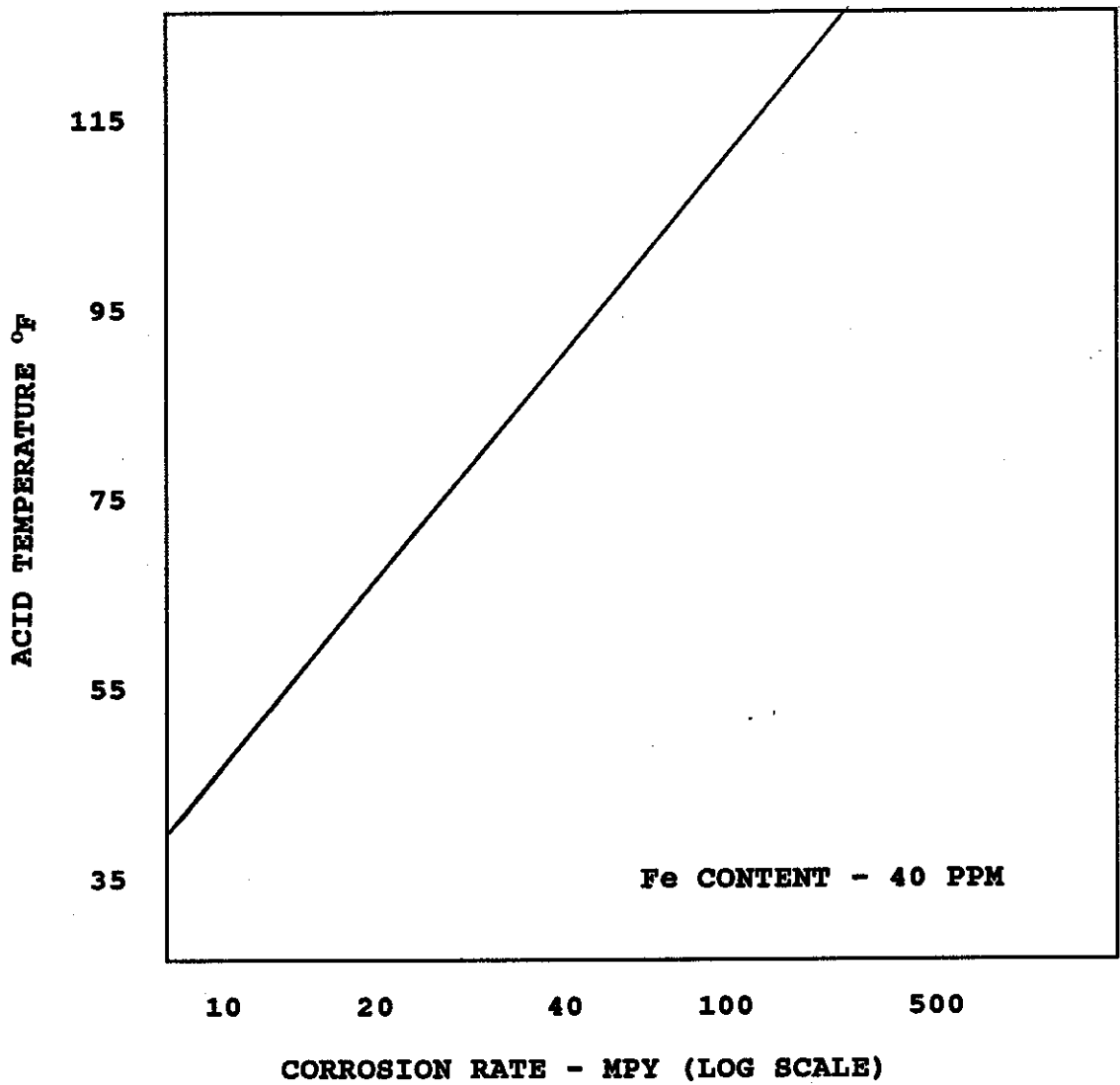
Other users who sell merchant grade acid report a much lower sludge content in their tanks since anodic protection was installed. This results from the lower corrosion rate, and less corrosion product being formed.

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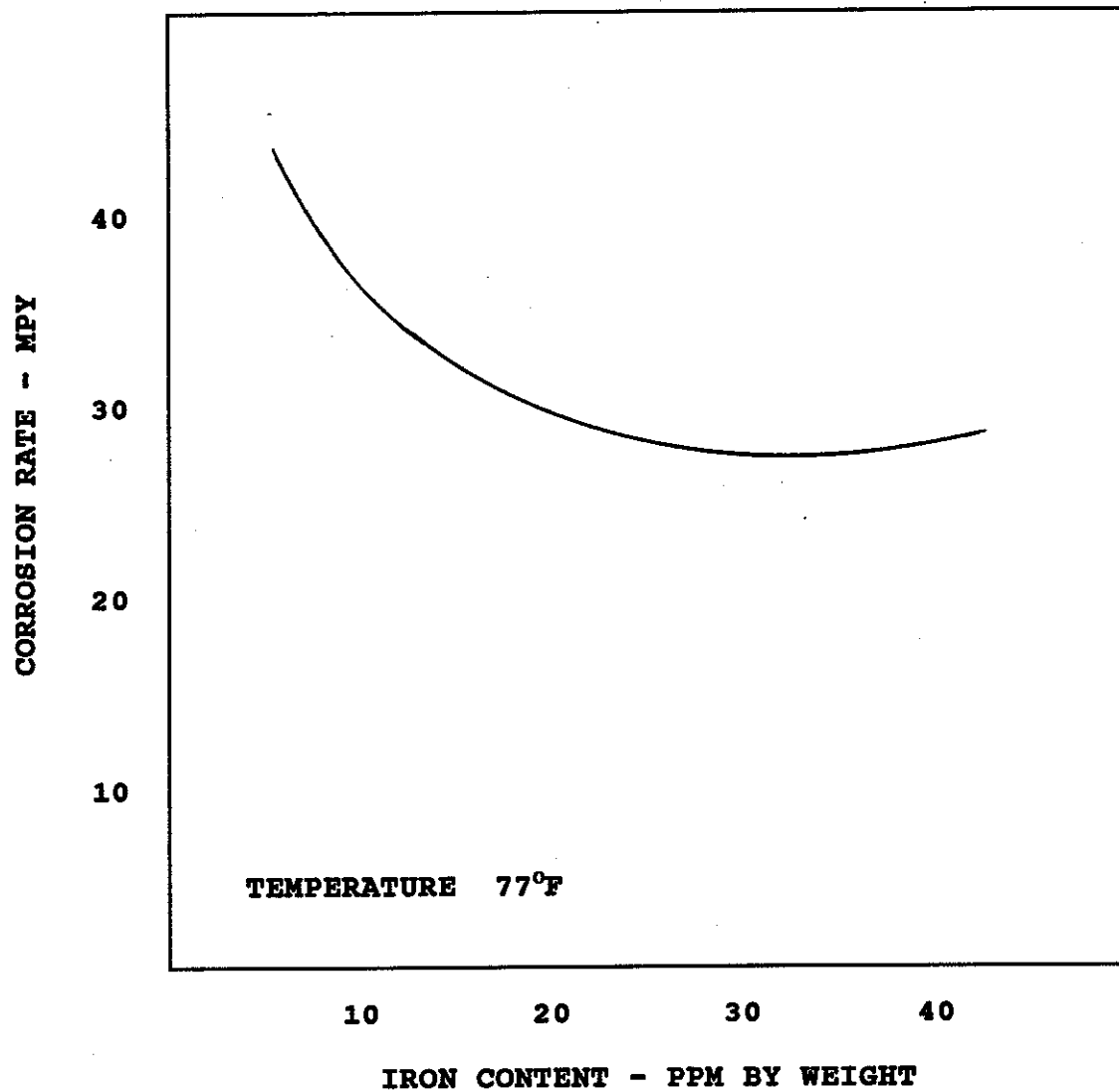
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## REFERENCES

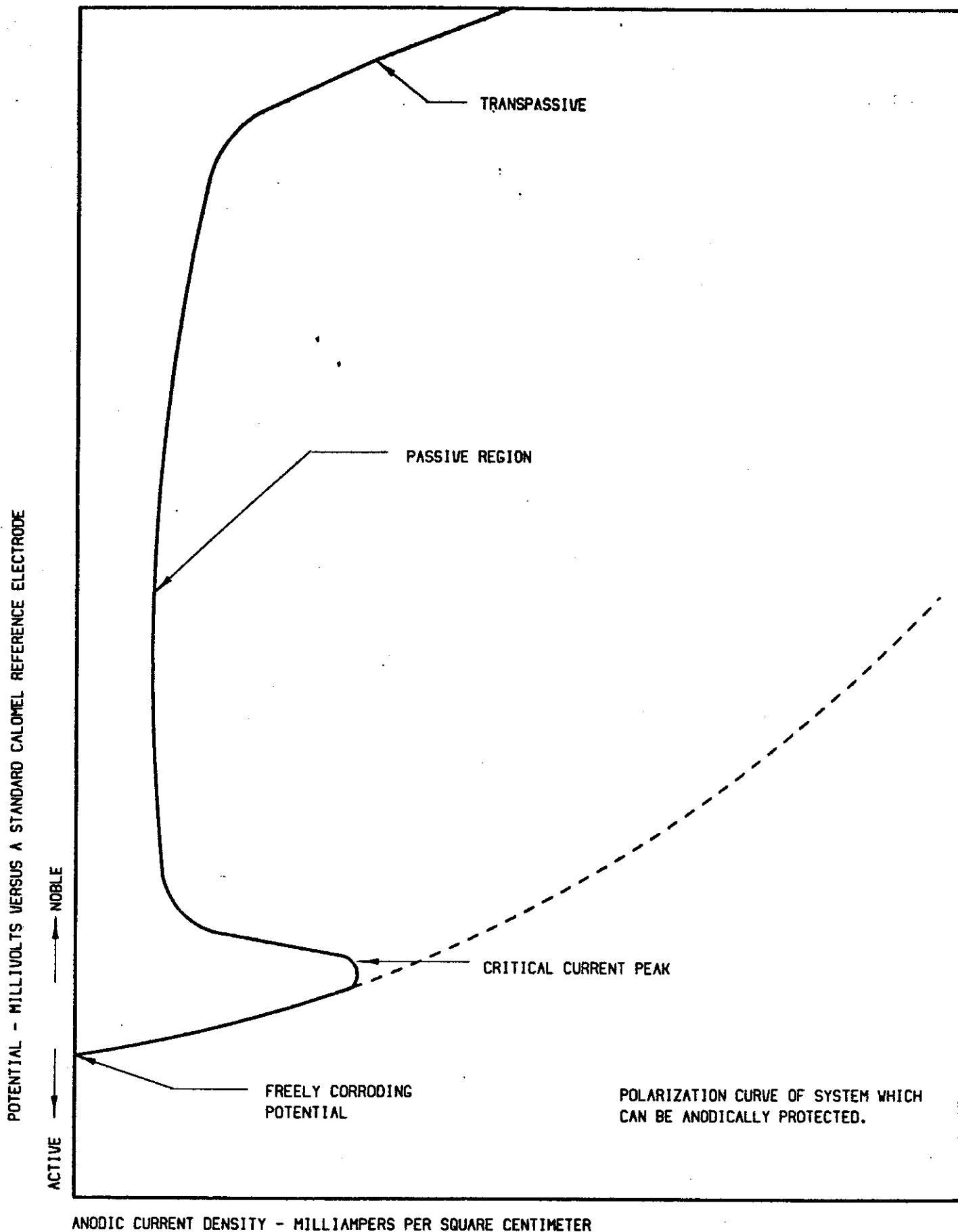
- (1) Futers, John R., "Rupture of a 3000 Ton Sulphuric Acid Storage Tank", A.I.Ch.E. Joint Meeting, Central Florida and Peninsular Florida Sections, May, 1977.
- (2) C-I-L Technical Manual, "Sulphuric Acid", 1980.
- (3) Rodda, J. and Vanderland, R.F., "Sulphuric Acid Storage Tanks", Research Contract Report, December 17, 1977.
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- (5) Tivel, M. and McGlynn, F., "Avoiding Problems in Sulfuric Acid Storage Tanks", A.I.Ch.E. National Convention, New Orleans, LA, April, 1986.
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**FIGURE 1. INFLUENCE OF ACID TEMPERATURE ON THE CORROSIVITY OF 93.5% SULFURIC ACID**

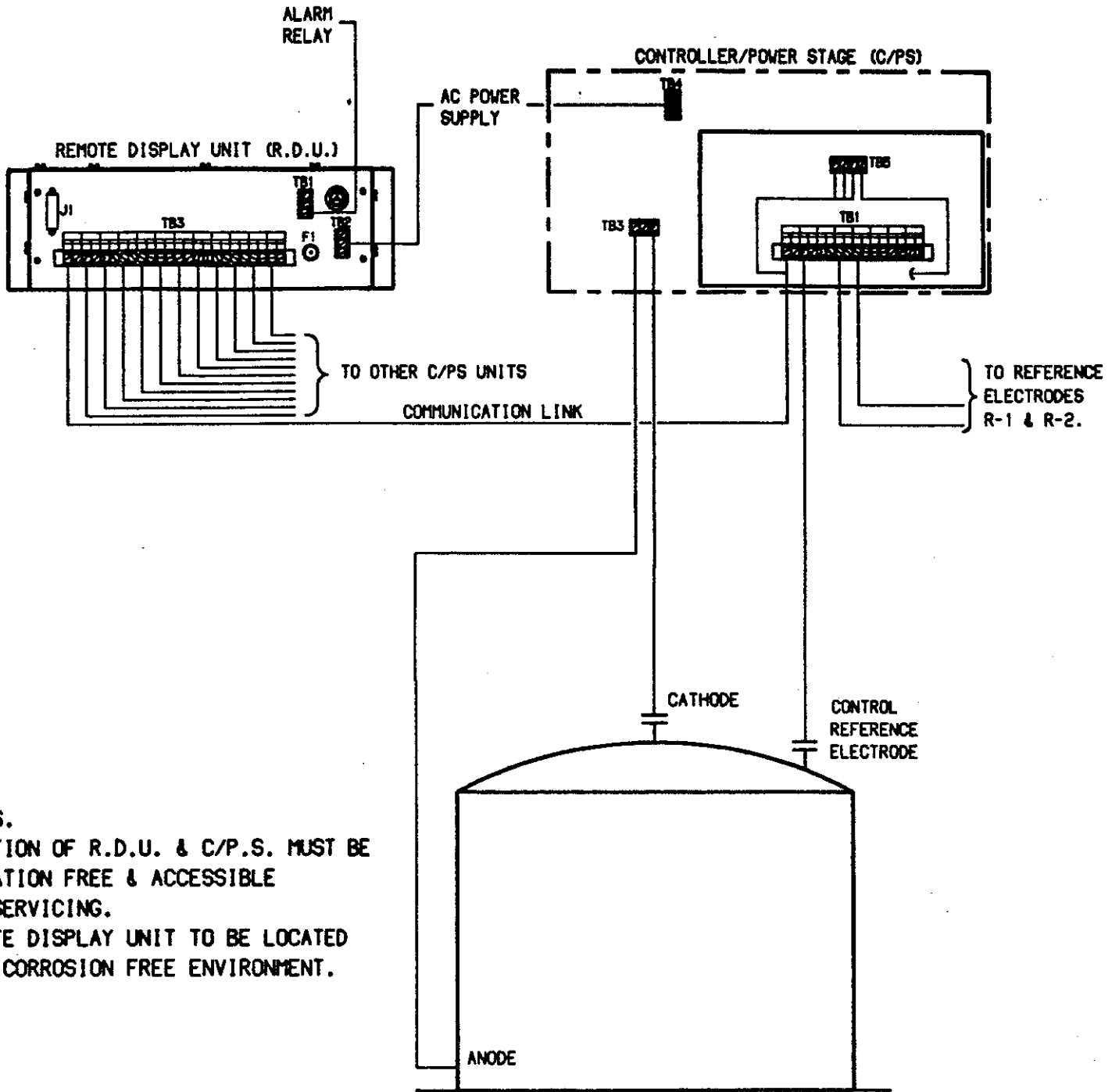


**FIGURE 2. INFLUENCE OF IRON CONTAMINATION ON THE CORROSIVITY OF 93.5% SULFURIC ACID**



**FIGURE 3. GENERALIZED POLARIZATION CURVE**





NOTES.  
 LOCATION OF R.D.U. & C/P.S. MUST BE VIBRATION FREE & ACCESSIBLE FOR SERVICING.  
 REMOTE DISPLAY UNIT TO BE LOCATED IN A CORROSION FREE ENVIRONMENT.

FIGURE 4. TYPICAL TANK ANODIC PROTECTION SYSTEM