Anodic Protection of NO_X-Contaminated Sulfuric Acid Tanks

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The efficacy of anodic protection (AP) on the wet/dry (tidal) zone of a sulfuric acid (H_2SO_4) tank wall has been in some doubt. The present work confirmed that AP is effective in mitigating corrosion of nitrogen oxide (NO_X)-contaminated H_2SO_4 in both the submerged and tidal zones of the tank.

Sulfuric acid (H_2SO_4) is a by-product of the smelting operation of sulfide ores. High-temperature burners may produce nitrate and nitrite impurities (NO_X) in the acid that cause a number of undesirable effects, such as contamination, pink/purple coloring due to the $Fe(NO)^+$ complex, and accelerated corrosion of storage tanks. The focus of this work is on the corrosion-mitigating effects of anodic protection (AP) on storage tanks that contain nitrogen oxide (NO_X)-contaminated H_2SO_4.

The by-product, 93 to 95% H_2SO_4 from the Phelps Dodge Corp., Miami Smelter Operations in Arizona, was stored at their own local facilities and at a number of other sites in the vicinity, including the Morenci (Arizona) operation. Maintenance personnel at the Morenci facility noted an alarming increase in the corrosion rate of their storage tanks (Figure 1). Ultrasonic thickness (UT) measurements in 2003 and 2004 indicated that the average thickness loss was in the range of 5 to 8% per annum. In addition, the wet/dry (tidal zone) of one tank experienced more than 30% loss per annum. The facility used steel plates varying from 7.5 to 15.9 mm (0.295 to 0.625 in.) thick for tank construction.

This corrosion rate was certainly higher than what would be expected from 93 to 95% acid even in the hot summer months of southwestern United States. The owner identified the cause as NO_X-accelerated corrosion and collected daily NO_X concentration data. The data from May 3, 2004 to June 12, 2005 (406 days) were used for this analysis (Figure 2).

Andersen, et al.[1] reported the corrosion rate of steel in concentrated reagent grade H_2SO_4, R (mm/y), as a function of NO_3^- concentration as:

$$R\ (\text{mm/y}) = 0.0071[NO_3^-]_{\text{mg/L}} + 0.447 \qquad (1)$$

Equation (1) is valid from 0 to ~1,000 mg/L of NO_3^- in H_2SO_4 at 50°C.

In an effort to test the validity of this equation, the daily equivalent corrosion loss using Equation (1) was calculated and summed over the 406 days of available NO_X information in Figure 2. Based on this computation, a total of 1.1 mm (44 mils) or 1.0 mm/y (40 mpy) would have been consumed at 50°C.

Field thickness readings on the storage tank were recorded on May 3, 2004 and August 17, 2005 (Figure 3.) To compensate for the additional 66 days over which this degradation occurred, an average daily loss was calculated based on representative sampling from 0 to 6 m elevation. The average daily loss was multiplied by 406 days for comparison purposes. The average wall loss over this period was 0.46 mm (18 mils) or 0.41 mm/y (16 mpy). The discrepancy between the calculated 1.0 mm/y rate and the normalized actual rate of 0.41 mm/y may be attributed to:

1) 50°C laboratory data vs the ambient temperature field data.
2) An average calculated loss was used to compare to multi-level wall thickness loss in a tank.
3) Equation (1) was derived specifically for $[NO_3^-]$ and the tank acid could contain other NO_X species.

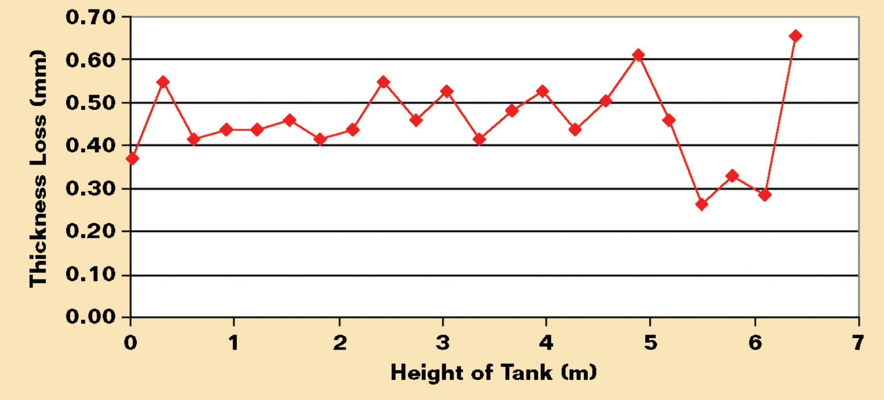
Nevertheless, the corrosion rates were in the right order of magnitude and Equation (1) may be considered as a good first approximation of actual corrosion rate.

Anodic Protection

AP is a proven and well-established technology[2] and has been employed to mitigate corrosion and control iron contamination.[3-5] None of these tanks suffered from NO_X-accelerated corrosion, however, because circumstances allowed those tank owners to keep NO_X levels at a minimum. For example, one plant in the province of Quebec, Canada, used AP in tanks with <10 mg/L of NO_3^-.

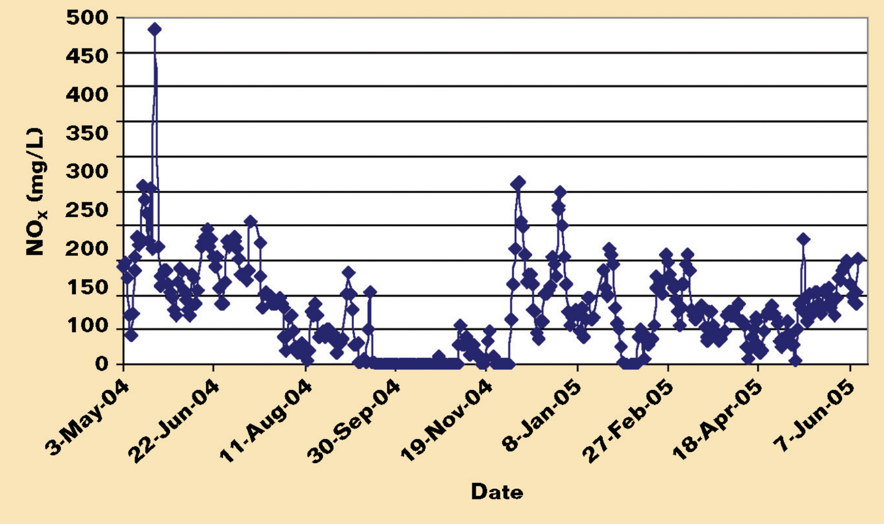
AP is very successful in mitigating corrosion. This is accomplished by shifting

FIGURE 1



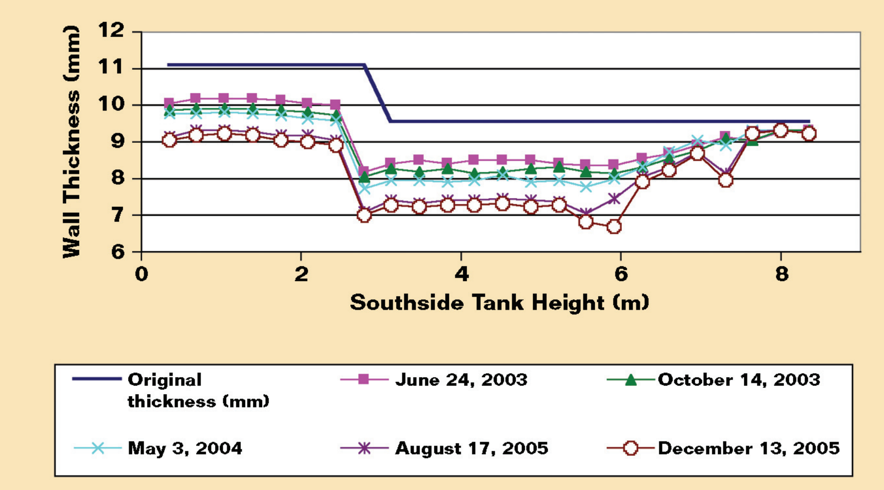
Average wall thickness loss over a period of 406 days derived from ultrasonic measurements taken on May 3, 2004 and August 17, 2005.

FIGURE 2



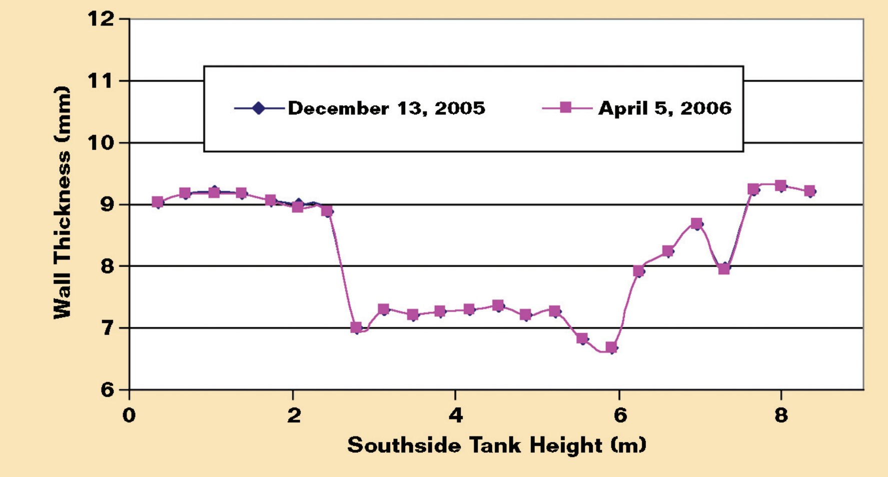
NO_X level in H_2SO_4 tank from May 3, 2004 to June 12, 2005 (406 days).

FIGURE 3



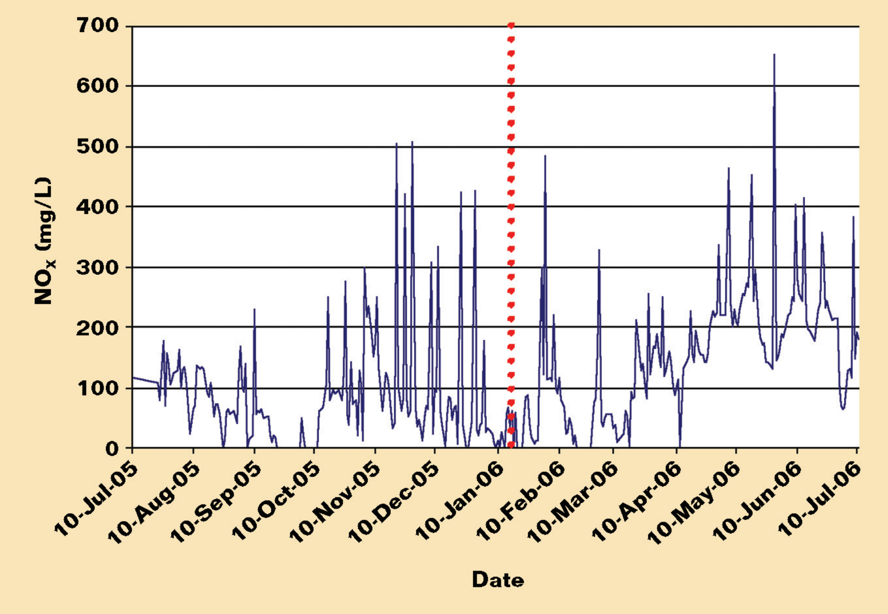
Summary of Southside tank wall thickness readings from 2002 (original thickness) to December 13, 2005.

FIGURE 4



Southside tank wall thickness readings before and after energizing the AP system on January 5, 2006. The lines overlap because no corrosion was detectable between the two surveys on December 13, 2005 and April 5, 2006.

FIGURE 5



July 10, 2005 to July 10, 2006 NO_x log. Note the increase in average daily NO_x levels from March to June 2006. The vertical dash line indicates energization of the AP system on Jan. 5, 2006.

the electrochemical potential of the tank wall from the "active corrosion" zone to the "passive" zone where the corrosion rate is limited.

While the current required to move the potential from the "active corrosion" to the "passive" zone is quite high, once passivity is achieved, the current required to sustain potential is very modest indeed. In fact, <5% of the current required to overcome the active/passive transition may be necessary to sustain passivity.

Basic AP equipment includes cathodes, reference electrodes, and a controlled current source. Some operators install a computer-based remote monitoring system (RMS) to streamline their maintenance requirements.

To ensure that no sparking occurs when the acid level falls below the cathode tips, AP may employ two independent safety systems. An active level sensor ensures that the AP system shuts down when acid levels fall below a preset minimum and a wicking mechanism is used on the cathodes to prevent the direct current (DC) circuit from being broken intermittently. This wick system essentially "wicks" the acid to the cathode and hence retards the speed at which the DC circuit resistance can change (i.e., from a closed to open circuit or vice versa) and thereby eliminates sparking concerns.

The tank is connected to the positive DC output of the controlled current source and the negative output is connected to cathodes suspended from the roof of the tank. A roof-mounted reference electrode is used for feedback potential control of the current source output. Roof-mounted hardware should allow for replacement and maintenance of equipment without taking the tank out of service.

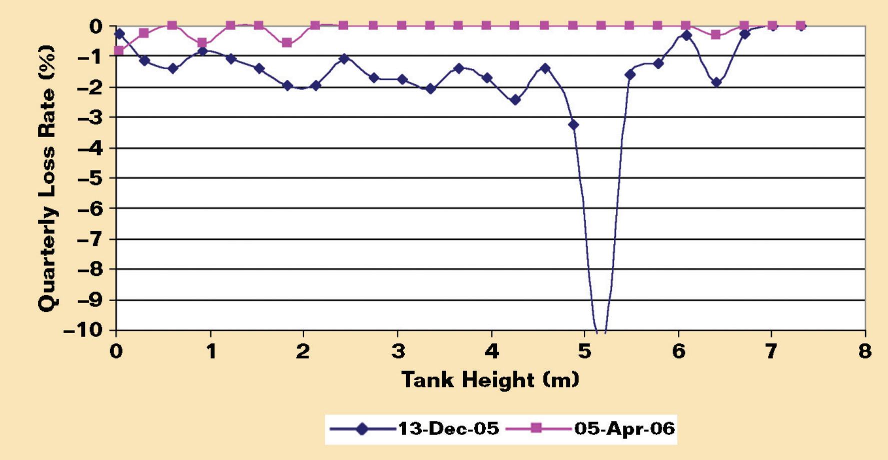
Further discussion of AP theory and hardware are available elsewhere.[2-5]

Installation at Facility

The Southside acid tank located at the Morenci operation in Arizona was constructed of A36 carbon steel and was commissioned in 2002. It is 10.06 m (33 ft) in diameter, 7.32 m (24 ft) high, and has a design maximum acid level of 6.25 m (20.5 ft). The nominal content acid strength is 95%. Plant personnel installed the AP system, which included a computer-based RMS for operating data. The system was energized on January 5, 2006.

The three-tier construction of the wall has plate thicknesses of 11.1 mm (0.4375 in.) at the lowest course and two 9.53-mm (0.375-in.) plates above. As shown in Figure 3, the wall thickness in 2005 in the wet/dry (tidal) zone between the 2.5 m

FIGURE 6



The April 5, 2006 wall thickness readings show that corrosion was halted after AP was energized in January 2006. No further corrosion occurred in the tidal zone (2.0 to 6.0 m level).

(8 ft) and 6.0 m (19.5 ft) levels lost between 2.41 mm (95 mils) and 2.92 mm (115 mils) in the three years since the tank was commissioned. These results represent an alarming average loss of 0.81 to 0.97 mm/y (32 to 38 mpy). The consistent thickness losses year-to-year indicated that the data were reliable and no anomalies were observed.

In Figure 3, the most severe loss occurred in the first year of operation. From tank commissioning in 2002 to the first UT measurement on June 24, 2003, ~1.1 to 1.3 mm (45 to 50 mils) were lost in the wet/dry zone (i.e., 2.5 to 6.0 m level). A high loss rate was also observed between the 0 to 2.5 m (0 to 8 ft) level (i.e., submerged zone) in the June 24, 2003 survey as compared to subsequent years. The very high corrosion rate during this initial period was caused by the new steel having yet to establish a passive layer. As the passive layer developed, corrosion slowed marginally but remained at an unacceptably accelerated rate.

The Anodic Protection System

The energization of the AP system on January 5, 2006 was routine (i.e., no unusual incidents were noted) and, as expected, once the system achieved passivation, only a modest amount of maintenance current was required to sustain the target potential.

The AP system remained effective through the Spring of 2006, at which time another wall thickness survey was conducted. The results in Figure 4 showed that AP had halted the corrosion of this NO_X-contaminated H_2SO_4 storage tank in both the submerged and tidal zones. The plotted data overlap because no significant difference in wall thickness was detected between the readings taken on December 13, 2005 and April 5, 2006.

To ensure that AP was effective in the presence of NO_X contamination, daily NO_X concentration data were collected. Figure 5 shows one year of NO_X data from July 10, 2005 to July 10, 2006. While the NO_X level is seen to increase from March to June 2006, Figure 6 indicated that the AP was effective in mitigating corrosion during that period.

In Figure 3, there was significant corrosion between the August 17, 2005 survey and the December 13, 2005 survey. The nominal NO_X level was fairly low during that initial period, as shown in Figure 5, fluctuating between 50 and 100 mg/L most of the time with some higher level excursions in November and December 2005. In early 2006, the NO_X level started increasing to a higher and sustained level. By March of that year, the NO_X level was 100 to 150 mg/L. As evidenced by the undetectable wall thickness loss in the April 2006 survey, the AP system was still effective at the higher NO_X levels.

These results clearly demonstrated that AP was effective in mitigating corrosion of concentrated H_2SO_4 storage tanks contaminated by NO_X. The benefit to the tidal zone was particularly evident.

The benefit of AP to the tidal zone of acid tanks has long been a topic of discussion and speculation. Although low iron contamination data in AP-protected tanks suggested that corrosion in the tidal zone was also mitigated, no direct proof was available. No definitive direct measurements prior to and after the energization of an AP system had been undertaken. The present data reveal that tidal zone corrosion was, in fact, mitigated. In Figure 6, the April 5, 2006 thickness survey showed no corrosion was detectable in the tidal zone (2.5 to 6.0-m level) after AP was installed. The small amount of corrosion detected in the submerged zone (0 to 2-m level) could be caused by noise and reading errors.

One possible explanation for the tidal zone corrosion mitigation is that when the acid level was high, the AP system created a passive layer on the wall surface; and as acid levels fell, this passive layer did not immediately dissipate. With this "remnant" protective layer intact, the wall remained shielded during this critical period. The wall was most vulnerable to the very corrosive condition that could occur when the acid-wetted wall was diluted by small amounts of moisture in the air. While the passive layer eventually dissipated as the wall dried, the "remnant" passive layer eliminated the peril created by the wetted condition.

Conclusions

The AP system was effective in mitigating corrosion of an NO_X-contaminated H_2SO_4 tank, in both the submerged zone and the tidal (wet/dry) wall zone.

One possible explanation for the system being effective in the tidal zone was that the passive layer established by the AP did not dissipate immediately when acid levels receded. Rather, this layer remained intact and protected the tank wall during the critical period when the acid was most aggressive. Without further AP current, the passive layer will dissipate as the tidal zone dries but conditions at that point are no longer of concern.

The equation presented by Andersen, et al.,[1] which was based on laboratory results of the corrosion rate of steel as a function of NO_X concentration in concentrated H_2SO_4 at 50°C, is a good first approximation for actual tank wall corrosion. Some allowance needs to be made for temperature differences between laboratory and field conditions.

Acknowledgments

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