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Benefits of Anodic Protection and Remote Monitoring on Sulphuric Acid Tanks Contaminated by NOX

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ABSTRACT

The corrosion mitigation benefit of Anotection® anodic protection (AP) systems in sulphuric acid tanks is well established. AP prevents tank wall wastage, iron contamination of acid and hydrogen grooving of tank walls. Yet, the efficacy of AP at the wet/dry (tidal) zone of tank walls has been in some doubt; and no published information is available on its effectiveness in concentrated sulphuric acid contaminated by NOX (nitrogen oxides). Laboratory tests reported that the corrosion rate of carbon steel increases by ten (10) times when exposed to NOX contaminated acid (at approx. 900 ppm) as compared to NOX-free acid. This paper presents wall thickness readings of a sulphuric acid tank contaminated by NOX at levels that would accelerate corrosion. Corrosion rates before and after the installation of an AP system are presented. The results indicate that AP is effective in mitigating corrosion of NOX contaminated sulphuric acid in both the submerged and tidal zones of the tank. Some recent advances made in the area of remote monitoring, including Internet based systems, are also discussed.

INTRODUCTION

Sulphuric acid is a by-product of the smelting operation of sulphide ores. The use of high temperature burners may produce nitrate and nitrite impurities (NOX) in the acid that cause a number of undesirable effects such as contamination, pink/purple colouring 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 on storage tanks containing NOX contaminated sulphuric acid.

The by-product 93-95% sulphuric acid from a smelter operation in south-western USA is stored at their own local facilities and at a number of other sites in the vicinity. Maintenance personnel at all the sites noted an alarming increase in the corrosion rate of their storage tanks after they started storing the smelter acid. Ultrasonic thickness measurements in 2003 and 2004 indicated that the average thickness loss was in the range of 5-8% per annum. In addition, one area in the wet/dry (tidal zone) experienced over 30% loss per annum. The original wall thickness of these tanks varied from 7.5 mm (0.295") to 15.9 mm (0.625").

This corrosion rate is certainly higher than what would be expected from 93-95% acid even in the hot summers of south-western United States. The plant identified the cause as nitrogen oxide (NOX) accelerated corrosion and collected daily NOX concentration data. The data from May 3, 2004 to June 12, 2005 (406 days) were used for this analysis.

Andersen et al[1] reported the corrosion rate of steel in concentrated reagent grade sulphuric acid, R (mils per year), as a function of NO_3^- concentration as:

$$R\ (\text{mpy}) = 0.28[\ NO_3^-\ ]_{\text{ppm}} + 17.6 \qquad \text{........................ (1)}$$

Equation (1) is valid from 0 to approximately 1000 ppm of NO_3^- in sulphuric acid at 50°C.

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

Field thickness data on the storage tank was recorded on May 3, 2004 and August 17, 2005. The thickness loss is presented in Figure 1. To compensate for the additional 66 days over which this degradation occurred, an average daily loss was calculated and multiplied by 406 days for comparison purposes. The average wall loss over this period was 18 mils (0.457 mm) or 16 mpy (0.406 mm/yr). The discrepancy between the calculated 40 mpy rate and the normalized actual rate of 16 mpy may be attributed to the 50 °C laboratory data and the ambient temperature field data. Nevertheless, the corrosion rates are in the right order of magnitude and Equation (1) may be considered as a good first approximation of actual corrosion rate. It should be emphasized, however, that Equation (1) was derived specifically for NO_3^- and acid can contain other nitrogen oxide species.

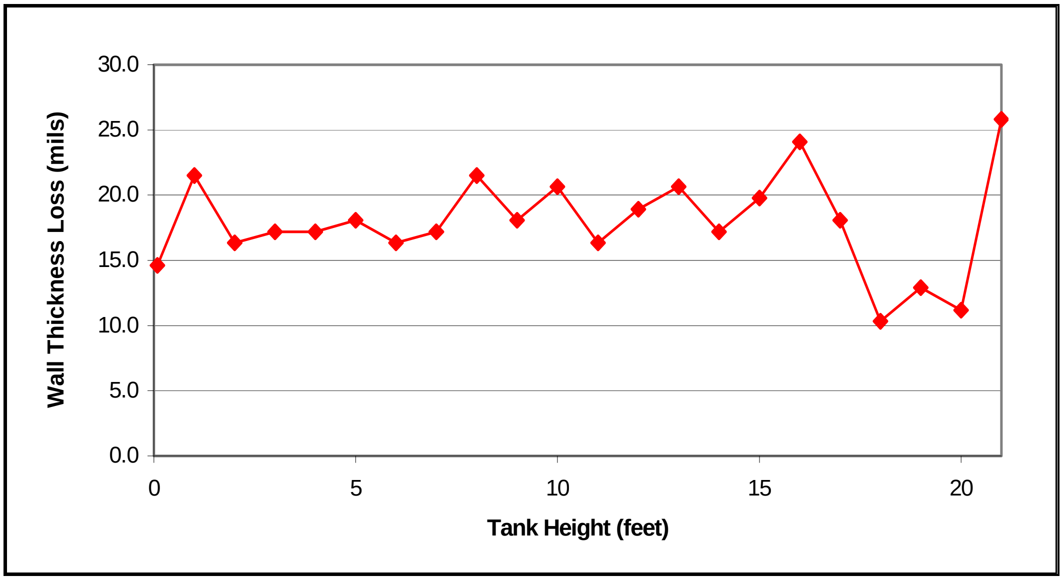

Figure 1. Average wall thickness loss over a period of 406 days derived from ultrasonic measurements taken on May 3, 2004 and August 17, 2005.

ANODIC PROTECTION

Since the 1970's, Corrosion Service has designed and supplied **Anotection®** anodic protection (AP) systems for approximately 100 sulphuric acid storage tanks globally. In all cases, this proven and well-established[2] technology was employed to both mitigate corrosion and control iron contamination.[3,4,5] However, none of the tanks suffered from NOX accelerated corrosion because circumstances allowed the tank owners to keep NOX levels at a minimum. One plant in the province of Quebec, Canada for example, uses AP in tanks with less than 10 ppm of NOX^-.

The application of AP has been very successful in mitigating corrosion. This is accomplished by moving the electrochemical potential of the tank wall from the "Active Corrosion" zone to the "Passive" zone where corrosion rate is limited. See Figure 2.

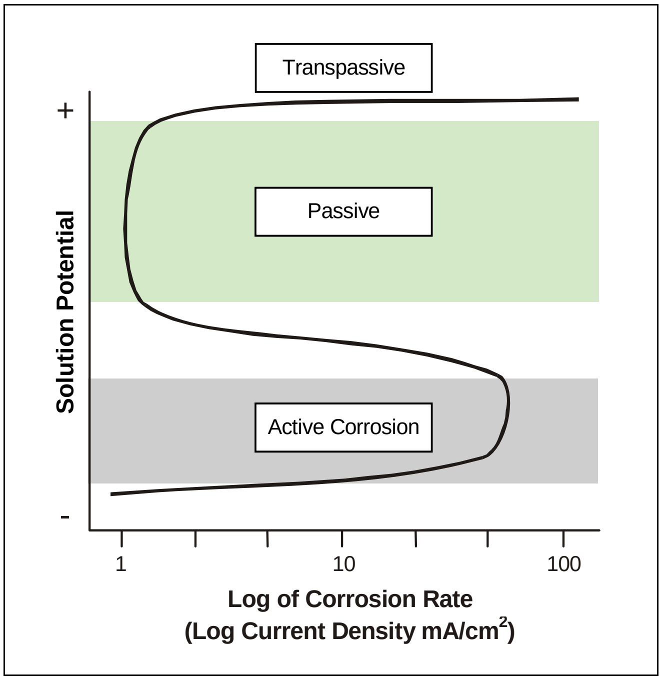

Figure 2. Polarization curve showing active/passive behaviour with corrosion zones identified.

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, less than 5% of the current required to make the active/passive transition may only be necessary.

Basic AP equipment includes cathodes, reference electrodes and a controlled current source. Some operators would install a Remote Monitoring System to streamline their maintenance requirements.

To ensure that no sparking occurs when the acid level falls below the cathode tips, the **Anotection® system** employs 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 patented 'passive wick' mechanism used on the cathodes to prevent the DC circuit from being broken intermittently. This passive 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 allows for replacement and maintenance of equipment without taking the tank out of service.

Further discussion on anodic protection theory and hardware are available elsewhere.[2-5]

Installation of Anodic Protection System

The plant initially tried to keep NOX level to below 100 ppm to ensure an acceptable corrosion rate. Unfortunately, this low level of NOX was not sustainable at their facilities without expensive equipment modifications and upgrades. Eventually, the plant decided to try anodic protection for one tank to test its effectiveness in NOX contaminated acid.

The acid tank being protected by anodic protection is constructed of A36 carbon steel and was commissioned in 2002. It is 33 feet (10.06 m) in diameter, 24 feet (7.32 m) high, and has a design maximum acid level of 20.5 feet (6.25 m). The nominal content acid strength is 95%.

The AP system used for this tank, which included a Corrosion Service Remote Monitoring System (RMS), was installed by plant personnel and energized by Corrosion Service on January 5, 2006.

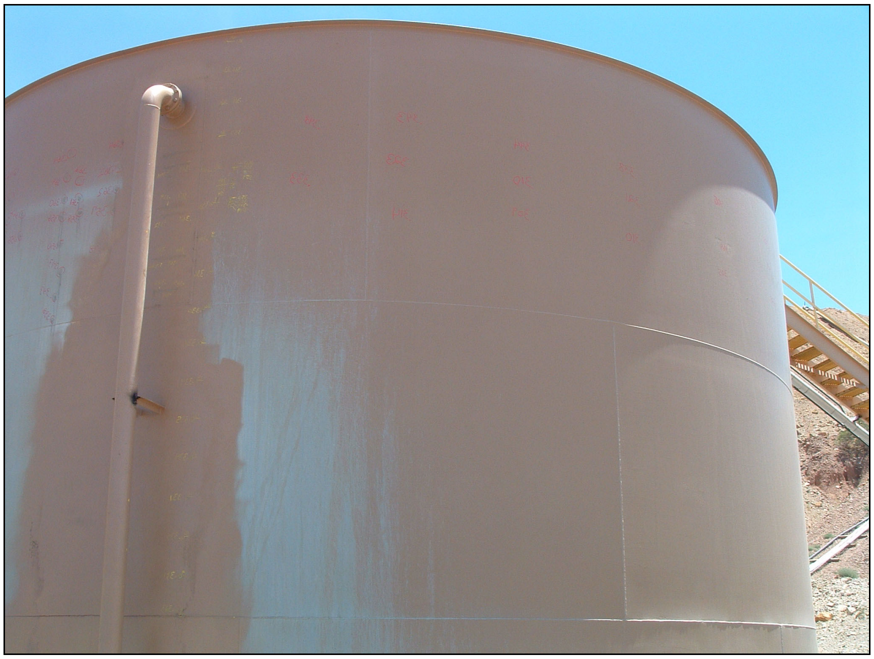

Photo 1. Sulphuric acid tank containing NOX contaminated acid.
Ultrasonic measurements revealed accelerated corrosion.

The three-tier construction of the wall has plate thicknesses of 0.4375 inch (1.11 cm) at the lowest course and two 0.375 inch (0.953 cm) plates above. As shown in Figure 3, the wall thickness in 2005 in the wet/dry (tidal) zone between the 8 foot (2.44 m) and 18 foot (5.49 m) levels lost between 95 mils (2.41 mm) and 115 mils (2.92 mm) in the 3 years since the tank was commissioned.

These results represent an alarming average loss of 32-38 mpy (0.81-0.97 mm/yr). The consistent thickness losses year-to-year indicate that the data is 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, approximately 45 to 50 mils (1.14-1.27 mm) were lost in the wet/dry zone (i.e. 8 foot to 18 foot level). A high loss rate is also observed between the 0 to 8 foot (0 to 2.44 m) level (i.e. submerged zone) in the 24/6/2003 survey as compared to subsequent years. The very high corrosion rate during this initial period may be due to the new steel having yet to establish a passive layer. As the passive layer developed, corrosion slowed marginally but remained at an unacceptable accelerated rate.

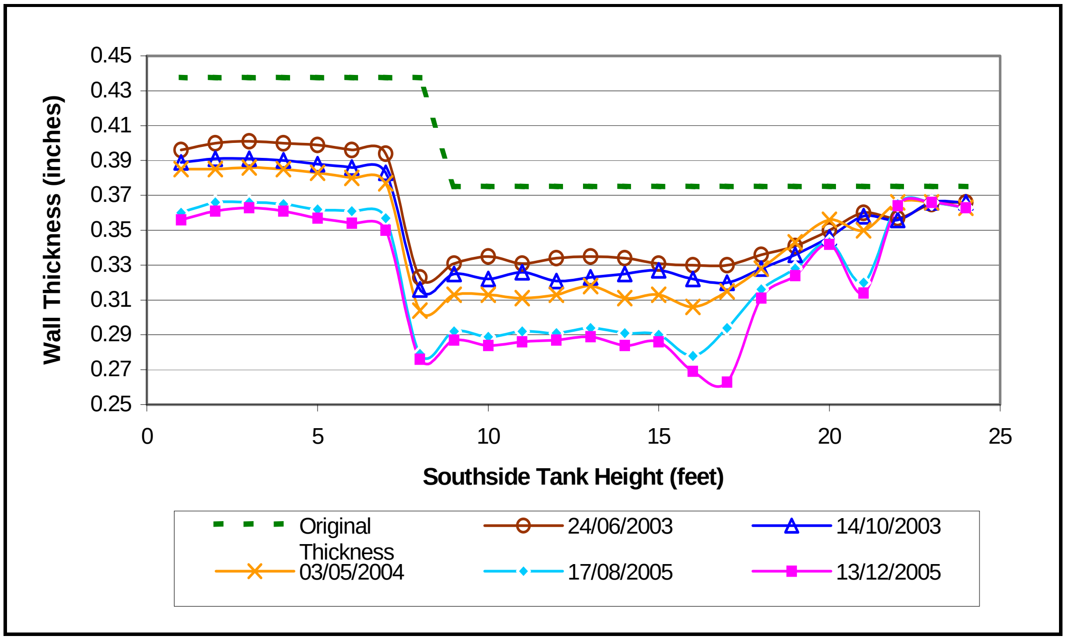

Figure 3. Summary of tank wall thickness readings from 2002 (original thickness) to Dec. 13/05.

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 potential.

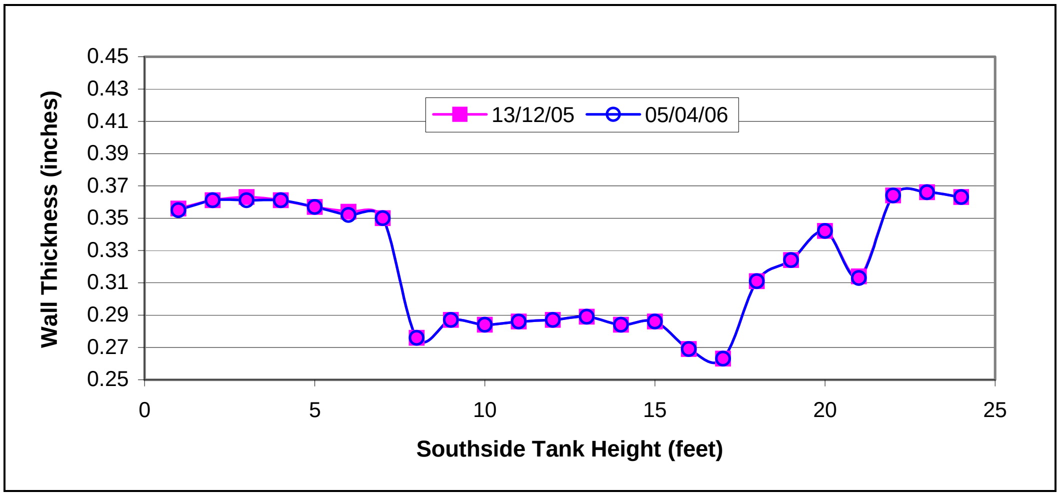

Figure 4. Tank wall thickness readings before and after energizing the anodic protection (AP) system on January 5, 2006. The lines overlap because no corrosion was detectable between the 2 surveys on December 13, 2005 and April 5, 2006.

The AP system remained effective through the Spring of 2006, at which time another wall thickness survey was conducted. The results in Figure 4 show that AP has halted the corrosion of this NOX contaminated sulphuric acid storage tank (including the tidal zone). The plotted data overlap because no significant difference in wall thickness was detected between the readings taken on December 13, 2005 and on April 5, 2006.

To ensure that AP was in fact effective in the presence of NOX contamination, daily NOX concentration data was collected. In Figure 5, one year of NOX data from July 10, 2005 to July 10, 2006 are presented. While the NOX level is seen to increase from March to June 2006, Figure 4 indicates that the AP was effective in mitigating corrosion during the same period.

Significant corrosion between the August 17, 2005 survey and the December 13, 2005 survey is depicted in Figure 3. The nominal NOX level was fairly low during that period (Figure 5), fluctuating between 50 and 100 ppm most of the time, with some high level excursions. In 2006, the NOX level started increasing to a higher and sustained level and by March of that year, the NOX level was 100-150 ppm. As evidenced by the undetectable wall thickness loss in the April 2006 survey, the AP system was still effective.

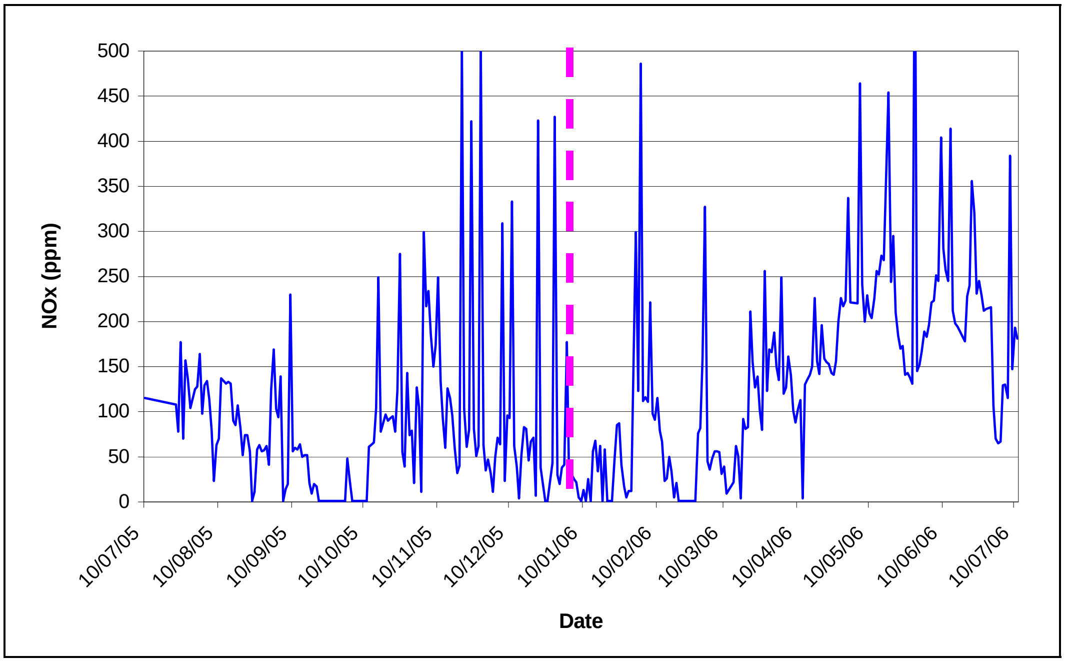

Figure 5. July 10/05 to July 10/06 NOX log. Note the increase in average daily NOX levels from March to June 2006. The vertical dash line indicates energization of the AP system on Jan. 5/06.

This result clearly demonstrates that AP is effective in mitigating corrosion of concentrated sulphuric acid storage tanks contaminated by NOX. The benefit to the tidal zone is 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 suggests that corrosion in the tidal zone is also mitigated, no direct proof was available. No definitive direct measurement prior to and after the energization of an AP system had been undertaken. This trial reveals that tidal zone corrosion is in fact mitigated. In Figure 6, the May 4, 2006 thickness survey should no corrosion was detectable in the tidal zone (8' to 18' level) after AP was installed. Small amount of corrosion detected in the submerged zone could be due to noise and reading errors.

One explanation for the tidal zone corrosion mitigation is that when the acid level is high, the AP system creates a passive layer on the wall surface; and as acid levels fall, this passive layer does not immediately dissipate. With this “remnant” protective layer intact, the wall remains shielded during the critical period. The wall is most vulnerable to the very corrosive condition that can occur when the acid wetted wall is diluted by small amounts of moisture in the air. While the passive layer eventually dissipates as the wall dries, the “remnant” passive layer eliminates the peril created by the wetted condition.

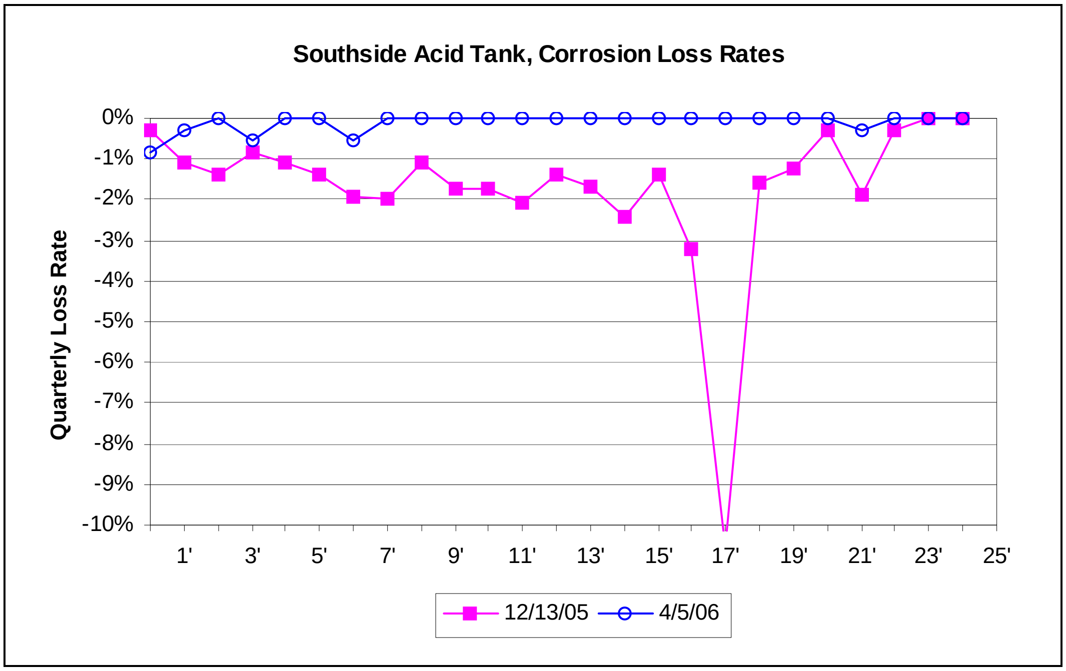

Figure 6. The April 5/06 wall thickness readings show that corrosion was halted after AP was energized in January 2006. No further corrosion in the tidal zone (8' to 18' level).

Remote Monitoring System

Remote monitoring technology has improved tremendously since our last presentation on the subject at Sulphur 98.[3] A Corrosion Service Remote Monitoring System (RMS) was installed at the customer's facility for the AP system. This proprietary RMS software was installed on a standard PC at the customer's plant and transmitted reference potential, current source voltage and current data via an RS-232 or RS-485 network.

Tank operators have the option to review operating parameters locally, have Corrosion Service monitor them remotely, or have the RMS store and package the data into a weekly email which is then sent to our office for review. This software was developed with the capacity for thousands of operating parameters and has the option of telephone-based or internet-based communication.

Shifting plant priorities and personnel changes can result in an unattended AP system. Remote monitoring ensures that the AP system is operating and that the full benefit of this investment is realized. More importantly, tank integrity is preserved and hence and the environment not compromised by leakage.

CONCLUSIONS

An **Anotection®** anodic protection (AP) system was effective in mitigating corrosion of an NOX contaminated sulphuric acid 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 is that the passive layer established by AP does not dissipate immediately when the acid level recedes. Rather, this layer remains intact and protects the tank wall during the critical period when the acid is 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 al1, which was based on laboratory results of the corrosion rate of steel as a function of NOX concentration in concentrated sulphuric acid 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.

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