A Case Study on Mixed Metal Oxide (MMO) Anode Failure of an Above Ground Storage Tank Bottom Plate

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Abstract
A case study on the failure of a cathodic protection (CP) system and consequent corrosion on the external surface of an above ground storage tank bottom plate is reported in this article. This tank was set on asphalt pad foundation. Also, it includes a none-metallic membrane one meter beneath the bottom plate, and a ring wall constructed around the tank perimeter. The space between the ring wall and bottom plate was filled with washed sand. An impressed current cathodic protection system was designed to prevent corrosion on ground contacting surface of the tank bottom. The Mixed Metal Oxide (MMO) anode system had been located in the fill area between the tank bottom and the membrane. After 8 years of service, a severe leakage on tank bottom was noticed and it has been decided to lift up the tank for close visual inspection. Visual inspection of anode system showed the failure of MMO anode wire loop. Further investigations by Scanning Electron Microscope (SEM) revealed that the MMO film on the titanium substrate is afflicted with localized loss because of hot spots in high current density or break-down voltage, which finally lead to interruption. Therefore, the CP system design calculations are compared to filed experience and preventive measures suggested.

Keywords
Above ground storage tank; cathodic protection; MMO; Wire anode; Current density;

Introduction

The cathodic protection (CP) system is used to protect the underground piping and storage tank bottom plate when those structures are exposed to soil. In order to minimize the environmental side effect in case of a leakage, a none-metallic membrane is used as secondary containment. Thus, preventing the cathodic shielding, the anodes of CP system are installed between the bottom plate and the none-metallic membrane in order to ensure the effectiveness of CP system. Since the anodes are not accessible after installation, most stringent precautions shall be taken in account to design and calculate the system based on the standards and best practices [1], [2]. In addition, the quality control of the anodes and cables shall be performed in advance in order to ensure the use of qualified products in the system since revamping requires an extensive costly and time consuming job [3]. Nowadays, the mixed metal oxide (MMO) anodes are used extensively with regards to their prolonged design life and low weight. Although the excellent stability of MMO coated titanium anodes are verified over almost 30 years of experience [4], but still there is CP system design without understanding the characteristics, limitations and evaluation method of such anodes; that the most important part is with the confusion regarding the breaking potential [5].

The main concern of MMO titanium anode is the breakdown of oxide film when it is operated at high DC voltage. Titanium possesses a wide potential window for the passive condition up to 8.35 volts with respect to copper sulfate reference electrode (CSE) [6]. However, when the voltage exceeds the upper limit of anodic potential, intensive oxygen evolution of the titanium surface occurs, resulting in passive film break-down and dissolution (pitting corrosion) of titanium [8]. The MMO film are mainly a mixture of titanium oxide (TiO_{2-x}), tantalum oxide (Ta_2O_5) in iridium oxide (IrO_{2-x}) or ruthenium oxide (RuO_{2-x}). In CP, MMO anodes provide a catalytic substrate to electrolyze water. It reduces the hydrogen, oxygen or chlorine and produces relevant gases. Produced gasses increases pressure in locally confined voids in soil (bubbling in water) and consequent turbulent movements can cause erosion [9].

The most important parameter considering design stage of a CP system, is the variable resistance during service period. Regarding the applied voltage limitation on the MMO anodes, the increment of resistance or local shielding, the protective current becomes inconspicuous and experience showed that the existing analytic methods for calculating this parameter are not always as accurate as desired [10], it is common to obtain data from field case studies. Considering lack of performance data, discrepancies between routine CP design calculations and field results are discussed in this paper; also, the failure root cause of the pertinent MMO anode are studied.

Case Problem

On March 2014, a severe leak was noticed on the north side of the Mono Ethylene Glycol storage tank bottom plate at a gas plant in Asaluyeh, Iran. In this regard, necessary precautions followed to enable field staff for close visual inspections.

The intake Mono Ethylene Glycol (MEG) content was contaminated with sour water, to be then stripped in next processes. The severe acidic corrosion on the carbon steel shell of the tank lead to rehabilitation. Hence, the tank with the diameter of 3 meter was lift up and the opportunity found to inspect the CP system directly. After close visual inspection, samples of MMO anode was sent to laboratory for microscopic investigations.

The CP system was supposed to perform 25 years of successful tank bottom protection, but in reality, the leakage due to corrosion found after almost 8 years. Based on previous survey results, the plate-to-soil potential dropped drastically below the acceptance criteria, which was -850 mv versus copper/copper-sulfate reference electrode (CSE). The CP system included MMO wire loop anode which was installed one meter beneath the tank bottom plate, and

above the High-Density Poly-Ethylene (HDPE) pad. The wire anodes include copper cored titanium wire with a MMO coating. A ring wall had been installed around the tank perimeter and filled with washed sand. A layer of sand bitumen mix with the thickness of 10 cm casted to cover the washed sand.

According to tank bottom inspection, corroded regions on the external surface (soil side) of bottom plate are reported as follow:

1) The first zone of corrosion was near the tank perimeter toward the center up to almost 40 cm, that severe corrosion due to water ingress or condensation occurred. The reason should be the gap between ring wall and bottom plate which was not sealed. Consequently, this gap promotes the water ingress beneath the tank in the radial distance of 40 cm (the resistance to more absorption of water to central areas is restricted by bitumen mixture).
2) The second zone of corrosion observed by evidence of corrosion products and metal loss, where the bitumen mix (asphalt) was no in full contact with tank bottom (almost 70% of tank bottom area). These gaps are caused by inevitable uneven surface of asphalt. The other cause for lack of full contact may be because of expansion in tank bottom during welding, hot weather in summer and high temperature of MEG input.

However, the developed gaps are most detrimental when filled by moisture and air. The air has a low conductance which shields the protective current toward tank bottom in that specific area. It allows the available moisture to react with steel and form ferro-hydroxides. Here the stimulating parameter is that the shielded area tends to reach the electronegative potential of neighbor sites (which pick up protection current), so that the corrosion reaction lets the iron ion to leave surface and holding the negative charges. The reaction continues and a localized corrosion leads to content leakage. It worth to note that no sign of corrosion was found on area, where bottom plate was in full contact with asphalt.

Table 1: Potential survey history

No.	Date	Bottom Plate Potential (mV vs. CSE)	T/R Voltage (V)	Protective Current
1	16-Jun-2007	-924	7.2	Average of 100 mA
2	18-Mar-2008	-924	7.1	
3	08-Jan-2009	-860	7.4	
4	20-May-2009	-245	7.8	
5	15-Nov-2009	-242	7.7	
6	18-Mar-2010	-248	7.8	
7	05-Nov-2010	-300	8	
8	02-Jan-2011	-300	8	
9	25-Mar-2011	-420	7.9	
10	18-Jun-2011	-285	8.3	
11	07-Oct-2011	-290	8.4	
12	13-Jan-2012	-351	8.7	
13	12-May-2012	-283	8.9	
14	16-Nov-2012	-404	9.4	
15	28-Feb-2013	-389	9.4	
16	17-Dec-2013	-250	9.2	
17	01-Feb-2014	-305	9.6	

Further excavation displayed the MMO anode mesh. Two anode loops, one in north side and the other in south side was plowed on sweet soil. The north side anode had a length of 45 cm whereas the south side anode was 80 cm in length, which based on design documents both

anodes was supposed to meet 80 cm of length. On reference electrode was implanted near the north side anode loop. Severe destruction observed on the MMO anode. In some cases, a hollow tube of titanium anode was found that shows dissolution of copper core wire. There were also locations of MMO film lost and deep localized corrosion (pitting) on the titanium surface so that in north side anode loop, deep-root pitting terminated the anode wire connection.

Materials and Methods

With reference to inspection data, the tank bottom was made of carbon steel plate of ASTM A283 grade C, with the thickness of 10mm, and fillet welded by E7018-G electrodes. The CP system design was based on impressed current technique which included a wire mesh of MMO anode, which in fact the core copper lead was covered with titanium tube, and then a MMO film deposited as a final layer. The CP survey data during the 8 years of service are listed in table I, and the protection trend is depicted in fig. 1.

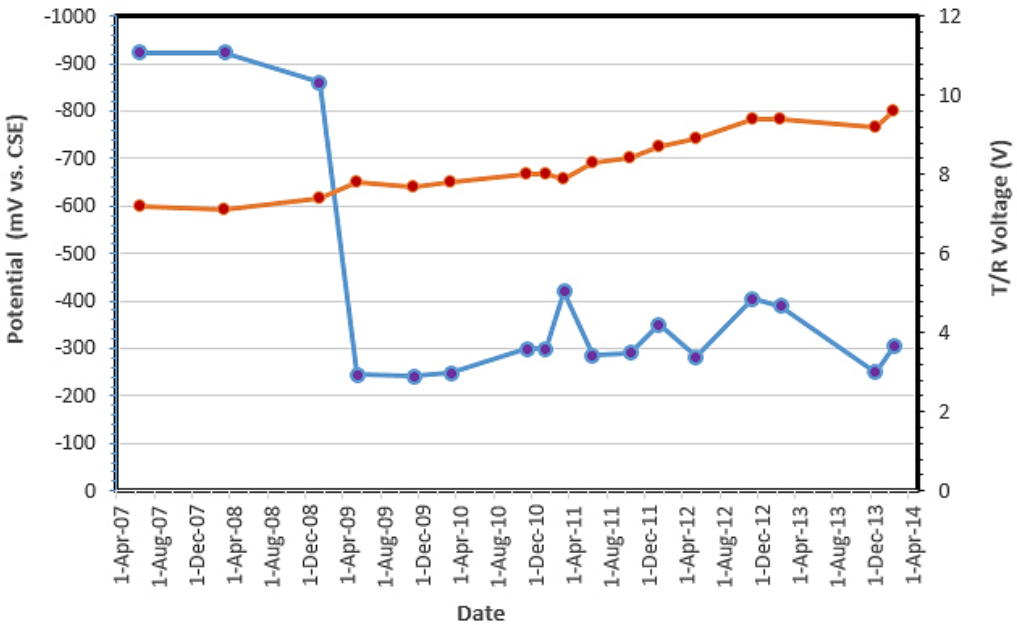

Figure 1: The T/R voltage and CP potential diagram of MEG tank bottom plate, from June 2007 to February 2014.

Although lack of protection with respect to standard criteria [4] was monitored, but the plant's work load and related costs, did not allowed for rehabilitation. Anyhow, designers consider that CP system of tank bottoms are not capable of easy and accessible repair. It becomes almost impossible where there is non-metallic membranes laid under the tank.

Two samples of failed anode selected and investigated by Scanning Electron Microscope (SEM) model Cambridge-360. The first sample sliced from the intact part of MMO wire, whereas the second sample chose from destroyed section. The resulted micrographs are shown in fig. 2 and fig. 3.

Discussion

SEM investigations are shown in Figure 2 and 3. The first one represents normal MMO wire anode with the MMO film thickness of about 5 um. In fig. 3 the anode wire miss the MMO film and depicts severe pitting corrosion on tube surface. The overall condition of anode

reveals that the local current discharge due to cathodic shielding is impressed on anode wire; which leads to higher current densities within the allowed potential boundary.
In this case the impressed current MMO anodes are implemented without considering any backfill. Introducing coke backfill to the dimensionally stable anodes (DSA) of MMO may prevent this phenomena by providing higher surface for cathodic reaction. High current density can cause local hot spots and even reduction (consumption) of mixed metal oxides. The superior advantage of these anodes is their chemical stability in low pH, even lower than1.

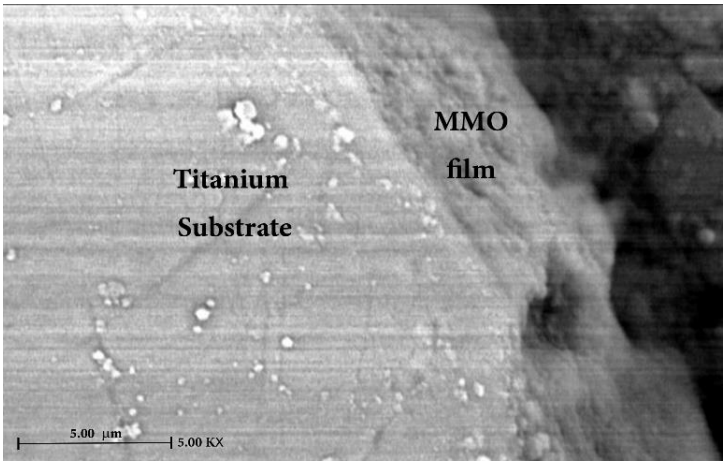

Figure 2: SEM micrograph of MMO anode wire, 5000 X.

Acidic environments create the possibility of higher current density discharge of MMO anode, which helps the anode consumption rate. So, in overall there was hot spots of high current density which tends to lower the potential difference between anode and cathode adjacent to shielded area which increased resistance broadens this potential difference. In low potential hot spots, the MMO film is consumed in faster rate, while in high potential spots the MMO film can confront breakdown potential.
Low voltage breakdown of MMO anodes in contrary to other impressed current anodes are reported to be 12 V according to [2]. However, in international standards this number is reported to be 8 V [7]. With reference to reported breakdown potentials, and considering the Trans Rectifier (T/R) potentials, that did not exceed 10 V, the system performance was not reported as abnormal by inspection division.

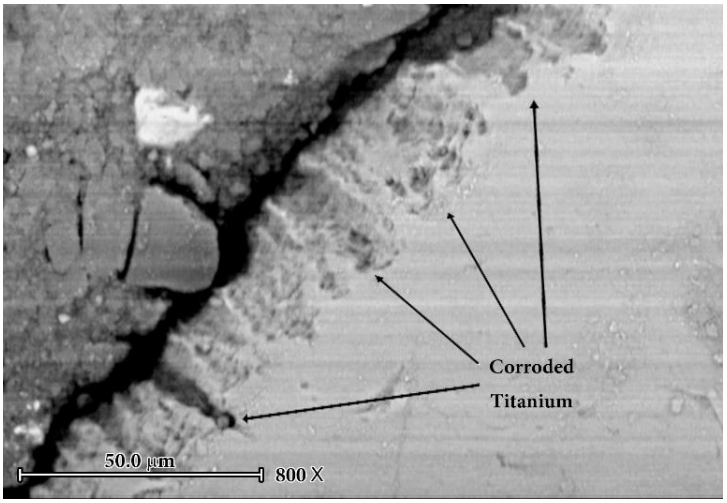

Figure 3: SEM micrograph of lost MMO film and corroded titanium, 800 X.

According to tank installation specification, a 10-cm layer of asphalt (mixed bitumen) was applied under the tank bottom. As mentioned in previous section, the tank bottom attachment to beneath asphalt was locally and caused cathodic shielding. Moreover, considering the asphalt morphology, microscopic shielding can also appear due to bigger mesh versus washed soil. Taking this to account, the surface contact percentage can reduce to lower percentages than reported 70% obtained from visual inspections. In addition, asphalt cracking can increase this number to higher values (air gap among asphalt cracks).
As figure 4 depicts, and with regards to CP system calculation sheets, and anode depth of 50 cm, the protection current coverage length is calculated as follow:

$$L = 2d \tan \theta \qquad (1)$$

where: d = 0.5 m and $\theta = 60^o$ then L = 1.73 m

The tank bottom diameter equals 3 m, which the total surface area would be: $\pi \times (1.5)^2 = 7.07\ m^2$. So, the anode wire length is calculated by dividing total surface area to coverage length. These simple calculations show that 4 meters of anode wire can cover all the tank bottom surface. In this case one 0.8 m anode wire is placed at northern side, and one 0.8 m at southern side. So, remained 2.4 m anode wire is implemented under tank bottom diameter crossing center.

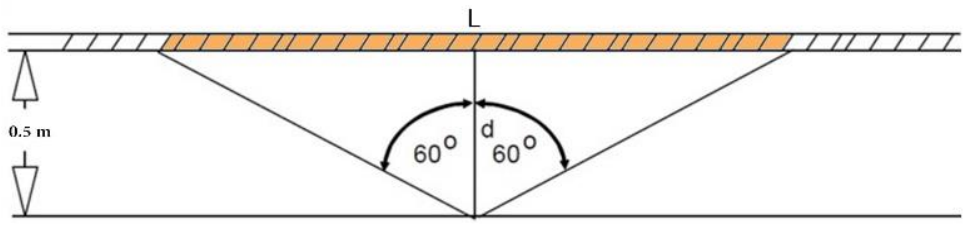

Figure 4: Wire anode coverage zone

All in all, by comparing the calculations of designer engineer and obtained field experience, one can understand that the only missed parameter is a corrective coefficient. This coefficient shall be considered in calculations where an asphalt layer will be applied beneath tank bottom. This coefficient will depend on the anode implementation lay out (spiral, parallel and etc.) bitumen type, mix ratio and mesh. This coefficient is not yet defined in reference literatures and can be obtained from field experience data gathering or laboratory testing. In this case, in order to prevent hot spots, a coefficient factor of 50% for a new CP system considered so that the required MMO anode wire length is doubled.

Conclusion

The asphalt layer beneath the above ground tanks are compulsory by some regional codes and regulations. This layer has a primitive protection on the vast tank bottoms during construction until the operation. On the other hand, this layer decreases the surface attachment to tank bottom and shields the protective current locally.
In addition, lack of MMO anode coke backfill jeopardizes the current distribution and can increases current density so that local high currents cause faster deterioration hot spots.
In conclusion, regarding above conditions the authors suggest routine internal inspection of tank bottoms in shorter periods (e.g. every two years) or consideration of an attachment coefficient (or coverage efficiency) by the designer engineer, who has the most significant responsibility in consideration of all the cost-effective parameters.

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