



CORROSION BY CONCENTRATED SULFURIC ACID IN
CARBON STEEL PIPES AND TANKS – STATE OF THE ART
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Abstract

PETROBRAS, allied to the policy of reduction of emission of pollutants, has been adjusting the processes of the new refineries to obtain products with lower sulfur content. Thus, the sulfur dioxide, extracted from the process gases of a new refinery to be built in the Northeast, will be used to produce sulfuric acid with concentration between (94-96) %. This acid will be stored in carbon steel tanks and transported through a buried 8-km carbon steel pipe from the refinery to a pier, where it will be loaded onto ships and sent to the consumer markets. Therefore, the corrosion resistance of carbon steel by concentrated acid will become a great concern for the mentioned storage and transportation. When the carbon steel comes into contact with concentrated sulfuric acid, there is an immediate acid attack with the formation of hydrogen gas and ferrous ions which, in turn, forms a protective layer of FeSO_4 on the metallic surface. The durability of the tanks and pipes made of carbon steel will depend on the preservation of this protective layer. This work presents a review of the carbon steel corrosion in concentrated sulfuric acid and discusses the preventive methods against this corrosion, including anodic protection.

1. Introduction

The need of reducing the amount of gas emission into the environment is becoming a worldwide concern. Several industrial segments have been studying the viability of combining the reduction of environmental pollution with profit gains. In this context, the petrochemical industry has been emphasizing the re-use of the sulfur compound contained gases coming from the petroleum extraction and refining processes by converting these gases to concentrated sulfuric acid.

PETROBRAS, as a known leader in environment protection issues, is planning to install a concentrated sulfuric acid production plant in the new refinery which will be soon constructed in the Brazilian northeast region. The production of this acid will be done using as a raw material the gases generated from the oil refinery process which are rich in sulfur and in nitrogen compounds. The nitrogen compounds (NO_x and NH_3) will be converted into gaseous nitrogen which, being nontoxic, will be released to the atmosphere and the sulfur compounds (mainly SO_2) will be converted into concentrated sulfuric acid.

However, one of the great problems faced in the sulfuric acid production is its storage and transportation. This acid is very aggressive and attacks the metallic materials used for the construction of storage tanks and pipes. Many types of metallic materials can be used for this purpose, but the most used are carbon steel and austenitic stainless steel. Each of these materials presents different behaviors in concentrated sulfuric acid. Table 1 shows the corrosion rates of these two metals in concentrated sulfuric acid.

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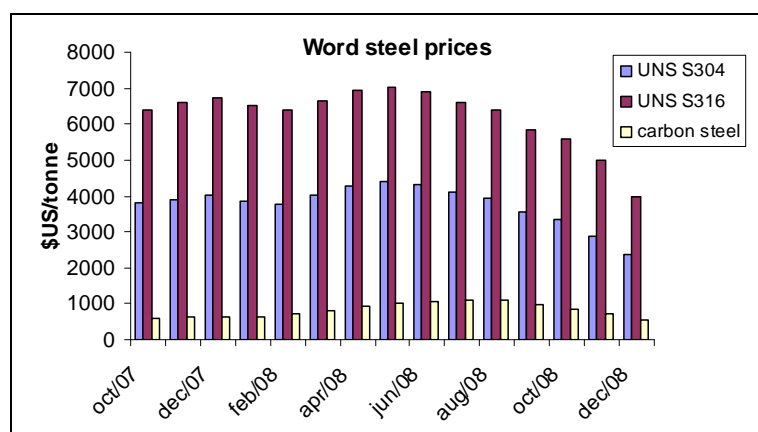
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Table 1 - Corrosion rates (mm/year) of carbon steel and UNS S304 and S316 austenitic stainless in H₂SO₄ (API 581, 2008)

| Carbon steel (33 °C e 2.0 m/s de flow) | | Austenitic stainless steel (30 °C e 2.1 m/s de flow) | | |
|--|--|--|--|--|
| 93.5 % (H ₂ SO ₄) | 98 % (H ₂ SO ₄) | UNS | 92.5 % (H ₂ SO ₄) | 98 % (H ₂ SO ₄) |
| 1.91 | 1.02 | S304 | 1.52 | 0.38 |
| | | S316 | 0.76 | 0.38 |

In Table 1, it can be observed that the carbon steel shows higher corrosion rates than the UNS S304 and S316 austenitic stainless steels. Despite this fact, many industries prefer using carbon steel due to its low cost. Figure 1 shows the values in \$US per ton of metal. It can be seen that the difference of price between the carbon steel and the UNS S304 and S316 austenitic stainless steels is very high, justifying the above mentioned choice.

**Figure 1** - Price in \$US/ton in 2007 and 2008 for carbon steel and UNS S304 and S316 austenitic stainless steels (www.meps.co.uk/world-price.htm, access in 04/03/2009)

Thus, aiming to adopt the necessary preventive measures in order to extend the maximum useful service life of carbon steel storage tanks and pipes, PETROBRAS decided to better understand the corrosion of carbon steel in concentrated sulfuric acid. For this purpose, a wide bibliographical research was done. The goal of this work is to describe the mechanisms of the carbon steel corrosion in concentrated sulfuric acid and to discuss the preventive methods against this corrosion, including anodic protection.

2. Corrosion of carbon steel in sulfuric acid

When the carbon steel enters in contact with concentrated sulfuric acid, there is an immediate attack with the formation of hydrogen gas and ferrous ions, which, in turn, forms a protective layer of FeSO₄ on the metallic surface, as shown in reaction 1.



This protective layer prevents the metal from a new attack by the concentrated sulfuric acid. Therefore, the durability of tanks and pipes made of carbon steel will depend on the preservation of the FeSO₄ layer.

It is well known that, when the corrosion of a metal is accompanied by the formation of a protective layer of corrosion products, the corrosion rate is determined by one of the following stages: the diffusion of the oxidant (in this case the sulfuric acid) to the metal surface through the corrosion product layer (FeSO₄ in the case of carbon steel); the corrosion reaction rate and the diffusion rate of the corrosion products from the metal surface toward the bulk solution. The slowest step will determine the corrosion rate. Additionally, any factor that causes acceleration of these stages will result in increasing the corrosion rate. In the case of carbon steel in sulfuric acid, the most important factors that cause the increase of the corrosion rate are:

- **FeSO₄ solubility in acid** - as shown in the graph of Figure 2, with the exception of sulfuric acid with concentration between (70-85) %, the greater the acid concentration, the greater the corrosion rate of carbon steel;

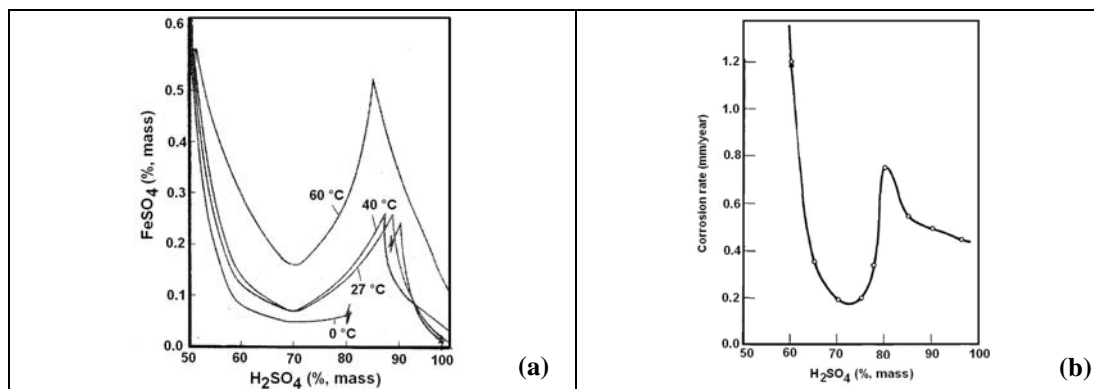


Figure 2 - (a) solubility of FeSO_4 in concentrated H_2SO_4 (DEAN; GRAB, 1985), (b) corrosion rate of carbon steel as a function of H_2SO_4 concentration, at 20 °C (HINES; WILLIAMSON, 1964)⁶

- **temperature** - the corrosion rate rises with the increase of temperature due to the increase in the solubility of the FeSO_4 layer. Figure 3 shows some examples. From this Figure, it can be noted that, for 70 % of sulfuric acid, the corrosion rate is slightly smaller than 0.5 mm/year at 24 °C while the rate increases about 10 times (5 mm/year) when the temperature is increased up to 107 °C. For 98 %, the corrosion rate is about 0.13 mm/year at 24 °C and less than 5 mm/year at 107 °C.

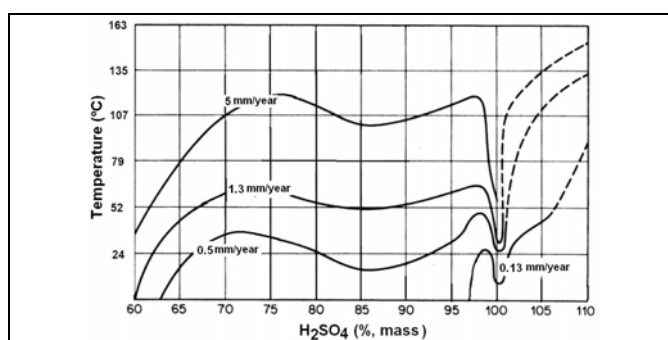


Figure 3 - Corrosion rate of the carbon steel tanks for different temperature and sulfuric acid concentration in static conditions (NACE SP0294, 2006)⁶

- **relative movement between the metal and acid** - the agitation caused by the acid flowing through pipes or by loading/unloading operations of tanks accelerates the mass transport of FeSO_4 from the metallic surface toward the bulk acid. Consequently, the corrosion rate of the carbon steel walls increases. The main factors that cause a mass transport increase are:

- ✓ **diffusivity** - this factor is related to the difference in concentration between the interface and the bulk solution. The coefficient of diffusion is dependent on the temperature and the viscosity, as shown by the equation below (DEAN; GRAB, 1985):

$$D = 1.68 \times 10^{-12} \frac{T}{\mu} \quad (1)$$

where:

D = diffusion coefficient of FeSO_4 ;
 T = temperature in K;
 μ = viscosity of H_2SO_4 ;

Therefore, the higher the viscosity, the smaller the diffusivity of FeSO_4 . The viscosity of H_2SO_4 , in turn, increases with increase of acid concentration and decreases with the increase of the acid temperature, as shown in Figure 4.

⁶ Adapted from reference.

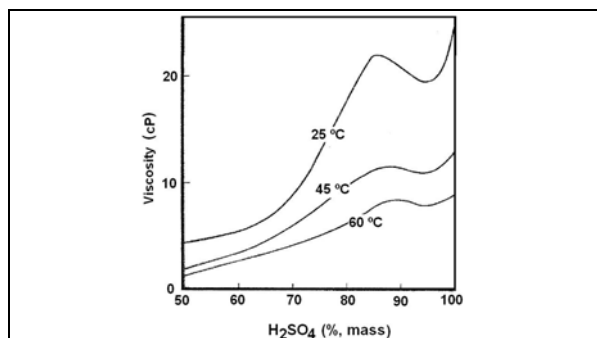


Figure 4 - Viscosity of H_2SO_4 as a function of its concentration for different temperatures (DEAN; GRAB, 1985)^{7,8}

- ✓ **thermal (or natural) convection** - because of the difference in internal and external temperature during the day, especially in tanks where the sulfuric acid is in stagnant conditions, there is the onset of thermal convection accelerating the removal by erosion of the FeSO_4 surface layer. Thus, in tanks located in courtyards exposed directly to sunlight present a higher corrosion rate. The influence of exposure to the sun on the corrosion rate can be verified in a practical case of a 9-year old carbon steel tank for H_2SO_4 storage (DEAN; GRAB, 1986). The corrosion rate of the wall exposed directly to the sunlight was 0.84 mm/year whereas the corrosion rate of the hidden walls from sunlight was 0.53 mm/year.
- ✓ **forced convection** - forced convection is provoked by mechanical stirring such as the one determined by the flow through pipes; by the tank loading/unloading operations; by the turbulence occurring due to the change of direction of flow caused by elbows and joints in the pipe; by the presence of valves; by the roughness in welds and by the lack of alignment of pipes. This agitation causes the removal by erosion of the FeSO_4 layer as thermal convection does. The difference being that the removal is greater due to more aggressive agitation. According to Dean and Grab (1985), the corrosion rate is proportional to the velocity of flow. Doubling the speed of flow, the corrosion rate is almost doubled.

3. Types of corrosion in carbon steel

Besides the uniform corrosion observed in carbon steel when in contact with sulfuric acid, depending on working conditions, there may be other types of corrosion, such as:

- **hydrogen grooving** - is a type of corrosion that can be found on pipeline walls (NACE RP0391, 2001) and on vertical and horizontal tank walls, being very common on inside walls of manholes and nozzles of storage tanks (FYFE; VANDERLAND; RODDA, 1977). This corrosion is caused by hydrogen bubbles from corrosion that accumulates on the inside walls of nozzles or manholes and when they rise, they create turbulence and remove the FeSO_4 layers along their paths leaving the area subject to corrosion and formation of a new protective layer. This cycle repeats itself provoking the formation of the grooves. Intense hydrogen grooving occurs especially along the top at the 12-o'clock position and less intense between the 3-o'clock and 12-o'clock position or 9-o'clock and 12-o'clock position. Figure 5 illustrates this type of corrosion.

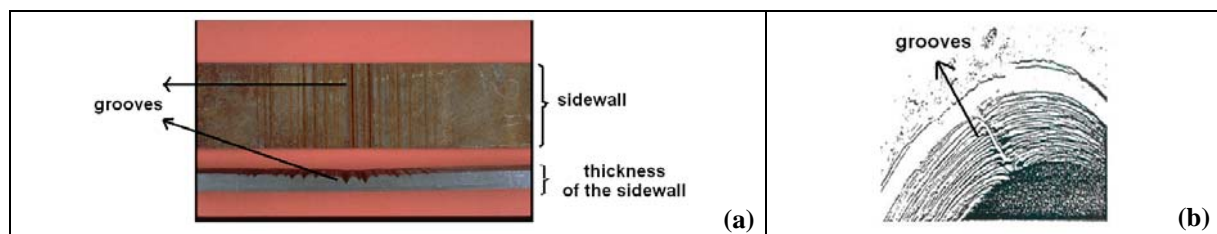


Figure 5 - Hydrogen grooving on the sidewall of a tank (a) and on the 12-o'clock position of a manhole of a tank (b) (FYFE; VANDERLAND; RODDA, 1977)

⁷ The unit used for the viscosity is cP (centipoise), where: $1 \text{ cP} = 10^{-2} \text{ g}/(\text{cm.s}) = \text{mPa.s}$ (milipascal.second).

⁸ Adapted from reference.

- **blistering** - is a type of damage caused by atomic hydrogen. When the cathodic reaction responsible for the corrosion of carbon steel is the reduction of hydrogen ions, blistering may occur. This cathodic reaction occurs in two steps. Hydrogen is first produced in atomic form. Two atoms then combine to form hydrogen gas molecules, as shown by the following reactions:



Some of the hydrogen atoms, however, do not combine to form hydrogen bubbles, but diffuse into the steel mainly towards discontinuities and combine there to form hydrogen gas. This gas is trapped within the plate and pressures of several thousand atmospheres build up slowly until the steel bulges to form a blister and eventually ruptures (FYFE; VANDERLAND; RODDA, 1977). Compounds such as H₂S, bismuth, lead, sulfur, tellurium, selenium, arsenic, phosphorus, antimony and cyanide cause the acceleration of atomic hydrogen penetration and therefore they are called hydrogen poisons (PANOSSIAN, 1997);

- **preferential weld attack** - according to studies of Dean and Grab (1986), acid holdup occurs in the roughened area of welds that was subsequently diluted by absorbing water from the air during unloading operation. This causes acceleration of the corrosion on roughed weld areas. Therefore it is advisable to smooth the weld before loading sulfuric acid tanks.

4. Preventives measure for carbon steel corrosion control in sulfuric acid

To increase the useful life of tanks and pipelines made of carbon steel, a detailed study of appropriate standards is advisable. Some of the recommended practices stated by sulfuric acid related standards are as follows:

- the concentration of sulfuric acid should be maintained between (88-99.5) % (NACE SP0294, 2006), preferably (98-98.5) % where corrosion rates are lower;
- the flow velocity of sulfuric acid in tanks and in pipelines should be limited to 0.9 m/s (NACE RP0391, 2001) and the temperature to 50 °C;
- a corrosion allowance for tanks and nozzle surfaces wetted by sulfuric acid should be between 3.2 mm and 6.4 mm (NACE SP0294, 2006). Corrosion allowance is defined as metal thickness above the design minimum thickness that may be consumed or otherwise removed without performing fitness-for-service evaluations;
- corrosion test coupons installed in critical tank locations is advisable as they can provide valuable quantitative data on types of attack prevailing in the specific locations at which the coupons are installed (NACE SP0294, 2006);
- precautions should be taken in order to avoid the ingress of water during loading/unloading operations (NACE RP0391, 2001; NACE SP0294, 2006);
- the mechanical properties of the carbon steel plates, welds and heat-affected zones (HAZ) must comply with applicable codes (e.g., ASME BPVC, Section VIII, Division 1) or standards (e.g., API650, Section 2, Materials or API 620 Section 4, Materials). The maximum tensile strength exceeding 620 MPa should not be used because of the potential for hydrogen damage. The hardness of heat-affected zones of the weld metal and base metal should be limited to 22 HRC (NACE SP0294, 2006);
- coatings should be applied to external surfaces of noninsulated tanks to minimize radiant heating from the sun and to keep the metal temperature as low as possible (NACE SP0294, 2006).

In cases where carbon steel presents low performance, lined carbon steel pipes may be considered. Fluorinated plastics are resistant to concentrated sulfuric acid at temperatures up to 50 °C, such as: polytetrafluoroethylene (PTFE); perfluoroalkoxy (PFA); ethylene chlorotrifluoroethylene (ECTFE); fluorinated ethylene propylene (FEP) and ethylene trifluoroethylene (ETFE) (NACE RP0391, 2001).

Polyethylene (PE) and polypropylene (PP) are subject to environmental cracking. Cracking probability increases with increasing acid concentration and temperature and a careful review of long-term performance of these materials should be performed prior to application (NACE RP0391, 2001).

Polyvinylchloride (PVC) and polyvinylidene chloride (PVDC) have been used successfully as piping for concentrated sulfuric acid below 96 %. Polyvinylidene fluoride (PVDF) may be used up to 98 % (NACE RP0391, 2001).

High temperature baked phenolic coatings are normally used to protect small sulfuric acid storage tanks in the range of (90-98) %. At acid concentration greater than 98 %, some types of baked phenolic coatings slowly carbonized may be used (NACE RP0391, 2001; NACE SP0294, 2006).

The most used protection method in reducing the corrosion rate of carbon steel in concentrated sulfuric acid is anodic protection. This method also guarantees the quality of the acid in terms of iron content which is an important feature where the acid purity is required such as the sulfonated product producers that use sulfuric acid as a raw material (FISHER; BRADY, 1963).

The essential condition for using anodic protection is that the metal must exhibit an active/passive behavior in a specific media, such as the carbon steel in sulfuric acid. Anodic protection is obtained by applying an anodic current to put the metal under consideration in the passivity domain.

Figure 6a depicts a typical polarization curve of an active/passive metal environment combination. As a positive potential is applied from the corrosion potential (E_{corr}), the current density increases up to a maximum value which is called critical current density (i_{crit}). The corresponding potential is called Flade potential (E_F). The potential range from E_{corr} to E_F concerns the active stage of the corrosion process. From point P, a range of potential (E_P to E_O) is reached. This range is characterized by low corrosion rates and is known as the passive region of the polarization curve. At point O, the evolution of oxygen becomes possible and the current density increases again.

In the case of carbon steel in sulfuric acid, the literature reports that the anodic polarization curves show two peaks of current density, as shown in Figure 6b (WILLIAMSON; HINES, 1964).

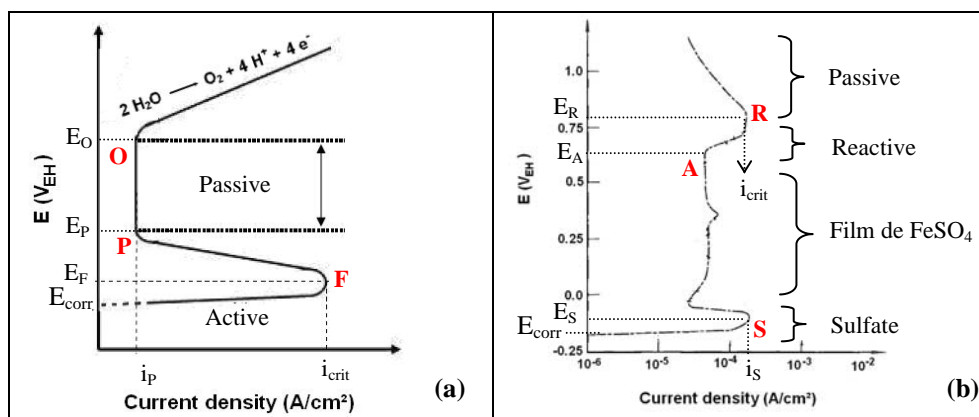


Figure 6 - (a) polarization curve of a metal in acid solution presenting an stable passive film, (b) polarization curve of carbon steel in 96 % H₂SO₄ (WILLIAMSON; HINES, 1964)^{9,10}

In Figure 6b, the first peak (point S) occurs as soon as the application of anodic potential from the corrosion potential starts. The range from E_{corr} to E_S is a typical activation process, known as the sulfating stage. This stage involves the formation of supersaturated FeSO₄ solution at the metal surface which leads to nucleation and growth of FeSO₄ crystals, followed by the formation of a FeSO₄ protective film (WILLIAMSON; HINES, 1964). At this point (S in Figure 6b), a sharp decrease of the current density is observed. It is worth mentioning that the described sulfation process occurs naturally on the surface of the carbon steel when it is brought into contact with a concentrated solution of sulfuric acid.

After the formation of the sulfate film, a potential increase will not determine an increase in the current density up to point A. However, at this point the current starts to increase again and a second peak is observed (point R). According to Williamson and Hines (1964), this step is called the activation step. However, it is believed that it is more suitable to call it as the reactivation stage as long as the sulfating stage is also an activation process.

During this stage, the Fe₂SO₄ film becomes unstable due to the oxidation of Fe²⁺ ions to Fe³⁺ ions, as observed by Banks and Sudbury (1963). This oxidation makes the film more porous and therefore less protective. This transformation is accompanied by a change in the film color: the dark color due to the FeSO₄ film disappears and a white color film starts to form, indicating the formation of Fe³⁺ ions.

According to Williamson and Hines (1964), at the second current density peak (i_{crit} at point R of Figure 6b), a process of nucleation and growth of a passive film occurs. This film is constitute by a crystalline film of Fe₂O₃ mixed with Fe₂(SO₄)₃·5H₂SO₄ and FeSO₄·3H₂SO₄. This stage is called the passivation stage being accompanied by a sharp reduction of the current density. The range of potential of the passivation stage is that in which carbon steel is maintained during anodic protection. It is important to mention that, in sulfuric acid, the water oxidation reaction occurs at a much higher potential being almost 5 V_{EH} (HINES; WILLIAMSON, 1994).

Therefore, in an anodic protection system of the carbon steel in contact with sulfuric acid, there are basically three important issues to be considered: first is the critical current density (i_{crit}) for the correct selection of initial current density to be applied in order to achieve the passivation state; second is the knowledge of the limits of the passivation range in order to maintain the carbon steel in the passive state and the third is the required current necessary to maintain the passivation state (SHOCK; RIGG; SUDBURY, 1960). Thus, two components of an anodic protection system are important. One: the source of an electric current necessary for applying a DC current between the cathode and the tank

⁹ Adapted from reference.

¹⁰ V_{EH} – Potential measured on the standard hydrogen electrode.

walls in a controlled way; two: a voltmeter installed between the tank walls and a reference electrode for measuring the tank/acid potential. Figure 7 shows a simplified diagram of an anodic protection system.

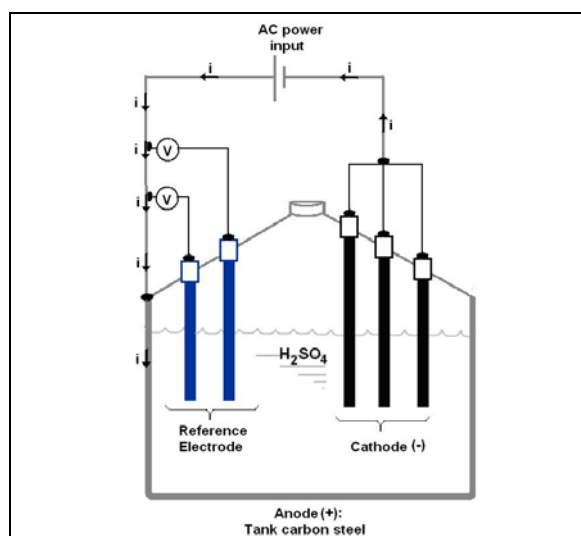


Figure 7 - Basic anodic protection system (SHIM; MUNRO, 2000)¹¹

For a suitable anodic protection system, initially, a relatively high current density is applied and the tank/acid potential is monitored. When the measured potential reaches a value within the pre-established passivation potential range, the applied current density is reduced to the minimum value necessary for maintaining the passive state (FISHER; BRADY, 1963).

The required time to achieve the passivation stage depends strongly on the intensity of the applied current density, the greater the current density the lower the required time. In order to maintain the passive state, a minimum current density must be applied continually to the system, otherwise a rapid drop of the tank/acid potential toward the active state will occur which determines an increase of the corrosion rate. Banks and Sudbury (1963) found that the time for the occurrence of this drop depends on the concentration and on the temperature of H_2SO_4 . Figure 8a shows some examples. From this Figure, it is possible to note that the potential drop is more rapid for more dilute solutions (56 % to 80 %). For more concentrated solutions (93 % to 97 %), the potential drop is much slower. On the other hand, by comparing Figure 8a to Figure 8b, it can be noted that the potential drop time decreases as the temperature increases. For example, in 96 % of sulfuric acid, the potential drop lasts almost 30 minutes at 27 °C (Figure 8a) and only 5 minutes at 49 °C (Figure 8b).

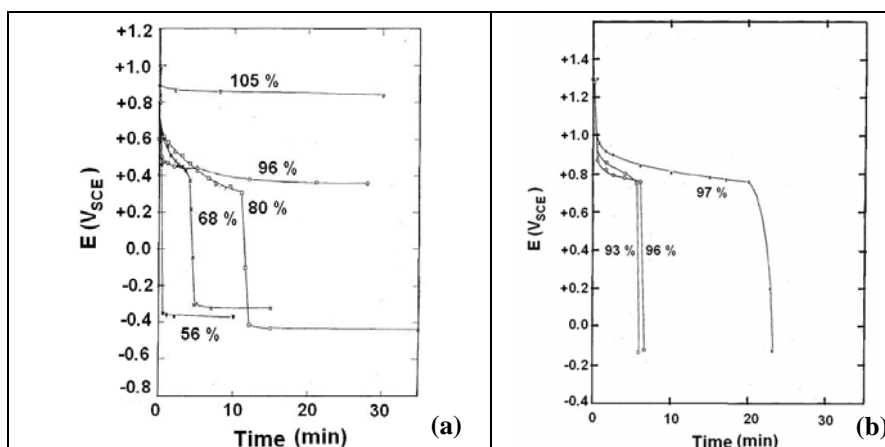


Figure 8 - Potential drop time after switching off the anodic protection current for different sulfuric acid concentrations at (a) 27 °C and (b) 49 °C (BANKS; SUDBURY, 1963)¹¹

¹¹ Adapted from reference.

5. Conclusions

Based on the presented literature review on the construction materials for storage tanks and transportation pipes, it is possible to conclude that, although the carbon steel presents several types of corrosion and damage when in contact with concentrated sulfuric acid, this metal can be used in the construction of this equipment due to its low cost. In order to extend the service life of carbon steel equipment, preventive measure must be adopted. The corrosion resistance of carbon steel in sulfuric acid is a consequence of the formation of a protective FeSO_4 layer. Thus, the preventive measures should be selected aiming to preserve this protective layer. Therefore, it is necessary to avoid: direct exposure to the radiant heating from the sun on the metal surface, high flow velocity of sulfuric acid, high turbulence and entrance of moisture. Furthermore, the use of anodic protection is very efficient in reducing the corrosion rate of carbon steel in concentrated sulfuric acid.

6. Acknowledges

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