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PROBLEMS IN INSURING MAINTENANCE OF TRANSPORT SYSTEMS OF FLUID HYDROCARBONS THROUGH METAL PIPES

BY

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Abstract. The structural continuity of the and the integrity of the metallic materials specific of pipelines guarantees their exploitation under proper technical conditions and with the minimum reduction of environmental risks, representing a permanent preoccupation and essential condition in the maintenance of the transport systems of fluid hydrocarbons through metallic pipes.

Metallic and non-metallic materials coming in contact with a certain environment suffer gradual degradation due to reciprocal interaction.

The nature of this interaction can be chemical or electrochemical and this, in time, makes the material unusable due to the structural, dimensional or continuity changes.

The resistance to corrosion of a metallic material is closely related to the composition and its structure, to its degree of purity, to the nature and characteristic of the corrosive environment, to the conditions in which the corrosion takes place.

When there is uniform corrosion, the behavior of the material is evaluated by the gravimetric index, the penetration index and the volumetric index.

The protection against corrosion represents the total measures taken to diminish the destructive action of the environment on materials in working

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concrete conditions, at the lowest possible cost and by meeting safety conditions.

The main means of protection or reduction of the corrosion intensity are the following: treatment of the environment (with the purpose of reducing its aggressivity), coating of the surfaces exposed to the corrosion, application of surface treatments, moving the electrochemical potential of the metal in the field of immunity or passaging and draining of dispersion currents.

The displacement of the potential of the metallic material protected in the field of immunity can be ensured by the realization of a galvanic pile with an active anode or by current injection, which opens, as an engineering practice, the way to ensuring the cathodic protection applied to the equipments in contact with an electrolyte (water, oil etc.), as the most modern method of preventing the loss of metallic material and of structural damage of the pipes destined for the transport of fluid hydrocarbons.

Keywords: corrosion; gravimetric index; penetration index; volumetric index; electrochemical potential; cathodic protection.

1. Introduction

General Considerations – Characteristics of the Corrosion Phenomenon

The metallic and non-metallic materials, which are in contact with a certain environment, undergo in time a continuous process of destruction due to the reciprocal interaction. The interaction may be of a chemical, electrochemical or fragile nature and this makes the material unusable after a period of exposure due to structural, dimensional or continuity changes.

Corrosion can be defined as a process of destruction of materials over time by chemical and / or electrochemical actions of the environment in which they are located (Haves, 1970).

Therefore, any reaction of the material with the environment is a corrosion process, characterized by its own mechanism of unfolding.

The environments in which the destruction processes take place are considered as corrosive or aggressive environments. Aggression is assessed by the intensity of the destructive action on the material. For the most part, corrosive media have non-metallic elements, with incomplete valence layers, which together with the metal ions passed into the solution form chemical compounds. Among the most active non-metallic elements are: oxygen, chlorine, sulfur. The free energy of the resulting chemical compounds is lower than the free energy of the metal. Therefore, the corrosion process translates into the passing of the metal into a more stable thermodynamic state. If the free energies of metal and chemical compounds are close, the corrosion process does not stop, but reduces its intensity. Starting from this difference of free energies, metals can be: corrosive or sacrificial metals, semi-noble metals and noble metals (Burkhalter, 1969).

The criteria underlying the classification of corrosion types are numerous:

The mechanism of development:
- chemical corrosion
- electrochemical corrosion
- microbiological corrosion

1. Nature of the environment
   - atmospheric corrosion
   - corrosion in gases
   - corrosion in liquids
   - soil corrosion
2. Place and character of destruction:
   - surface corrosion
   - deep or penetrating corrosion
   - brittle fraction corrosion
3. Application form:
   - corrosion under tension
   - corrosion fatigue
   - fretting corrosion
4. Metallurgical processes:
   - corrosion by decarburization
   - corrosion by carburization
   - graphitic corrosion
   - nitrate corrosion
   - galvanic corrosion

According to the behavior of the material in the corrosive environment, the most unfavorable situations are when the corrosion occurs locally or under the protective layer (Krause, 1976). Their highlighting involves the use of much more laborious means of detection, of high sensitivity. The local forms of corrosion must be known before proceeding with the installation of the equipment or machinery in order to take the necessary control measures.

Fig. 1 – Defective type of loss of material caused by corrosion.

Corrosion resistance is the ability of a metal to maintain its functional characteristics under the conditions given by the destructive action of the corrosive environment (Tullmin and Roberge, 1995).

The corrosion resistance of a metallic material is closely related to its composition and structure, its degree of purity, the nature and characteristics of the corrosive environment, the conditions in which the corrosion takes place.

From the summary enumeration of the factors involved in the corrosion destruction process one can conclude that their actions cannot completely characterize the material except for concrete test conditions. Any modification of the parameters leads to changes in the behavior of the material to corrosion.

The corrosion trials are aimed at:

– elucidation of the corrosion mechanism

– knowledge of material behavior in different aggressive environments

– checking the manufacturing technology according to the corrosion behavior of the manufacturing elements

– the most accurate assessment of the operating time of the material under the given operating conditions

Regardless of the purpose pursued, the test method must be simple, not require a high consumption of materials, chemicals and energy, to be carried out in a time that can fully characterize the corrosion process, to ensure rigorous control of working parameters, to allow the simple interpretation of the results obtained, etc.

The most important parameters that are followed before and during testing are:

– composition of liquid or gaseous environment (PH)

– the state of movement of the solution (rest, agitation)

– working temperature

– the humidity of the gaseous environment

– condition of surfaces exposed to corrosion

– the state of tension in the material

– microstructure and purity of the metallic material

– metallurgical processes that can intervene in heating and cooling material in the presence of aggressive environment

– how to prepare the surface in order to apply corrosion protection

– nature and state of protective layers (Durham and Durham, 2005).

Depending on the carrying out conditions, the corrosion tests may be:

– laboratory trials - in which the tests are performed on special installations, in artificial environments or similar to those in operation.

– operating tests - in which the tests are performed on real installations, under normal operating conditions.

The corrosion tests in laboratory conditions are carried out on simple test tubes such as plates, disks, etc., especially prepared for the existing apparatus or installation.

The trial performed directly by the operating equipment is the most convincing method.

The materials in the form of samples are placed in the working areas using supports with dielectric qualities and resistant to the aggressive environment. After the test time expires, the samples are extracted and examined in the laboratory.

Corrosion assessment by visual examination is only suitable for qualitative determination of the type and appearance of corrosion. The investigation by optical means proves insufficient for some forms of local corrosion.

In the case of a uniform corrosion, the behavior of the material is evaluated by the gravimetric index, the penetration index and the volumetric index.

The gravimetric index Kg is defined as changing the mass of the sample subjected to corrosion in the time unit and on the surface unit:

$$Kg = \Delta G / t = (G\text{-}G) / At \qquad (1)$$

where: Gi – initial mass of the sample; Gc – mass of corroded sample; A – the area exposed to corrosion, t – the shutter speed.

The penetration index p represents the average depth of corrosion penetration in the sample wall in the unit of time:

$$p = 8.76\ Vcor / \gamma \qquad (2)$$

where: Vcor – corrosion rate; γ – the specific weight of the trial material; 8760 – the number of hours in a year

In the chemical and petrochemical industry, the assessment of the corrosion behavior of the materials is based on the penetration index, as follows:

Perfectly resistant materials $p < 0.5$mm / 10 years
– resistant materials $p = 2$mm / 10 years
– acceptable materials $p = 4$ mm / 10 years
– improper materials $p > 5$ mm / 10 years

For tubular material (pipes), the assessment of corrosion resistance is made on the basis of the penetration expressed as a percentage of the wall thickness:

– resistant materials p = 0-15% / year

– materials with average resistance p = 15-25% / year

– materials with low resistance p = 25-50% / year

– non-resistant material p> 50% / year

Ideally, all the technological constructions and installations in the oil industry will be made of materials recognized as corrosion resistant. However, such a construction is economical only if the corrosion leads to the destruction of the installation in a very short time (Al-Hajri, 2008).

As stated before, according to the mechanism of development, the corrosion can be chemical, electrochemical, or microbiological.

In order to consider a chemical corrosion to be pure, the aggressive environment must not conduct the electrical charges, and must not modify its characteristics during the process, as this will trigger an electrochemical process of passing the metal into the solution.

Chemical corrosion is characteristic of metals existent in dry gases and dielectric liquids.

The purely chemical action of gases is manifested only at temperatures greater than 200-300°C, when a film absorbed by water cannot form on the surface (Aliev and Trifel, 1961).

The main characteristic of chemical corrosion is the formation of compounds that remain adherent on the surface. The chemically formed film has the crystalline structure and dielectric qualities that may have more or less protective action, depending on the formation conditions and the diffusion possibilities of the corrosive agent or the metal. Through this film, the metal ions and atoms of non-metallic elements can move more easily. The smaller the radius and the higher the electric charge of the metal ions is, the higher their mobility.

The protection against corrosion is the totality of the measures that are taken to diminish or stop the destructive action of the environment on the materials in concrete working conditions, at the lowest cost and full safety in operation.

In the action of designing the protection against corrosion, the aspects related to the safety of the service personnel, the protection of the environment, the risk of explosion should not be neglected.

The main means of protection or reduction of corrosion intensity are the following:

– treating the environment, in the sense of reducing its aggressiveness

– coating the surfaces exposed to corrosion

– applying surface treatments

– displacement of the electrochemical potential of the metal in the field of immunity or passivation

– drainage of dispersion currents

The protection of metals by electrochemical methods is part of the group of active protection methods (Oniciu and Constantinescu, 1982).

Cathodic protection is applied to equipment and machinery in contact with an electrolyte (water, soil, etc.). Pipes, cables, oil rigs, tanks, heat exchangers, etc. can be cathodically protected (Artanova and Galubnici, 1976).

The displacement of the potential of the metallic material to be protected in the field of immunity can be ensured by:

– making a galvanic cell with an active anode

– current injection

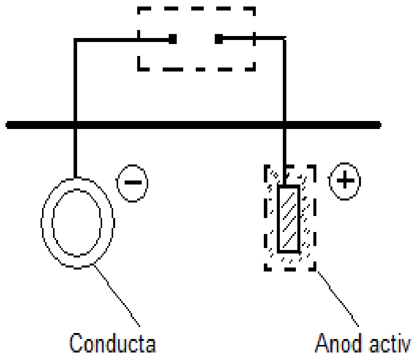

Fig. 2 – Cathode protection with active anode.

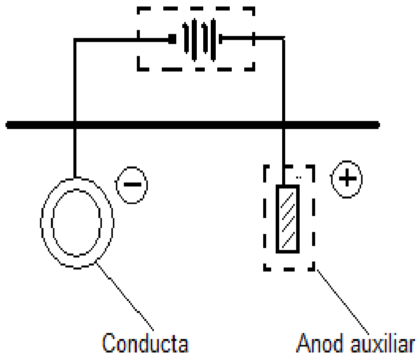

Fig. 3 – Cathodic protection with current injection.

The first procedure is called cathode protection with active or consumable anode. The second is called cathodic protection with current injection protection station, the cathode being the protected construction, and the auxiliary anode, a sacrificial material (Baeckmann, 1962).

Both methods have both advantages and disadvantages.

The main advantage of the **cathode protection method with active anodes** is that it can be used in most environments where corrosion occurs, even in areas with an explosion hazard, due to the low currents it provides.

As a major disadvantage we can remember the very high cost of execution in case of a high current requirement (for example the protection of a tank park).

Among the main advantages of **the current injection protection station,** we can mention the possibility of providing a high protection current at relatively low execution costs as well as the low maintenance costs due to the possibility of maintaining a constant potential automatically.

One disadvantage is that it cannot work in explosive environments. This is due to the lack of a current injection station that can work in explosive environments.

Among the most affected by the lack of a current injection station that can work in explosive environments are the parks of tanks and the tanks in general.

The reservoir parks consist of several storage or transit reservoirs, disposed underground or overground, connected by pipelines, provided with product transfer devices, overflow devices to prevent spillage, leak detection devices, prevention installations and fire extinguishing, protection systems against electric shock. The entire tank park is served by its own pumping station.

The tank parks are installed in fenced and supervised premises and are subject to precise authorization regulations. When establishing the location, it takes into account a number of conditions, of which the most important are: the quantity and nature of the products stored, the possibility of pollution of the underground water, air and soil in case of damage, the possibility of fires, the connection to the road and rail network, connection to units (electricity, compressed air, steam sources, sewage) etc. The authorized access inside the tank park must be free and permanent all year.

The tanks built within the park must comply with the conditions stipulated in API Std. 620 and 650 (mineral oil storage), 651 (cathodic protection), 652 (sealing) and 653 (inspection, repair, modification and reconstruction).

The main criteria on the basis of which the classification of the oil industry tanks are made are the following:

destination:

– crude oil tanks;
– injection water tanks;
– tanks for refined petroleum products;
– liquefied gas tanks.

location:

– tanks placed on the ground;
– tanks above the ground;
– underground tanks.

Reservoirs for the storage of liquid petroleum products work at atmospheric pressure, and those for natural gas work at high pressures, both being underground or overground.

The partially underground and overground tanks are generally provided with a double mantle and those situated on the ground with a double bottom. Single-walled underground tanks are always located in a concrete enclosure (Hausmann, 1970).

When determining the location of the tank park, the following must be taken into account:

– the characteristics of the terrain from the point of view of the geological structures, of the phreatic access, the resistance to shearing or compression, so that the movement, sinking or overturning of the tanks is prevented;

– the location area must be free from dispersion currents;

– visual inspection during the integrated course of reservations must be allowed

– the site must be protected so that the tanks are not affected by the movement of heavy vehicles;

– in the location area, the level of phreatic water and the possibility of floods must be anticipated so that they don't interfere with the construction of the reservoir.

Prior to commissioning, as well as periodically, tank mantles are checked non-destructively for any possible manufacturing defects or corrosion created which would determine the leakage of the product or the ingress of water from outside. An electronic system for signaling leakage of water is placed between the double walls.

The entire storage system of the tank park is protected against corrosion by coating and cathodic protection. The corrosion protection system of the tanks must comply with the API and standard NACE TM0101 - 2001 (measurement techniques related to the criteria for underground cathodic protection or metal systems with submerged reservoir), NACE PR 0169-2002 (Corrosion control on underground or submerged) metal pipes), NACE RP0193 -2001 (External cathodic protection of quality metal storage tanks), NACE RP0285 -2002 (Corrosion control of underground cathodic protection systems).

The cathodic protection of each tank is checked periodically with the help of a reference electrode. When using the cathodic protection station, the auxiliary anodes supply for the tanks is separated from other cathodically protected components. The cathodic protection station is provided with an acoustic and visual warning system in case of interruption and with a recorder for the injected current and the interruption duration.

Synthetic, coating layers, which protect the tank against internal corrosion, with a thickness of up to 2 mm have a relatively low electrical conductivity. In the event of a strong stirring of the liquid, these protections are charged with electrical charges. For this reason, the reservoir and the associated pipes must be connected to the earth socket. If it is considered that the electrostatic charge is active, dangerous, the filling of the reservoir is done at the base or through a tube that descends until approaching the bottom and is limited from flow through the filling and drainage pipes below 1 m/s (Pickelmann, 1980).

Underground cylindrical tanks can be single wall or double wall and work at pressures depending on the product stored. Thus, when storing liquid refined petroleum products, the pressure in the tanks is equal to the hydrostatic pressure, and for those for liquefied petroleum gases, the working pressure reaches and exceeds 10 bar (1 MPa). Underground tanks are located at a depth of min. 1 m measured from the upper generator of the metal body.

The single-walled tank, together with its accessories, is installed in a concrete, clean, watertight underground room that holds the leaked product. The capacity of this enclosure is 5 to 10% higher than the capacity of the hosted tank. To allow inspection, the distance between the tank and the wall of the concrete room, regardless of position, must be min. 50cm. The bottom of the tank should not come in contact with the concrete plate. For this purpose, the tank is placed on metal supports. An electrically insulating material is placed between the supports and the reservoir.

Double walled metal tanks are placed directly in the ground and are intended for the storage of flammable products. The wall that doubles the underground tank is recommended to be made of stainless steel. The space between the two walls is filled with a non-corrosive fluid (gas or liquid) and having a very low freezing temperature. And these tanks are also provided with safety devices that allow the detection of any leakage or leakage of liquid between the walls. In the event of leaks, these devices automatically trigger the optical and acoustic alarm, and the service personnel immediately take the necessary measures to prevent other undesirable situations from occurring. Detection and alarm devices are subject to a thorough check at least once a year. The distance of the reservoir from other underground constructions must be greater than 1 m. The placement of the reservoir must be secure, so that it is not lifted from the supports by increasing the groundwater level or in case of flooding.

Between 70 and 80% of the leakage of the underground tanks is due to the loss of the tightness of the pipes, connections and joints. These components are made at the location of the tank and for this reason may have defects difficult to detect. Filling pipes through free fall and drainage pipes are recommended to be with double walls and have a 1% downward inclination towards the tank. All these must be protected against corrosion.

In the case of several buried tanks, not cathodically protected, it is necessary to be connected together by an equipotential connection, which limits the potential difference through the earth socket (Rucareanu, 1989). The main equipotentiality conductor must be as short as possible, have a sufficiently large section, not be parallel to other underground electrical power cables and easily recognizable from other cables. Also, this cable should not be used for grounding the neutral or protection against atmospheric electrical discharges (Kulman, 1959).

During filling with slightly flammable liquids, for example gasoline, diesel or diesel fuel, an equipotential electrical connection between the unloading tank and the underground tank is required.

At underground cylindrical tanks, the position of the overflow probes is mounted at a depth of min. 10% of the inside diameter. This corresponds to approx. 95% of the total capacity of the tank. The overload probe has as a sensitive element a temperature-sensitive electrical resistor, of thermistor type, fed from a source of low voltage current. As long as it does not come into contact with the liquid, the heated thermistor has an electrical resistance specific to its material (Carradi, 1973). As soon as the probe is flooded, the thermistor cools and its electrical resistance changes. It is precisely this difference of electrical resistance that is the main feature of the probe. The response time must be very short to command the filling system to stop. As a safety measure, if the probe is defective or the control system fails, filling of the underground tank cannot start.

Underground tanks that communicate with the atmosphere are provided with an inlet air duct and an overflow system.

Underground tanks for liquefied gas are generally cylindrical with a horizontal axis, have a capacity of 120 – 3500 m^3 and are provided on the outside with an insulating layer consisting of polyethylene fibers, whose thickness reaches 50 - 60 cm.

The capacity of a tank for liquefied gases is established by weighing or by volumetric measurement of the quantity of water when filling, the measurement error not exceeding 1%. Capacity determination by calculation based on tank dimensions is not allowed.

The pressure for checking the sealing of the underground tank working at atmospheric pressure is 1.3 bar, for 24 h, using as carbon dioxide or another neutral and non-combustible gas as working agents. For those working under pressure, the leakage test is done with compressed air, at pressures 0.4 MPa - 0.8 MPa (4 - 8 bar), but not lower than the working pressure. The test pressure of the resistance of the underground tank is set so that the voltage σ in the mantle is not exceeded:

– for $0.66 < Rp02 / Rm < 0.85$ $\sigma \leq Rp02$

– for $Rp02 / Rm > 0.5$ $\sigma \leq Rm$

During the hydraulic sampling of reception or commissioning it is recommended to use the acoustic method of tracking the behavior of the tank, and the result obtained constitutes the zero point for future periodic checks.

After performing the hydraulic tests, a flaw-detection control of the welded joints is performed and the wall thickness and continuity of the protective layer are measured. The ultrasound control is performed along the entire length of the butt welds and the welds of the connections (Grafen, 1973). The wall thickness is measured on the seating area on the sand bed with an opening of about 120 degrees and close to the support rails. In case of defects, after repair, the non-destructive flaw-detection control is repeated 100%. Also, the position of the reservoir is checked, as it can be modified by soil compaction and the possible permanent deformations at the level of the upper, medium generators and in the support area are measured. In case of finding large displacements or deformations after the hydraulic test or after subsequent checks, the dimensioning calculation is restored and based on the obtained results the tank is re-qualified.

Periodically, liquefied gas tanks are subjected to qualification tests. The first qualifying test is done at max. 2 years after commissioning and consists of an ultrasonic control at min. 10% of the length of the welded cords, and in the areas considered critical, wall thickness measurements are made. The position of the tank and the cathodic protection parameters are checked whenever it is considered necessary, without exceeding 12 months between two successive checks. The verification program includes the removal of water and deposits and the control of overflow and leak detection systems.

Checking the tightness of the space between the walls of the underground tank, is done with inert gas or under vacuum, at least once a year. The moment of pursuit of the state of tightness begins after stabilizing the pressure.

For long storage periods without movement, it is recommended to fill the tank to the maximum level to reduce the amount of water vapor condensing on the interior walls. In case of prolonged non-use, the empty tank is filled with nitrogen at a pressure above atmospheric pressure. The overground tanks are much more numerous than underground tanks (ratio 3/1), due to the lower costs at the same capacity, the ease with which the technical state can be verified and the possibility of intervention in case of losses (Constantinescu, 1986).

A tank is considered to be overground if 90% of its volume is above the ground and works at pressures between atmospheric pressure and a pressure dependent on the stored gas. Most of the above-ground metal tanks are provided with a double bottom in which a leak detection system is installed. Periodically, during the operation of the cylindrical overground tanks, a series of checks are carried out, of which the most important are: the ultrasonic flaw-detection control and the measurement of the wall and bottom thickness. Every two years the tanks are subjected to technical reviews, with the purpose to discover the damage created by deformation, corrosion, usage or aging, the evaluation of the future behavior and the establishment of the measures that are necessary to prevent the pollution of the environment and the production of damage or fires (Tudor and Rapeanu, 2002a; 2002b). During the revisions, both checks of the outside of the inside of the tank are carried out. The control of the exterior of the overground tanks consists of:

– visual examination of the tightness of the connecting parts, the welded joints, the protective components and the exterior of the overground tanks;

– control of the operation of the safety devices: breathing valves and filling limitation probe;

– checking the tightness of the pipes, including those for leak detection, under a pressure of 0.2 bar;

– the test of resistance of the double-walled pipes, of the connection between the tanks and pumps at an air pressure of 1.5 times greater than the maximum service pressure, but not less than 3 bar, the joints and connections being covered with a foamy product.

The control of the interior of the underground tanks consists of checking the tightness of the vertical cylindrical tanks, with flat bottom, without leakage monitoring system. Corrosions deeper than 2 mm and perforations of walls and bottoms must be announced to the authorized services. Pressure testing of the connections between the tanks and the pumping station is done using a liquid, usually water, the entire sewerage, including the pumps being drained from the stored product. The test pressure is 1.5 times higher than the maximum operating pressure. The time of keeping under pressure, measured after the thermal stabilization, is greater than 1 hour and during the whole duration the possible losses are tracked. Losses lower than 0.38 L/h do not indicate significant leaks due to leaks.

The internal control is done in detail when an oil product containing hydrogen sulphide was stored in the tank. The rust powder is collected by scraping and the presence of iron sulphide in it is analyzed. If the collected powder, introduced into arsenic acid, results in a yellow precipitate, it means that the powder contains iron sulphide.

The materials used in the execution of the metal tanks, are established by the designer according to the operating conditions. Steel tanks provide good resistance to many oil products. Problems may occur when storing oxygenated fuel products, such as alcohol or methanol, which tend to dissolve the inner protective resin- based coating.

The metal tanks have corrosion damage both inside and outside. In order to meet the environmental conditions, the cathodic protection must be doubled by placing an impermeable membrane under the reservoir, which will ensure the collection and the directing of the possible losses to a sealed external collector (Bashi *et al.*, 2003).

Inside, the corrosion of the metal tanks is generated by aggressive deposited agents. In the most general case, the vapors and the condensate act above the stored liquid, and in the immersed area the corrosion is caused by the liquid itself.

The bottom of the overground cylindrical tank is considered as a critical element due to the corrosive action of the deposited liquid, of the decanted impurities and of the soil on which it is laid. Inside, both at the level of the vertical walls and at the bottom, the main form of corrosion is that of points, cave-like, which continues until the wall is perforated (Beizadea, 1981).

Atmospheric corrosion occurs outside, and corrosion produced by the soil occurs below the reservoir.

If, at the above vertical cylindrical tank, the leaks at the level of the ferrules are easy to observe, those that occur at the bottom of it are difficult to detect in a timely manner.

At underground or overground tanks, the corrosion in points is detected when carrying out the internal inspection, included in the preventive-planned maintenance plan.

The prevention and control of tank corrosion are required for the following reasons:

a) Economic. The loss of product stored increases over time due to the spread of defects created by corrosion and requires the emptying and repair of the tank, operations made with significant expenses that can exceed 1/8 of the replacement value. Introducing the repair involves removing the tank from the normal working cycle of the storage or transit park.

b) Ecological. Product losses are infiltrated into the groundwater and contaminate it for a very long time. Within the reservoir park, several groundwater quality check points are established.

c) Safety in operation. The loss of flammable products, even in very small quantities, raises the risk of fire. Monitoring and monitoring of wall thickness is a permanent concern. Special security measures are taken in case of repair with open fire.

Avoiding the loss of petroleum products and the possibility of starting fires, require the application of several protection systems, of which the most important are: passive protection by coating, cathodic protection and protection against electric shocks of any kind.

2. Modern Methods for Anticipative Maintenance of Fluid Hydrocarbons Transport / Storage Systems

2.1. Protection Against Corrosion of Underground Reserves

a) Internal protection by lining

Underground cylindrical tanks with an advanced degree of corrosion can be restored to the normal state of use by interior lining with an additional wall made of an elastic membrane of plastic material, resistant to the stored product. This protection system can be applied to all tank sizes under conditions of safety of operation.

To cover, the tank is first emptied, washed and if necessary, the cracks and holes created by corrosion are repaired by welding. After these operations, the inner wall is covered with polystyrene or polyurethane foam, thus obtaining a continuous and smooth surface. The preformed lining according to the type of tank and the new interior dimensions, is inserted through the visiting mouth and is fed from a compressed air source until it takes an interior shape of the tank. Then, the supply of compressed air is interrupted and the membrane is sealed at the level of the visiting mouth. Behind the membrane is created a permanently maintained depression, which brings it even closer to the metal wall.

In case of leaks, the depression behind the shirt changes and this is a signal of degradation and intervention.

b) External protection through cover and insulation

The outer protection by covering and isolating the underground tanks is provided with at least two layers thick enough and watertight made of fabrics made of glass fiber impregnated with oil bitumen, coal tar, epoxy resin or polyurethane. Oil bitumen cannot be admitted if an oil product is stored in the tank. The dielectric control of the insulation is mandatory before lowering the tank into the excavated cavity.

It is particularly important that the protection layer is not degraded when the tank is launched.

The outer walls of the buried tank should be surrounded by a layer of fine, washed sand, devoid of stones, well-beaten, with a minimum thickness of 0.20 m. The outer upper generator of the horizontal cylindrical tank must be at a depth greater than 0.80 m.

Cover protection does not solve the problem of contact corrosion, when connections and pipes from materials other than the wall are attached to the tank. To prevent contact corrosion, the use of electrically insulating connections is recommended.

c) External cathodic protection

External cathodic protection of underground tanks can be done using galvanic anodes or an external current source. The soil around the reservoir may not contain materials likely to affect cathodic protection. Cathodic protection with a current source, should be well analyzed at the tanks placed in a potentially explosive area.

Before proceeding to the establishment or measurement of the cathodic protection parameters, the technological pipes corresponding to the tank are isolated by means of the electrically insulating flange or nipple joints. Their electrical resistance must exceed 1m Ω (STAS 7335 / 7-87).

To determine the parameters of the cathodic protection system, first determine the own or resting potential of the tank in relation to the Cu / $CuSO_4$ electrode.

The protection parameters are established with the help of the mobile cathodic protection station connected to 3-4 steel electrodes placed in the ground at a distance of approx. 4 m around the tank. By the progressive increase of the electrode supply current, it is expected that the potential of the tank will reach -0.85 V compared to the non-polarizable Cu/$CuSO_4$ electrode. The series-linked ammeter indicates the value of the current required to ensure the minimum protection potential. Depending on the quality of the external insulation, the density of the protection current is between 0.1 and 1 mA/m^2.

For design, when all the necessary data is not known in detail, the current density is determined according to the degree of protection that must be ensured.

In the case of using galvanic anodes, the specific resistance of the soil is measured and according to this, the number of anodes is determined.

The burial depth of the anodes is established so that their middle is at the level of the central area of the reservoir. The connection between anodes and the reservoir is made through a potential outlet.

The cathodic protection system with current station is equipped with a total operating and shutdown time totalizer. The supply of the cathode protection station is done independently of the supply of pumps or signaling systems.

2.2. Protection Against Corrosion of Overground Tanks

The outside of the tank, which comes into contact with the atmosphere, is subjected to generalized atmospheric corrosion. The flat bottom of the tank placed on the ground, is subjected to strong external corrosion as a result of the differentiated aeration. In order to reduce this form of corrosion, the foundation on which the tank is placed has a slight rough outer slope, of 1-2%, in order to facilitate the drainage of water and possibly the lost products through the leaks of the bottom.

The foundation of the tank is covered with a waterproof layer which also ensures some leakage in case of loss.

The water-repellent layer is made of a mixture of sand and 10% (by volume) coal tar, for tanks in which petroleum products are stored, and of oil bitumen, for other products. The sand used is dry (maximum humidity 5%) and has a granulation of less than 2 mm. The mixing of the sand with the oil bitumen or the coal tar is done at a temperature of 70 - 80°C. After stretching, cooling and cylindering, the waterproofing layer is covered with a layer of fine sand, with a thickness of 10 - 20 mm.

Before starting the bottom construction, the sheets are covered with primer on the side that sits on the foundation.

The boards are welded automatically and only locally manually. Welding is done on one side, the root of the weld remaining under the bottom of the tank.

The lack of defects in the welding cords of the plates forming the bottom of the tank and of those created by corrosion can be established by the blowing of ammonia under a pressure of about 20 mm, the water column through the pipes radially inserted under the bottom of the tank. Inside the tank, the weld cords and the adjacent areas of the bottom, well cleaned, are covered by brushing with a solution based on phenolphthalein (2.5% phenolphthalein, 27.5% ethyl alcohol, 70% water, by weight). In case of leakage, the phenolphthalein solution will be colored locally in red, thus marking the spot of the defect.

The bed on which the bottom of the tank is placed can be considered as relatively homogeneous (composition, structure, permeability), but it cannot be accepted that in the radial direction, its degree of aeration to remain constant. The minimum oxygen concentration is in the central area of the tank bottom. Here, the steel acquires a pronounced anodic character in relation to the peripheral area. The corrosive effect of the macropile formed by the difference in concentration in oxygen, increases at the same time with the increase of the tank diameter.

The deviations from the flatness of the bottom also act directly on the intensity of the galvanic macropile. The surface of the foundation is not perfectly smooth, and the sheets that make up the bottom still show large deviations from the flatness. The main sources of deviations are the transport conditions of the sheets and the remaining tensions resulting from the welding.

When filling the tank, the hydrostatic pressure created tends to deform the bottom, so that it acquires the shape of the foundation. During this time the air beneath the bottom of the tank is evacuated to the outside.

When emptying, the situation is reversed. By lowering the hydrostatic pressure and the elastic relaxation of the plates, the air accompanied by moisture, possibly even water, is vacuumed under the tank bottom. This results in the repeated maintenance of the galvanic macropile created by the difference of concentration in oxygen below the bottom of the tank.

The aggressiveness of the bed on which the tank is placed cannot always be neglected. In order to establish the aggressiveness of the bed, the value of the cathodic polarization of the tank bottom can be taken. Cathodic polarization is dependent on the permeability and specific resistance of the soil or bed. Aggressiveness can be estimated by the ratio $i/\rho s$, where i is the current density corresponding to a peripheral potential equal to -1100 mV.

To extend the operating life of a metal tank, it is necessary to apply passive protection of the exterior and interior and the cathodic protection of the interior and the bottom of the tank.

2.2.1. The External Protection of the Above-Ground Tanks

2.2.1.1. Passive Protection

The external protection of the overground reservoirs is mainly ensured by priming with an oil-resistant primer, followed by coating with one or more layers of paint and an enamel layer. The surface to be covered is first cleaned, degreased and blasted, the roughness after blasting being between 50 and 100 μm (Bohni, 1973).

When choosing the outer coat of paint, the power of reflection of the wind rays is taken into account. A fresh black paint has an overall reflection coefficient of about 3%, a brown or brownish one 12%, and a white-silver one 84%.

Under the weather conditions of our country, the dark color resulting from the external corrosion can lead to a heating of the product stored up to 25°C, compared to the situation when it has a white-silver, reflective appearance. Even under these conditions, during the summer, the temperature of the product reaches + 45°C. Depending on the volume of the product stored, the temperature between day and night can vary by up to +25°C. The primer, in a dry state, contains fine zinc powders up to 95% in weight or 50% in volume. The zinc powder prevents rust from spreading in the case of the paint layer alteration to the metal surface. The subsequent layers of paint and enamel based on epoxy resins contain fine aluminum powders that ensure the reflection of the sun rays and reduce losses in this way by evaporation as a result of heating the stored product. In case the external corrosive action is considered to be strong, apply two coats of primer with zinc powders, respectively paint, followed by an enamel layer. In all cases the surface must be freshly blasted (max. 4 h). Each layer applied is allowed to dry well before a new layer is applied. All coating materials will be well shaken before use. Paints of two components and metallic powders, after the dosage indicated by the supplier, will be mixed with the help of mechanical stirrers, not electric and will be applied during the validity period. Before use, diluted products are filtered through 120Mesh (0.125 mm) metal meshes (Maniu, 1987).

The application can be done with the brush or roller, by spraying with air free of water or oil vapor or by injection. When applied, the temperature of the atmosphere must be higher than +5°C and the relative humidity of the air max. 85%. During drying, the temperature of the coated metal surface must be at least 3°C higher than the dew-point. Coverage is not recommended when the surface exposed to sunlight exceeds 40°C.

Particular attention is paid to the coverage of welding edges and cords where at least the minimum thickness of the protective film must be ensured.

The external passive protection can be doubled by the thermal insulation of the tank. Exterior insulation is mandatory for heated tanks to reduce the variation of indoor temperature and the loss through evaporation and as fire protection. The materials used must not be combustible. That is why, mineral fibers are used without plastic compounds, reinforced with metallic wires, and on the outside it is covered with aluminum foil.

The passive insulation applied on the outside of the sheets forming the bottom, is destroyed at least partially by welding. The welded joints are the most sensitive to corrosion. On the other hand, the organic insulation materials on which the bottom of the tank is placed undergo a natural aging process, which causes the protective properties to be reduced by half about 5 years from installation.

2.2.1.2. External Cathodic Protection

The external cathodic protection is applied to the bottom placed on the ground.

Prior to the connection of the cathodic protection, the technological pipelines related to the tank are isolated using flange-type electrically insulating joints having an electrical resistance greater than 1 MΏ (STAS 7335 / 7-87). They are mounted at a height of about 1 m above the ground. In case the atmosphere presents a danger of explosion, the electrically insulating joints are insulated on the outside with cold adhesive strips. The exterior metallic constructions (stairs, stands), are insulated against the tank and the foundation, using textolite plates and bushes and electrically insulating rounds for screws (Brown and Ellis, 1988).

Two types of Cu / $CuSO_4$ electrodes are used to measure the potential of the bottom. The exterior ones are placed on the ground and have a classic construction. Those in the center of the tank, placed in the bed of the tank, have a more special construction. The 2 to 9 central electrodes are in the form of a copper spiral surrounded by a thick layer of crystallized copper sulphate. Outside the bag that holds the copper sulphate, there is another bag in which there is a hygroscopic powder material, such as gypsum or chalk.

In the case of disconnection of ground connection or of the groups of protection anodes, the disconnection of the cathodic cable or the use of the alternating current bridge when carrying out the potential measurements for the measurement of the resistance of the ground connection electrical sparks can produced.

In order to avoid explosions, in all these cases it is necessary to disconnect and connect using special switches (ATEX). In addition, outside the tank, the connecting cables are protected by buried steel pipes, and the potential socket is located outside the risk of explosion or fire.

In many situations of capital repair of the tanks, a new bottom is created while keeping the old one.

The addition of corrosion for the new bottom is at least 4mm.

Experience shows that the new bottom, placed above the old one, placed at a distance of 300 – 600 mm, is corroded twice as fast as the old one, due to maintaining moisture in the enclosed space formed by the two bottoms. If the space between the two bottoms is filled with cement or sand, the wetting is ensured by the defects of the old bottom found on the foundation and a strong galvanic macropile is maintained through the difference in oxygen concentration. For this reason, the old defective bottom must be sealed and the cathodic protection of both bottoms be applied.

Cathodic protection of the bottom of the tank can be done using galvanic anodes or an external power source. Power source protection should be well analyzed at tanks placed in an explosive atmosphere.

For the outer protection of the bottom of the above-ground cylindrical tanks an anodes of Al-Zn 6.5 are used, placed symmetrically around the foundation, at a distance of 1-1.5m from the contour of the bottom at a depth of 1.5-2.5 m.

Before launching the anodes, the perforated hole walls are soaked with water. The watering operation is repeated after launch. If anodes from Zn 99.99 are used, it is allowed to reduce the resistivity of the soil by adding NaCl in the water to moisten the hole walls.

Given the fact that the surface of the bottom is large, it is recommended to use magnesium anodes, more expensive, but more efficient in terms of durability of protection. A magnesium anode with a weight of 1 kg can provide 1080 Ah, compared to 740 Ah in the case of zinc. The consumption of magnesium anodes is 7-9 kg /A. year, and of zinc 12-13 kg/A. year.

The current density required for the bottoms without a protective layer of coal tar or oil bitumen is 10-50 mA/m^2, while for those with such a quality layer, a density of 2-5 mA/m^2 is required. The current density can reach 100 mA/m^2, if the soil on which the reservoir is soaked with salt water.

The experiment established that in order to obtain in the central area of the bottom the protection potential of -0.85 V, on the whole periphery the potential must be brought and maintained at the value of -0.95 V.

The verification of the resistance of the earth connection of the tank through galvanic anodes is done according to the methodology presented in STAS 6119-78. Such verification is also required due to the fact that the anodes also serve to ground for the discharge of electrostatic loads. The external protection of the bottom of the tank with the external source of current is applied when the resistivity of the soil exceeds 1500 Ω/cm and when the current required for the protection is high, as is the case with the protection of an entire tank park.

The cathodic protection station is located outside the area in danger of explosion. The station and all the metal parts that can accidentally gain voltage are connected to the ground, the dispersion resistance of the socket being max. 4 Ω.

Initially, the cathodic protection station is set to a potential tank-soil of -1200 mV/Cu/CuSO$_4$ and left in operation for 48 - 72 h to polarize the tank. Following the correct adjustment of the station considering that after max. 3 s from the stop of the station, the potential OFF is between -850 and -1200 mV, at any point on the periphery of the bottom.

By using the cathodic protection station it is not necessary to reach the modification of the potential of the other underground metallic constructions with more than 70 - 100 mV. Otherwise, it is necessary to increase the depth of placement of the auxiliary anodes.

The main shortcoming of the cathodic protection of the bottom of the vertical cylindrical tanks is the unequal distribution of the protection current.

The central area of the bottom has a potential different from its periphery. If the potential difference between the center and the periphery is greater than 30 - 50 mV, a strong galvanic macropile is formed.

To overcome this shortcoming, either a deep-socket anode socket is used, or a modern protection procedure consisting of placing a flexible anode under the tank bottom which ensures a uniform distribution of the protection current.

The use of the flexible anode has other advantages:

– eliminates the interference with the other metallic structures in the vicinity of the reservoir, the drainage stations of the dispersion currents not being necessary.

– reduces the risk of cathodic detachment of the isolation due to overprotection;

– the necessary current of protection has a reduced value.

The negative terminal of the cathodic protection station is connected to the reservoir, and the positive terminal, to the anodic outlet located in the immediate vicinity of the reservoir and where the two ends of the flexible anode arrive. The flexible anode ends are joined by tightened metal bushes by local plastic deformation. The connection area is first isolated by wrapping a heat shrinkable strip that is contracted by heating and then the heat shrink tube is pulled out at the bottom of the anode, the length of which exceeds the length of the joint and which is also contracted by heating with the flame.

The multi-wire central conductor is made of copper and has a diameter of about 6 mm. Around the cable is a conductive polymer with a thickness of about 4 mm, which has the role of protecting the conductor, but which allows the passage of electric current. The conductive polymer is surrounded by finely chopped oil coke and this constitutes the regulatory mixture of the anode. Maintaining the coke around the conductive polymer is ensured by the synthetic fiber fabric resistant in aggressive environments. The bending radius of the anode must be greater than 20 outer diameters (Pietrareanu, 1972).

The flexible cylindrical anode, modeled in zigzag shape, is placed under the bottom of the tank at a depth of approx. 0.5m in a bed made of metallurgical coke. The characteristics of this coke are:

– maximum granulation 10 mm;

– content in coke powder max. 10%;

– 0.25 Ωm electrical resistivity;

– the normed quantity of coke 42.5 kg/m electrode.

Lately, anode production has developed in the form of mesh. It is made of titanium wire with a diameter of approx. 2 mm and is placed in the form of strips under the bottom of the tank in an activation layer.

2.2.2. Internal Protection of the Tank

The internal corrosion of the tank depends largely on the nature of the product stored. In the crude and total crude oil reservoirs, the corrosion manifests mainly in the lower part where there is a permanent layer of reservoir water. Also, at these reservoirs, there are significant corrosions at the water-crude oil limit and at the oil level and on the lid where the atmosphere inside operates.

The tanks for the storage of injection water are characterized by a generalized internal corrosion. Their duration of service is 4 - 10 years. For the well water, the corrosion rate of the metal wall of the tank is 0.2 - 0.5 mm/year, and if the water also contains hydrogen sulphide, it reaches over 1.5 mm/year. Within the capital repairs of the tanks destined for the storage or transit of the injection water, the superior collars and the cap are replaced after 3-7 years. The heating coils are mainly placed in the vertical cylindrical tanks thermally insulated or non-insulated on the outside in order to reduce the viscosity or to prepare the desalination or demulsifying operations of the crude oil. The heating agent, in case of cracking or breaking of the coil, should not react or affect qualitatively the product in the tank nor lead to the evaporation of water from the bottom of the tank. The current materials from which the coils are executed are carbon or weak alloy steels for seamless pipes. Joining several sections of the coil is done by welded flanges at the ends of pipes. The curves welded to the rectilinear pipes have a minimum radius $r \geq 1.5d$ (d being the diameter of the pipe).

The coil is mounted on welded supports, sized so as to provide a rough slope outside the tank of 2%, for the natural drainage of the condensate. After installation, the coil is subjected to a non-destructive flaw-detective microscopic control and then to the sealing samples (3 - 5 bar) and the internal pressure resistance (4.5 - 7.5 bar), using water as a working agent.

The heating coils are exposed to an intense corrosion process, due to maintaining the temperature at approx. 60°C. According to EN 50014, the outside surface temperature of the coil must be at least 10°C lower than the ignition point of the stored product. Also, by heating, the pressure in the tank should not increase by more than 200 mbar. In special cases, the heating coil is placed in a rather inflammable liquid, whose boiling point is higher than the maximum heating temperature of the stored product, at the same time not being miscible in the liquid stored in the tank.

The stored product is heated by the circulation of steam or hot water through the coil located above the bottom of the tank. Here, in the crude oil reservoirs, the coil is practically placed in the crude oil-reservoir mix.

For this reason, the maximum corrosion rate is on the outside of the heating coil. The strongest external corrosion of the coil appears at the entrance of steam or hot water in the coil, where the temperature is highest.

The inside of the coil is corroded by oxygen and carbon dioxide from the condenser. The higher the frequency with which the steam supply is interrupted the shorter is the operating time of the coil.

There are cases when the coil pipes, made of carbon steel or weak alloy, do not last more than 1-2 months (Chesa,1984).

For the inner protection of the coils, the water used to obtain the low pressure steam should be treated to reduce the concentration in oxygen and to contain additives adsorbed and stable on the metal surface (Hagymas *et al*., 1963).

In the case of short periods of stopping the heating, the coil is filled with water containing sodium sulphite, and for longer periods of stopping, nitrogen is introduced into the coil at a pressure greater than atmospheric pressure.

In the tanks for refined petroleum products, strong corrosion also manifests in the upper area of the tank, where the water vapor condenses through the breathing valve. The amount of water in the air entering the tank increases with temperature.

By cooling, the water vapor condenses on the walls and the droplets formed leak into the product in the tank.

The ability to dissolve water by petroleum products is dependent on their nature and temperature. Thus, the fuel for combustion (unrefined oil), can dissolve at 15°C an amount of water up to 0.1% in weight or 0.1 mL/m^3, and by cooling to +5°C, saturation water is separated min. 25%. Gasoline at 20°C dissolves 0.005% water in weight. By cooling the gas at 0°C between 25 and 30% of this water is separated, resulting in a quantity of free water of 25 – 30 mL/m^3. Research in this regard has shown that in overground tanks, the amount of separate water is greater than in underground tanks of the same capacity. The reason is the greater variations in the temperature of the above-ground tanks (Van Oeteren, 1969).

The water penetrated through the leaks of the lid, the one coming from the condensed vapors and the free water are deposited at the bottom of the tank and maintain the corrosion.

The metallic structures inside the tank (poles to support the lid, staircase, floats, etc.) are exposed to corrosion from the stored environment. Their maximum corrosion speed is observed in the fluctuation zone of the product level, where it has values exceeding 0.3 mm/year. The most corroded are the structures that have flat or slightly inclined horizontal surfaces, and the least corroded are the surfaces placed upright. The thickness losses are at least 50% higher on the horizontal surfaces on which the aggressive product stagnates, than on the vertical surfaces from which it flows slightly. All these processes of internal corrosion require the application of a complex system of protection against corrosion.

2.2.2.1. Protection by Cover

The inner protection is ensured by the multilayer system of resins or by lining with strips or sheets of synthetic materials. Epoxy resins, as shown, are resistant to petroleum products (gasoline, diesel, oils, unrefined oil) and water (drinking water, sea water, reservoir water). Due to these qualities, the most suitable interior protection system is the one consisting of a first layer of epoxy primer, a second layer of epoxy resin and an enamel layer, with a total thickness of 0.30 mm. Such a coating system is sufficiently elastic and withstands a long time at temperatures up to 6°C. The duration of protection increases from 3 to 5 years to 6 to 9 years, if the coating is made on a metallized layer of zinc or aluminum.

At thicknesses greater than 0.3 mm, the multiple layer is reinforced with glass fibers, because otherwise, it can detach due to the large difference between the coefficients of thermal expansion.

The inner coating with epoxy resins ensures the reduction of the expenses imposed by the frequent cleaning of the tank and maintaining the purity of the stored product.

At the tanks for petroleum products in operation, the technological flow of periodic interior coating with resins includes:

- emptying the tank;
- drainage of water and sludge;
- gas evacuation by steam injection;
- absorption of the remaining products with specific absorbents or by aspiration;
- drying and air conditioning from the inside;
- checking the quality of the interior atmosphere before entering of the execution personnel
- wet sanding until the crust and rust are completely removed;
- removing the sand and dusting the blasted surfaces with the help of an industrial vacuum cleaner;
- application of the grout with a grouter in the areas where the bumps or traces of corrosion are deeper than 2 mm;
- successive application of the resin layers, with cold hardening;
- glass fiber reinforcement of the covering layer on the bottom and possibly of the one on the first ferrule;
- control of the thickness and adhesion of the multiple layer and the absence of pores.

Prior to the application of synthetic resins to the interior, the reservoir is compulsory grounded to ensure the discharge of electrostatic loads.

During the interior work, the atmosphere in the tank is permanently conditioned until the complete drying of the coating. In the tank works a team consisting of two workers equipped with protective materials and oxygen mask and tied with ropes that pass out through the visiting mouth. From outside, another worker supervises the condition of those who perform the cleaning and coating. Such a work protection measure is required because the atmosphere inside the tank is toxic. The tools used indoors must not produce sparks.

In the case of the non-wetting of the boards, it is recommended to apply a layer (primer) based on epoxy resin reinforced with polyamidoamines, as well as epoxyphenolic resin. Being two-component, the ratio of the basic resin to the hardener is 4: 1. Some primer qualities contain zinc silicate up to 85% in weight, which also provides cathodic protection of interior surfaces.

The application of the primer is done at temperatures of 20 - 30°C and a relative humidity of max. 65%, the curing time being 10-12 h. The curing time reaches 6-7 days if applied at temperatures of 5-10°C. The thickness of a single layer is 0.1 mm and its increase is obtained by applying a new layer, the previous one not being completely reinforced, when touched by hand giving the feeling of stickiness. Dilution at spray application can be done in 2-4% diluted increments until the fluidity required by the spray apparatus is reached, but not more than 15% diluent.

In the case of improper surface preparation or the application of a coating incompatible with the stored product, degradation of the protective layer is achieved shortly. The aggressive product diffused through the coating reacts with the metal, and the resulting hydrogen creates a pressure high enough to detach and crack the layer. Under the film, corrosion manifests itself as a cavern. In tanks with a permanent variation of the level of the stored product, the destruction by detachment of the protective state is stronger. By evaporating the product penetrated under the film, the remaining salt crust continues to maintain local corrosion. It is expected that in small detachments, the depth of the cavern will be greater, because the evaporation time of the penetrating agent is smaller, and the duration of action of the corrosion by the difference of concentration in oxygen in the salt layer is greater.

When lining with wide strips or adhesive foils, the stability of the stored product, the adhesion to the steel and the thermal regime of the tank will have to be taken into account.

The adhesion to the steel of polyethylene and polypropylene without adhesive is weak. When using such materials, applying two layers of foil becomes mandatory, the first being made of polyisobutylene which ensures adhesion. Coats thicker than 0.8-1 mm cannot be applied, because between these and steel there is a big difference in the coefficients of thermal expansion leading to the detachment of the protective lining.

The operation of repair by welding at the tanks that have petroleum products deposited is risky and extremely expensive, due to the necessity of compulsory conditioning of the interior atmosphere. For this reason, in case of deep local corrosion, the local repair is carried out by applying successive layers based on adhesives.

The repair using the adhesives includes the following works:

- conditioning the atmosphere inside the tank (if applicable);
- surface preparation;
- preparation of the adhesive;
- application and hardening of the adhesive.

Surface preparation consists in removing by brushing or scraping impurities and rust on a surface that exceeds 30-50 mm the defect limits. Local cleaning can continue chemically. The old paint is removed with a solution consisting of 30% acetone, 10% ethyl alcohol, 30% ethyl acetate, 30% benzol (in volume). The solution is applied locally with the brush. The corrosion products can be removed with a solution consisting of 30-35% phosphoric acid, 10% ethyl alcohol, 10% hydroquinone, 20% butyl alcohol, 25-30% water. The solution is applied by brush and after 2-3 min. the treated surface is washed in water, brushed and neutralized with a 0.5% ammonia solution, 40% ethyl alcohol, the rest of the water and degreased with acetone by removal.

The coating of local defects is made with an adhesive based on epoxy resins modified with a polyamide resin (up to 40% in weight), which contains fine aluminum powder (15% in weight compared to resin). The adhesive being composed of two components, it is prepared with a maximum of one hour before application. The reduction of the viscosity upon application is obtained by adding a specific solvent in the ratios of max. 2% of the volume of the resin. The thickness of the adhesive layer is 0.3-0.5 mm and the covered area exceeds the area affected by corrosion. For deeper defects, a fiberglass fabric is pressed into the adhesive layer. The hardening of the adhesive is made hot at temperatures higher than 15°C, the heating is done with hot air, bags with heated sand, steam etc.

2.2.2.2. Inner Cathodic Protection

The inner protection of the tank only by covering with resins or foils is not completely safe. The insulating layer applied on a very large surface can present many defects or different degrees of degradation. For this reason, the cover protection is doubled by the cathodic protection.

The inner cathodic protection of the tank is possible if the stored product or the decanted product on its bottom is an electrolyte. The proper functioning of the cathodic protection implies the existence of an electrolyte layer that exceeds at least 3-5 cm the height of the anodes placed on the bottom of the tank. The cathodic protection is provided only in the flooded area, not in the upper area, which comes in contact with the atmosphere and vapors of the stored product.

The presence of the synthetic protective layer makes the current need for cathodic protection decrease much.

The reduction of the corrosion rate is obtained by lowering the corrosion potential until the protective potential range is reached using galvanic anodes for this purpose, and less often current injection.

The algebraic value of the potential difference E_M between the reservoir material and the reference electrode is given by the relation:

$$E_M=E_H-E_R \tag{3}$$

In which: E_H is the protection potential with respect to the standard hydrogen electrode of the material, in mV; E_R – the potential difference between the reference electrode and the standard hydrogen electrode.

The effectiveness of the inner cathodic protection with galvanic anodes is influenced by a number of factors, of which the most important are:

- the material from which the tank is executed;
- the type and characteristics of the protective layer (if there is any);
- the minimum and maximum water level from the bottom of the tank;
- compatibility of active anodes with the deposited fluid;
- the time interval after which the tank inspection is performed.

For tanks made of a single material, the potential for protection can be relatively simple to set. If the materials are different, the protection potential for less noble material must be assured. However, before setting the value of the protection potential, it must be determined whether the materials are compatible. Compatibility from the point of view of cathodic protection means that the ranges of potential protection to overlap (Zamfir *et al*., 1994).

If the inside of the tank is covered with a protective layer without defects, the need for cleaning decreases greatly. During the operation, the detachment of the protective layer may occur, as a result of the weak adhesion, the exaggeration of the protection potential when hydrogen (cathodic detachment) accumulates beneath the layer, or saponification of the protective layer material. When cathodic protection is applied to a tank already covered indoors, the deterioration of the layer must first be examined.

The tanks destined for the storage and transit of crude oil and reservoir water are the most exposed to the damage by internal corrosion and the two protection systems, passive and active, become obligatory for them. The current requirement is approx. 80 mA/m^2, if the cover is missing and 5-30 mA/m^2, if the interior is covered with a protective flawless layer. The application of cathodic protection must not lead to the release inside the tank of oxygen and corrosive products at its anode or of hydrogen at the cathode. In the tanks for petroleum products, the internal protection with magnesium anodes should be well analyzed, and the one by current injection should be avoided, because during the exploitation it takes about 5 m^3 of chlorine for 1A. year. Hydrogen reduces the ignition point of the gas mixture underneath the lid, and the chlorine triggers a severe erosion of the lid and is toxic to operators. The compatibility of the galvanic or sacrificial anode in relation to the electrolytic medium refers to the possibility of altering the deposited product by increasing the concentration in metal ions, as a result of the electrochemical reactions that intervene (Ciortea, 1955). The design of the internal cathodic protection starts from the plane of the metallic structures inside the tank, the quality characteristics of the protective layer, the chemical composition of the electrolytic environment and the stored product, the working conditions (stability of the electrolytic medium height, temperature, pressure). The galvanic anode inside the tank is positioned so that it <<sees >> the area it protects. Basically, an anode protects a limited surface, which can be adjacent to the one protected by the neighboring anode. In the case of an inappropriate placement, the existence of unprotected or insufficiently protected areas occurs. One of these insufficiently protected areas is the passage from the bottom to the first ferrule.

The steel heart of the anode is welded on ferrules, bottom, interior construction, coil. After cleaning, the welded joints and the metal heart of the anode are covered with protective layers identical to those of the inside of the tank.

Between the interior structures are made equipotential connections using insulated cables with materials resistant to the stored product.

Direct local measurement of the internal polarization is practically impossible and for this reason, fixed points of location of the non-polarizable reference electrodes are established. With their help, the local potential is measured before and after the cathodic protection is applied. It is recommended that these electrodes be placed in areas susceptible to poor or over-protected display and in areas where anodes can be screened. Such areas are established on the basis of potential distribution curves. In the case of installation of several reference electrodes, the variation of the potential between these electrodes must not exceed the range +50 mV, when the cathodic protection is in operation.

The effectiveness of the cathodic protection system is determined by potential measurements, current protection, specific resistance of the protective layer, insulation resistance or by placing corrosion control samples.

The potential measurements are performed with and without the cathodic protection in operation using a DC current voltmeter with an internal resistance greater than 10 MΩ. When the protection current is interrupted, the metal potential changes more slowly and the value measured immediately after the interruption constitutes the correct electrode potential. The speed at which the potential difference decreases after the power interruption gives an indication as to the validity of the potential measured immediately after the interruption. The fair value of the protection potential implies that depolarization is slow.

The measurement of the current protection is done with a series-mounted ammeter in the circuit that has a small electrical resistance. In the case of current station protection, the current supply of each anode must be measured. The measurement of the insulation resistance is required in the case of the current injection for the insulation materials of the cables passing through the mantle or bottom. An insulation resistance greater than 100 kΩ is considered appropriate for a cable voltage of 500 V in the absence of the electrolytic solution. The placement inside the tank of some corrosion control samples allows the tracking in time of the corrosion rate change. All the results of the measurements obtained by specialized personnel are written in the periodic control sheet of each tank. After the commissioning of the cathodic protection, the above mentioned measurements are performed monthly and then annually. The state of anodes and their consumption are also examined annually. The introduction of the reference electrodes through the access holes on the tank lid is almost impossible and presents many risks. Upon descent, the porous mass of the electrode is impregnated with the deposited petroleum product and its characteristic changes. In tanks with a floating cap, such a measurement method is impossible. The installation of the long-term reference electrodes in the established points, requires the passage of the cables through watertight seals practiced on the mantle or bottom. Sensors for cathodic protection placed on the mantle are used to increase the operational safety. The electrodes are made of Ag / AgCl or pure zinc with max. 0.0018% Fe. In the case of the Zn electrode, the zinc bars are inserted into a vegetable fiber bag to support the activation mixture consisting of 75% bentonite, 20% ground gypsum and 5% sodium sulfate.

The galvanic anodes used in particular are those of magnesium, zinc or aluminum, Zinc is not in all cases recommended, because it requires the electrolytic medium to have a high electrical conductivity, and when the temperature increases to values of the order of 60°C greatly changes its potential, when the reservoir wall can become anodic and thus greatly increase the corrosion rate.

The number of galvanic anodes is determined according to the area that a single anode can protect with a certain mass of active metal. The potential provided at any point of the flooded area must be -0.80 V, measured against the reference electrode Ag / AgCl.

In the tanks for the storage of refined petroleum products, the electrolyte in which the anodes are to be placed is water. If these products contain little water, in the form of dispersed droplets, the effect of cathodic protection is practically null because the anode cannot fulfill its function due to the lack of electrical continuity.

In the tanks that store products from which the water cannot be separated, the introduction of special electrolytes is required. These electrolytes do not dissolve in the products located inside and have a higher density than these.

At the cathodic protection with a galvanic anode immersed in the deposited electrolytic product, there is a large potential drop near the anode and near the metal wall. For this reason, it seems that the area insufficiently protected from the flat bottom to the vertical wall of the tank, where the distance from the anode is maximum. In order to improve the potential distribution in the lower area of the tank, it is necessary to place several anodes suspended by insulated conductive cables externally or to place several anodes on the bottom of the tank and on the first ferrule of the tank.

At spherical or small diameter vertical tanks, in which a product is stored that conducts the electric current and in which there are no metallic constructions, the cathodic protection can be provided by a single central anode.

If the cylindrical or spherical tank has interior metallic constructions (stairs, supporting poles, heating coils, etc.), the use of multiple anodes is required. When placing them, it must be taken into account that the current density on the cathode varies inversely proportional to the square of the distance from the active anode. At the reservoirs where crude oil is stored at room temperature, on the interior constructions, a current density of 15-25 mA/m^2 must be ensured. For tanks that store only products containing dissolved water, on the interior constructions, a current density of 8-12 mA/m^2 must be ensured. If the working temperature is 60-70°C, on the heating coil, a current density of 110-150 mA/m^2 must be ensured over the entire length. If the coil is made of a material other than that of the mantle, the passage through the mantle must be provided with an electrical insulation system due to the different potential need.

To reduce the cost of cathodic protection of the tanks in which non-flammable products are stored, the cathodic protection with the external source of current can be used, in the following cases:

– the stored environment allows the application of a high current density on anodes;

– the tank has a breathing valve that allows the permanent evacuation of the large quantity of hydrogen released. The station's anodes are made of silicon steel, graphite, platinum titanium, platinum niobium, platinum tantalum.

3. Conclusions

3.1. Control of Cathodic Protection

Cathodic protection control is imperative, especially when it is provided by current injection. The voltage and the output current, the electrode potential corresponding to the specific current density, as well as the depolarization that occurs when the power supply is interrupted are checked.

The purpose of the control is to determine the effectiveness of the cathodic protection during the life span of the tank. The main parameter measured is the potential OFF. The frequency of checks depends on the importance of the tank. In the case of the current injection, it is recommended to perform monthly the state of protection by the service personnel. The annual control is performed by specialized personnel who have the specific equipment.

The main works carried out during the control are the following:

– checking the electrical continuity of the tank-station protection system-anode and examining the status of the apparent cathodic protection materials;

– measuring the voltages on both sides of the electrically insulating joints;

– measuring the potential of each galvanic anode;

– measuring the voltage and intensity when leaving the station rectifier;

– measuring the ON and OFF potentials on the permanent electrodes;

– measurement of the current flow on each anode;

– calibration of the permanent reference disconnected electrodes;

– modification of the potential of the unprotected neighboring metallic constructions in the case of the functioning of the cathodic protection station (Hossam-Eldin and Mokhtar, 2008).

In the case of cathodic protection with current station, the main anomalies are specific to the rectifier, which is sensitive to current shocks and possible interference. If significant changes in the protection parameters are observed, the anode supply current regulation is required to maintain the potential between the set limits. A safer state of cathodic protection is obtained by providing the tank with an automatic station that allows the regulation of the anode supply current according to the signal given by the reference electrode whose characteristic remains constant for a long time.

The protection system with galvanic anodes is more stable, but after a few years the amount of current provided and the replacement of those who have exceeded their life expectancy must be checked. Another important point of the control program is that of the reference electrodes. Even if their potential is not considered to vary over time, they are sensitive to repeated drying and contamination with salts or petroleum products. The interior metallic structures (poles, stairs, heating coil, floats, etc.) must be characterized by equipotentiality. This condition is ensured by secure bonding by cables, so that it does not reach a potential difference, which would lead to the formation of galvanic macropiles. The equipotentiality is practically impossible in the case of protection with galvanic anodes, because the current flow is low. The potential of the mantle and the bottom of the tank should not be influenced by the potential of the service pipes. Their connection with the tank must be made by electrically insulating elements.

3.2. Protection Against Electrostatic Loads

The electrostatic loads are generated by the water-free hydrocarbons which move through pipes and in the tank perfectly isolated from the ground and can generate spark that can trigger fires or explosions. Avoiding accumulators of electrostatic loads is ensured by grounding the bottom, the mantle, the support poles, the floating or fixed cover, the stairs, etc., the resistance of the socket being of maximum 4Ω.

Besides this measure it is recommended to eliminate the cushion gas through:

– decrease of oxygen content in the cushion gas

– elimination of the flow inside the tank in the form of a jet, which forms disparate droplets which are easily electrostatically charged.

At the cathodic protected reservoirs it is also recommended to ground each part of the electrically insulating joint and seal the metal flanges between the electrically insulating joint and the reservoir.

In the case of constructions with large surfaces to protect, the most efficient method is the one with current injections. However, in some cases, like for constructions built in explosion-prone areas, the use of external injection stations is excluded. In such cases, the only method to be used (for example, the outer surface of the flammable fuel tank) is the one with active anodes.

In the case of very large reservoirs, the cost of active anodes is several times higher than that of an installation with current injection station.

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I have met the PhD student eng. Robert-Gheorghe VLĂDESCU, since 2014, from the point of view of my capacity then as scientific leader of the license work, for which he obtained mark 10 (ten). During this period, Mr. Eng. Robert-Gheorghe VLĂDESCU carried out an extensive research activity, which he successfully continued as a doctoral student. He was admitted to the Doctoral School, as a result of taking the admission examination at IOSUD at the University of Petroleum-Gas in Ploiești in 2017. As the scientific supervisor of the doctoral student, I inform you that so far he has taken all the exams and research reports. provided in his training program, with very good results. The theme of the doctoral thesis that is currently being prepared is "Contributions to improving the maintenance technologies of pipeline transport systems of fluid hydrocarbons in order to increase the degree of safety in operation".

On this occasion I had the opportunity to get to know him better. I should mention that, the PhD student eng. Robert-Gheorghe VLĂDESCU has shown interest, concern and permanent involvement and an adequate behavior during the years of studies, obtaining remarkable professional results.

In view of the above, I recommend the PhD student. eng. Robert-Gheorghe VLĂDESCU with all confidence and conviction, in order to participate and publish a series of specialized articles in the TUIAȘI Doctoral School Conference from 7 to 9

May 2020 in Iaşi. If you would like further information, as well as other references in the future, I am pleased to inform you at flgdinu@upg-ploiesti.ro

Ploiești, 09.02.2020
Prof. univ. habil. Dr. Dinu Florinel

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PROBLEME ÎN ASIGURAREA MENTENANȚEI SISTEMELOR DE TRANSPORT HIDROCARBURI FLUIDE PRIN CONDUCTE METALICE

(Rezumat)

Continuitatea structurală și integritatea materialului metalic propriu conductelor petroliere garantează exploatarea acestora în condiții tehnice adecvate și cu reducerea la minimum a riscurilor pe linie de mediu, ceea ce a reprezentat o preocupare permanentă și un deziderat esențial în mentenanța sistemelor de transport hidrocarburi fluide prin conducte metalice.

Materialele metalice și nemetalice, aflate în contact cu un anumit mediu, suferă în timp un proces continuu de distrugere ca urmare a interacțiunii reciproce. Interacțiunea poate fi de natură chimică, electrochimică sau de fragilizare şi aceasta face

ca după o perioadă de expunere, materialul să devină neutilizabil ca urmare a modificărilor structurale, dimensionale sau de continuitate.

Rezistența la coroziune a unui material metalic este strâns legată de compoziția și structura acestuia, de gradul său de puritate, de natura și caracteristicile mediului coroziv, de condițiile în care se desfășoară coroziunea.

În situația unei coroziuni uniforme, comportarea materialului se apreciază prin indicele gravimetric, indicele de penetrare și indicele volumic.

Protecția contra coroziunii reprezintă totalitatea măsurilor care se iau pentru a diminua sau stopa acțiunea distructivă a mediului asupra materialelor în condițiile concrete de lucru, la un cost cât mai scăzut și deplină siguranță în funcționare.

Principalele mijloace de protecție sau de reducere a intensității coroziunii sunt tratarea mediului (în sensul reducerii agresivității lui), acoperirea suprafețelor expuse coroziunii, aplicarea de tratamente de suprafață, deplasarea potențialului electrochimic al metalului în domeniul de imunitate sau de pasivizare și drenarea curenților de dispersie.

Deplasarea potențialului materialului metalic de protejat în domeniul de imunitate se poate asigura prin realizarea unei pile galvanice cu un anod activ sau prin injectarea de curent, deschizând, ca practică inginerească, calea asigurării protecției catodice aplicată echipamentelor și utilajelor aflate în contact cu un electrolit (apă, sol etc), ca cea mai modernă metodă de prevenire a pierderilor de material metalic și de afectare structurală a conductelor destinate transportului de hidrocarburi fluide.