Corrosion Protection in Hazard Reduction

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Abstract. In this paper stopping corrosion and hazard reduction were analyzed. Metal coatings and corrosion resistant improvement were studied to stop corrosion and decreasing hazard. Hydrogen absorbed and adsorbed in gas pipelines were examined. Rates of the possible reactions was derived. Hazard reduction by corrosion resistant improving was provided. The obtained results have shown how seek out parameters for corrosion control. Corrosion control expression was derived.

Keywords: Corrosion, control, hazard decreasing, parameters, hydrogen absorbed, hydrogen adsorbed.

1. Introduction

The essence methods for stopping corrosion are change material, change environment and protect material.

While these may be an oversimplification, they tell the maintenance engineer, with the assistance of the materials engineer, the steps to carry out in stopping corrosion.

In the category of changing material to minimize or stop corrosion is the practice of using a more corrosion resistance material, usually achieved by alloying or occasionally achieved by upgrading the material to a more resistant material based on reported experiments. In addition to changing by alloying, one can also change to nonmetallic materials such as plastics, with and without reinforcement, elastomers, ceramics, stoneware, glass, carbon, graphite, rubber, and wood, among other. The matter of changing material is not merely a function of selecting a material that has improved corrosion resistance, other factors such as thermal and electrical properties, ease of fabrication, strength, ease of joining, availability, and cost must be considered.

When one speaks of changing the environment to reduce corrosion, the easiest and the most obvious method is to lower the temperature. Since corrosion processes are chemical reactions, every 18 degrees decrease in temperature reduces the reaction rate by half. Thus, if one can lower the temperature, the rate of corrosivity will be retarded. In addition, atmosphere can be changed by use of gases, in the sense that some metals are corroded in the absence of air and others in the presence of air. Other environmental changes involve agitation, aeration, and velocity, all of which have a decided influence on many materials. Behind these, a fairly easily made change in some processes is that of adjusting the pH which is a measure of the acidity or alkalis of the solution.

The presence of trace additives is a change in environment which can be good or bad for certain metal systems. It is necessary to know the behavior of the metal in the system toward various additives to establish whether this is a

positive or negative effect. For example, the presence of copper ions in solution improves the corrosion resistance of stainless steels in certain environments, while the presence of copper ions in solution will cause localized pitting and attack of aluminum alloys in other solutions. There is yet the wider option of adding inhibitors which suppress the corrosiveness of the main species in the solution.

2. Metal coating and hazard reduction

Protecting the material to reduce corrosion often means isolating the metallic surface from the corrosive environment. This can be done with either organic or metallic surface coatings on the surface. Organic coatings can be thick or thin and can be either paint film or solid linings or, further, can be plastic in their form of the tape, a sheet, or a powder fused to the surface. Metallic coatings are often applied as electroplated materials, though some metals can be deposited by chemical means in an electrode less deposition similar to silvering glass to make a mirror. A metal may be coated by diffusion at moderate temperatures such as the application of zinc in galvanizing or aluminum in aluminizing or metalizing of the surface by spray application of partially melted materials. Selecting of any one of these protective methods depends on service factors, environmental condition, economics, ease of application of material, complexity of parts, etc.

In addition, one can protect the metal surface by applying an electrical potential under conditions that make the surface either cathodic or anodic, depending on the environment and the metal being protected. The more widely used of these two methods is that of cathodic protection, often applied to underground pipelines, tank bottoms, water boxes on exchangers, etc. The application of cathodic protection is sometimes done with a sacrificial anode of magnesium or zinc or by the application of an applied potential from a rectifier or battery where one users a more permanent anode of graphite or platinum-titanium.

Protective coating are probably the most widely used and, at the same time, the most controversial material employed for minimizing corrosion of steel and certain other materials. Because of its

importance, the subject of protective coating and painting is discussed later. It is important here to emphasize that it is unwise, and generally uneconomical, to try to use steel equipment with a chemically resistant coating for cottoning chemicals that are quite corrosive to the steel. This results from the fact that it is almost impossible to avoid some pinholes or holidays in the coating. Rapid attack of the steel will occur at such points, and continued maintenance attention will be required. This is the reason for the more stringent requirements on coatings for continuous immersions service such as tank linings. Such requirements include thickness, sometimes minimum sometimes maximum, number of coats, freedom from pinholes, and degree of cure.

The chemically resistant coatings, such as the baked phenolics, baked epoxies, and the air dry epoxy, vinyl, and neoprene coatings, are ideal for minimizing contamination of chemicals handled in steel equipment. They should not be used where 100 percent protection from corrosion is required. An excellent material for immersions service has been developed that consists of flakes of glass dispersed in a polyester resin. This is applied by spray to a properly prepared surface and the wet coating is rolled with a paint roller to orient the glass flakes in a plane parallel to the substrate and to provide maximum resistance to chemical attack.

Glass lined equipment is available from a chemically resistant standpoint for handling all acids except hydrofluoric and concentrated phosphoric acid, at ambient at elevated temperature, and many alkaline conditions and ambient and slightly higher temperatures. The glass lining is resistant to all concentrations of hydrochloric acid at temperatures up to 118.88°C, to dilute concentrations of sulfuric acid at their boiling points, to concentrated solutions of sulfuric acid, up to about 232.22 °C, and to all concentrations of nitric acid up to their boiling point. An acid resistant glass with improved alkali resistance is commercially available for use under alkaline conditions up to pH = 12 at temperatures of 93.33°C .

Equipment items such as tanks, pressure vessels, and reactors, pipelines, valves, and accessory equipment are available. Improved resistance to impact has been developed for the glass linings. Methods of field repair of glass linings have been developed which include the use of cover plates and plugs of tantalum in combination with resin cements and teflon.

3. Increasing corrosion resistance

All woods are effected adversely by acids, particularly the strong oxidizing acids, but they are regularly used in dilute hydrochloric acid solutions at ambient temperature. Improved corrosion resistance can be imparted to wood by impregnating the wood under pressure conditions with certain resin solutions that include asphalt, phenolic, and furan. This greatly extends the area of application of woods in corrosion services. Strong alkaline solutions, particularly caustic, generally cause disintegration and can not be used with impregnated wood. Weak solutions can be used with wood equipment with reasonably good service life.

Inhibitors are very important for corrosion of irons and other metals. The corrosion of irons and other metals in aqueous solutions can frequently be minimized or inhibited by the addition of soluble chromates, molybdates, silicates, and amines or other chemicals, singly or in combination. Such materials are called inhibitors and are generally attractive for use in recirculating systems or closed systems. They are also used in neutral or very slightly acid solutions. The concentration of an inhibitor for maximum control depends upon the solution, composition, temperature, velocity, metal system, and the presence of dissimilar metals in contact in the solution. Care should be taken in the selection and application of inhibitors, since in some instance they can increased localized attack. Although chromate treatment is widely used, it does require attention to keep concentration at the required minimum for specific environmental conditions. In addition, there is the always present danger of pollution from loss of chromate to the surrounding environment.

One of the most common uses of inhibitors is in brine systems. When calcium or sodium chloride brine is used in steel equipment, it is generally recommended that sodium dichromate be used. Where chromates can not be used, disodium phosphate is recommended for sodium chloride brines. While aluminum equipment is used in service, it is recommended that present as much sodium be used as there is chloride present.

For recirculating water systems made of steel, it has been found that 0.2 ml of sodium silicate per liter is effective in inhibiting corrosion. Sodium dichromate at 0.01 present concentration is also effective and can be used where toxicity effects are not important.

For preventing corrosion of steel in ferrous base materials, particularly in protecting machine parts and storage and equipment, the use of volatile or vapor phase corrosion inhibitors has been found to be effective. These materials are amine nitrite salts. They inhibitors are slightly volatile at atmosphere temperature, the protection obtained results from the diffusions and condensation of the vapors on the surface of the items being protected.

Cathodic protection fundamentally, has used of an impressed current to prevent or minimize the corrosion of metal, by making the metal a cathode in the system. This current is provided either by the use of rectifiers or by sacrificial galvanic anodes. Graphite, titanium, and high silicon iron are used as anodes in conjunction with rectifiers. The most commonly used sacrificial materials are magnesium, zinc, and aluminum. Cathodic protection is recognized as a proved method of control of corrosion of steel and other metals under many environmental conditions. It has been used successfully for minimizing corrosion of equipment such as buried pipeline, water storage tanks, condensers, heat exchangers, and dock piling.
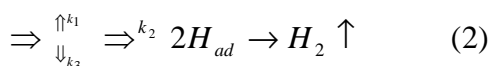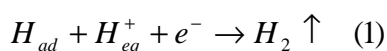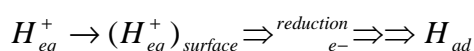
Stopping corrosion is very useful for hazard reduction and the quantitative assessment of a hazard. If corrosion occurs it can induce explosion. Damage caused by the above mentioned events comes about through two distinct processes: direct action of chemicals on

humans and the environment and indirect action of liberated energy.

4. Hydrogen absorbed and adsorbed induced cracking

The absorption of atomic hydrogen at temperature below 100 °C changes the toughness and ductility of steel, the effect increases with increasing steel strength. This can be recognized by the disappearance of the distinctive yield point and the loss of reduction of area and elongation in tensile testing.

The quantity of hydrogen H_{ab} being absorbed by metallic phase from an electrolyte solution in which hydrogen ions are discharged, corresponds only to the hydrogen gas pressure in the solution, generally 100kPa, given undisturbed equilibrium between H_{ad} and H_2 gas.

$$H_{eq}^+ \rightarrow (H_{eq}^+)_{surface} \Rightarrow^{reduction}_{e-} \Rightarrow\Rightarrow H_{ad}$$

$$H_{ad} + H_{eq}^+ + e^- \rightarrow H_2 \uparrow \quad (1)$$

$$\Rightarrow \begin{matrix} \Uparrow^{k_1} \\ \Downarrow_{k_3} \end{matrix} \Rightarrow^{k_2} 2H_{ad} \rightarrow H_2 \uparrow \qquad (2)$$

$$H_{ab} \qquad\qquad (3)$$

Reaction rates can be defined:

$$\frac{dc_{H_{eq}^+}}{dt} = -k_1 c_{H_{eq}^+} \qquad (4)$$

$$\frac{dc_{H_{ad}}}{dt} = 1/2 k_2 c_{H_{eq}^+} \qquad (5)$$

$$\frac{dc_{H_{ab}}}{dt} = k_3 c_{H_{eq}^+} \qquad (6)$$

Only when the steps involving recombination of atomic hydrogen are inhibited can an increased H_{ad} concentration and hence a higher value for H_{ab} occur.

Some substances result in a particularly high retention of atomic hydrogen on a steel surface in corrosion reactions by inhibiting recombination. They are known as promotors or poisons, and include compounds of S, P, As, Se, Te, and Sb, e.g., thiocyanates and thiosulfates, as well as CO and cyanides. They cause a considerable increase in the concentration of hydrogen absorbed in the metal, which formally correspond to an increased hydrogen pressure in the gas phase. This can give rise to considerable embrittlement of steel even under normal pressure. Apart from AsH_3, COS, HCN, and CO, above all H_2S is responsible for many cases of damage, in particular in the chemical, petroleum, petrochemical, and electroplating industries.

In the mild steels, blisters, cracks, and terraced fractures, caused by slag and sulfide lines, can occur under sufficiently high hydrogen uptake and static tensile stress below the yield point at low temperature, room temperature. This results form the formation of high pressure hydrogen in structural defects as shown in Fig. 1. Residual stress is often sufficient to generate local plastic deformation and initiate cracking.

Cracking occurs far more readily and rapidly in intermediate strength steels. In cold parts of high-pressure petrochemical plants, cracks are often found in shaped components made of heattreatable steel through the attack of condensates containing H_2S. The same applies to equipment for drilling and extracting natural gas.

Hydrogen induced embrittlement in high steels is less dependent on the occurrence of local internal hydrogen pressure zones, because they cannot induce local plastic deformation in such steels. It depends on the interaction between dissolved and mobile hydrogen and stress fields, precipitations regions, and crack tips during a local plastic deformation process.

Fig. 1. Terrace shaped fractures in natural gas pipeline caused by condensate containing H_2S

With pure molecular hydrogen, atomic hydrogen can originate on places of plastic deformation, notches, starches, by interaction between molecules and the resulting active surface of steel [19]-[21]. The absorbed hydrogen causes crack initiation and propagation. This occurs particularly under low-cycle fatigue conditions. Damage occurs, at inner marks in high pressure gas cylinders for hydrogen transport that are often filled and emptied.

A purely optical differentiation between hydrogen-induced cracks and cracks produced by anodic stress corrosion cracking is often extremely difficult.

5. Control corrosion to reduce hazard

The resistance parameters needed to select a material can be obtained in two ways, incorporating suitable test specimens in test plants or existing, not yet optimally designed production plants, and corrosion testing in the laboratory.

Both methods of corrosion testing are similar in that on the corrosive medium side a number of important parameters such as concentration, temperature, dissolved gases, impurities, solids, and the flow rate must be carefully considered. Because of the many parameters involved, when material specimens are incorporated in a test or production plant, effort should always be made to ensure that the specimens are incorporated in a test or production plant, efforts should always be made to ensure that the specimens are subjected as close as possible to operating stress. The material specimen is geared to the types of corrosion expected.

Material specimens are mostly attached to internals, for example, to an agitator or a thermometer protection tube. To avoid unwanted polarization of the specimens though contact with plant components and a subsequent incorrect measurement, the specimens are bolted with insulating sleeves. At low flow rates and low temperatures the specimens can be incorporated with the help of plastic binding or tape.

If corrosion tests in pilot plants are not possible, laboratory tests sufficiently close to practice should be carried out. These should also be carried out when operating tests do not clearly indicate the time function of corrosion processes and thus more intense corrosion conditions can complete the picture.

Three groups of variables determine the corrosion of metallic materials. material variables: chemical composition, heat treatment, and surface condition; corrosive medium variables: pH, temperature, flow rate; and potential.

In laboratory test used as the basis for material selection the biggest problem is the correct choice of these variables, which is the determining factor for simulating operating conditions.

Chemical corrosion tests focus primarily on resistance to surface and selective corrosion. In general the effect of material and corrosive medium variables can be understood with these methods. The variable potential, on the other hand, is more or less undefined and can experience time changes depending on the properties of the various partial reactions involved in corrosion. The fluctuation range of

the potentials found in practice can not be taken into account in the immersion test. Often, therefore, the results obtained in chemical corrosion testing using electrochemical methods must be further differentiated to take account of the variable potential. If the corrosion rate determined in chemical corrosion testing has little to offer, but if there is only little potential dependence it is more reliable.

By means of electrochemical corrosion tests, the dependence of corrosion on the potential can be investigated and indicators obtained as to the parameters which influence the potential. There can be fundamental differences between the results of chemical and electrochemical corrosion tests. This is due to the fact that in chemical tests the potential can change with time. This is deliberately avoided in electrochemical tests, with partly increased predictability and partial restriction of the potential practical uses, for example, in the event of strong time dependence. Dependence on the following variables is a major consideration in electrochemical corrosion tests: potential U_H in relation to the standard hydrogen electrode, current density i in relation to the geometric surface of the specimen, and time t.

Corrosion control can be expressed by the following equation (7):

Material corrosion = f(chemical composition, pH, surface conditions, heat treatment flow rate, temperature, potential)   (7)

As mentioned above, tests to determine the corrosion resistance of materials in industrial corrosive media can be performed in the laboratory, in pilot plants, and in existing production plants. With regard to the choise of locations for specimens it should be borne in mind that reactors and other apparatus may be attacked differentialy by the liquid and vapor phase of the corrosive agent and at the three phase interface of the liquid, vapor, and material. As rule, therefore, material specimens must be exposed at each of these phases.

Opportunities may exist to reduce the volume of waste catalyst by reusing the catalyst through several hydrogeneration batches, however experts disagree on the final benefit of this. The measurement of this can be made by measuring hydrogeneration efficiency versus catalyst disposal costs. Other catalysts have been explored, however their costs and effectiveness are less desirable. These catalysts have environmental problems of their own since they are heavy metal based.

Grain and metal solids is an area in which the improvements in solid waste can be made through loss control. Transport of these materials is highly mechanical, involving conveyors, elevators, pneumatic systems and trelated mechanisms. Losses tend to occur at transfer points along the conveyance system as well as at loading and unloading points barge, railcar and truck. In addition, building dust collectors, cyclones and similar air emission control devices are a constant source of grain and meal solids losses due to plugging and overflow. Of importance is that many of these points are located on building roofs, therefore the losses may go unnoticed and undetected. This situation will receive better focus in the near future due to developing regulations on control of pollution in stormwater.

6. Conclusion

In this paper corrosion protection methods were studied. Corrosion as the special type of hazard. can be controlled.

Hazard reduction by stopping corrosion was examined. Corrosion of the metallic materials determines chemical compositions, heat treatment, surface conditions, pH, temperature, flow rate, and potential.

Hydrogen H_{ab} being absorbed by metallic phase from an electrolyte solution in which hydrogen ions are discharged, corresponds only to the hydrogen gas pressure in the solution. Equilibrium between H_{ad} and H_2 gas has determined rate of corrosion.

Stopping corrosion is very significant method for hazard reduction and the quantitative assessment of a hazard, because of corrosion can induce often explosion.

This paper shows corrosion control system, and their application.

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