

Stainless steels as Corrosion Resistant Materials in Pulp and Paper Industry

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SUMMARY

Basically, the corrosion resistance of the common stainless steel is due to the presence of chromium, with other alloying elements like Nickel, Molybdenum etc., contributing specific properties. Chromium supplies the fundamental passivity by forming an inert layer of chromium oxide on the surface of the steel which resists the further corrosion and actually makes the steel stainless. If less than 12% chromium is present, the steel is not considered stainless and will rust in the atmosphere. Chromium content may be increased to a maximum of 28% depending on the capacity required to resist corrosion.

Most metals require refining to convert them from their natural state to a usable form. In one sense corrosion is a recombination with other materials to revert to a non-refined state so that a corresponding release of energy occurs. This release of free energy is the driving force in corrosive reactions.

Stainless are corrosion resistant because they are passive, which means that they have an oxide film on the surface and this film must be maintained.

Types of corrosion—Intergranular—galvanic—pitting—stress—cracking—erosion.

Practical observations of corrosion in pulp and paper industry that cover SS clad sulphate digesters, bleach plant equipment, SS Pump impellers, agitators, piping and fittings, barometric shell and leg of M.S., flue gas ductings of M.S., Recovery Boiler, causticizing plant valves, piping and fittings, chlorine gassifier piping and milk of lime tank piping at Hypo Preparation plant, and sulphuric acid pumping system at stock preparation plant are among the equipment affected by corrosion so severely in APPM that some of them had to be replaced with FRP.

INTRODUCTION

Corrosion in general corresponds to an ionization of the metal and the setting up of an equilibrium between the metal, its ions and the available electrons. Assuming the metal to be bivalent the reaction can be written.



Corrosion phenomena consists of electro-chemical reactions between an electrolyte and a metal surface and it will thus be appreciated that modifications of the surface may play an important role.

THE MECHANISM OF CORROSION IN STAINLESS STEEL

Stainless steels play a very important part in many pulp and paper processes. Stainless steels are used because they are resistant to corrosion attack in many

of the environments encountered in the manufacture of pulp and paper, and they do not contaminate or discolour the product.

Many people think of 'Stainless Steel' as a magic formula offering a cure-all for almost every problem encountered in corrosion, abrasion, or heat resisting application. This may be true to some extent, but a thorough knowledge of properties is essential to obtain the proper application for the best results. Proper application is actually selection of the most economical stainless steel that satisfactorily resisted the corrosive conditions in a specific environment. Each combination of corrodent and temperature produces a different corrosive result.

The designation of the American Iron & Steel Institute are those most commonly used for identification of wrought steel grades. These A.I.S.I. type numbers have three digits and range from the 300 series upto the 500 series.

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The steels in the 300 series are the Iron-Chromium-Nickel grades and they are the most widely used types. They are non-magnetic, austenitic, and generally not hardenable except by cold deformation. Those in the 400 series are mostly the straight Iron-chromium types of steels. They are ferritic and magnetic and are either hardenable or non-hardenable by heat treatment, depending on composition. The 500 series types are relatively low alloy steels, more closely comparable to SAE types and are not usually classified as true stainless steels by the accepted definition.

Basically, the corrosion resistance of the common stainless is due to presence of chromium, with other alloying elements contributing specific properties. Chromium supplies the fundamental passivity by forming an inert layer of chromium oxide on the surface of the steel which resists the further corrosion and actually makes the steel stainless. As more chromium is added to the steel, the capacity to resist corrosion increases. If less than 12% chromium is present, the steel is not considered stainless and will rust in the atmosphere. Chromium content may be increased to a maximum of 28%.

The second most important alloying element is nickel. Again, increasing nickel content increased resistance. In fact pure nickel is exceptionally resistant to some environments. Molybdenum is often used in pulp & paper mill alloys to reduce the tendency of acidic environments to produce pitting type corrosion.

A necessary alloying element is carbon which is useful in producing hardness. However, Carbon consumes 17 times its weight in chromium to form chromium carbides, so carbon must be carefully balanced in the composition to achieve the desired properties of the alloy.

MECHANISM OF CORROSION

Most metals require refining to convert them from their natural state to a usable form. In one sense corrosion is a recombination with other materials to revert to a non-refined state, so that a corresponding release of energy occurs. This release of free energy is the driving force in corrosive reactions.

The rate of change in free energy determines whether or not a corrosion reaction will start spontaneously. The rate of change is related to the electromotive force (emf) of the corrosion reaction and emf can be calculated from the free energy change and vice-versa. The 'Quarter-Volt-Criterion' states that corrosion will not occur unless the emf is atleast 0.25 volts. The emf can get as high as 1.8 V.

Usually corrosion is an electrochemical reaction, involving anodic and cathodic parts. Each part involves an oxidation-reduction system with its own reversible potential. An electrochemical reaction requires that an electrolyte be present to carry a current. The electrolyte may be any solution from moist air to strong acid. Corrosion will not occur in a totally dry environment unless high temperatures are involved. In the latter case the temperature

increases ion-activity to the point where ion exchange can occur without an electrolyte.

Stainless Steels are corrosion resistant because they are passive, which means that they have an oxide film on the surface and this film must be maintained. In today's industrial usage, we have become accustomed to a classifying corrosion into five different groups.

1. Intergranular
2. Galvanic
3. Pitting
4. Stress Cracking
5. Erosion.

INTER GRANULAR CORROSION

Intergranular corrosion is a selective attack on the grain boundaries of metal or closely adjacent material without appreciable attack on the grains themselves. This attack will destroy the mechanical properties of the metal for the depth to which it has progressed. It is possible for entire metallic grains to fall out of a place of steel.

Intergranular corrosion in austenitic stainless steel is usually caused by the carbon present in the steel precipitating out of solution during slow cooling. As the carbon collects, it combines with chromium to form chromium carbides. Sufficient chromium is absorbed in the carbides so that the chromium-depleted areas lose their ability to form a passivating film which interferes with the electron flow, and hence lose their corrosion resistance. Any time an austenitic stainless steel is heated above approximately 1200° C, even momentarily, or held for a time at temperatures over about 800° F, and cooled slowly, the carbon precipitation occurs. This can occur during solidification, welding or in process applications. Fortunately the carbon and chromium may be redissolved in the steel by heat treatment, eliminating the carbides and restoring the chromium to a desirable condition. Heating to 1900-2000° F will dissolve the chromium carbides and rapid cooling will maintain the dissolved condition.

Intergranular corrosion can also be prevented by lowering the carbon content to 0.03% rather than the usual 0.08% in 18-8 type steels.

GALVANIC CORROSION

Galvanic corrosion can occur any time dissimilar metals are in electrical contact while immersed in an electrolyte.

When electrical contact is made, a current flow begins. The more active metal of the galvanic couple is the anode. Here, the reversible potential shifts to increase the oxidation reaction (formation of metallic ions and electrons) and decrease the reduction reaction. On the more noble metal, the potential shift is in other direction and the current flow produces cathodic protection.

If the difference between the metals in the galvanic series is large enough, the more noble metal may act as a cathodic, but not be affected by the reaction.

This property of galvanic corrosion makes area relationships important. Since it is current density that determines corrosion rate, it is unwise to combine a small area of the cathodic member, while the reverse relationship is generally not troublesome.

As long as stainless steels are passive with an unbroken surface film of chromium oxide they will not be attacked when coupled with other metals in any solution. If the stainless steel loses its passivity, for instance by abrading away the chromium oxides film, severe attack can occur. In this case the adjoining passive surface serves as a cathodic to the active anode area.

PITTING CORROSION

Pitting corrosion is probably the most prevalent type of corrosion found in Pulp & Paper Mills. By definition pitting is corrosion confined to a small area as compared with a whole surface. However, the pits may be small or large, few or numerous, smooth or rough empty or filled with corrosion products.

The primary cause of pitting corrosion is the formation of an electrolytic cell. In this cell an emf is developed which is large enough to initiate the anodic cathodic corrosion reaction. Ion concentration pitting can be minimized by careful design and fabrication to eliminate crevices, by polishing the exposed surfaces of equipment and by passivating the components involved.

Another form of Ion concentration pitting is caused by impingement of a stream of solution on a surface. The flushing action of the stream can remove ions to the point where the area becomes anodic and corrosion will occur. In the ion concentration cell the corrosion occurs outside the pit. The active passive cell is a result of the effect of oxygen on the passivity of stainless steel. A high oxygen concentration promotes the concentration of heavy chromium oxide film, increasing the cathodic potential of the surface. An area shielded from oxygen may lose its oxide film and becomes active. As soon as the difference in potential between the active area and the passive area becomes large enough corrosion begins.

Any deposit on a stainless steel surface sets up conditions favourable for cell formation. The area outside the deposit is continually replenished with oxygen by movement of the solution. The area under the deposit cannot be replenished with oxygen because it is shielded from the solution and it becomes anodic. If corrosion product remains in the pit, the situation gets worse and worse, since oxygen can be completely depleted under the deposit.

The same factors which minimise Ion concentrations tend to reduce the formation of deposits. In addition periodic cleaning is useful. Metallurgically the addition of molybdenum is particularly beneficial in reducing pitting. For instance, with acidic sulfite liquors, it is necessary to maintain a higher level of molybdenum in 18-8 type alloys than is normally available silicon additions are also beneficial, but carbon, selenium and titanium are detrimental.

STRESS CORROSION

Corrosion by itself will not cause cracking but only in combination with stress. The crack initiates at a point on the surface where stress is sufficient to disturb the surface film. When stress is present, the corrosion crack proceeds at a far higher rate than corrosion would proceed without stress. Complete removal of the stress will usually completely stop the growth of the crack.

A great deal of work has been done to develop preventive measures. One remedy is to produce cast austenitic alloys so that delta ferrite pools occur in the metallurgical structure of the steel. These ferrite pools act to stop cracks before they have any appreciable depth. Thus, the crack stopping ability is available only on the cast 18-8 type steels. A second remedy is to use materials so corrosion resistant that corrosion does not occur, even under stress. Since the austenitic stainless steels are more prone to cracking in presence of chlorides, the high resistance of titanium to chlorides makes it a good choice. Alloys containing more than 30% nickel such as alloy 20 CB3, are not subject to stress corrosion.

EROSION CORROSION

Erosion-corrosion is, as the name implies, corrosion resulting from erosion of the surface. We have repeatedly seen that a chromium oxide film on the surface is necessary for a steel to be passive. If the film is removed, the surface in that area becomes anodic to the passive areas and corrosion occurs. Erosion very effectively removes the oxide film. Erosion may be caused by high-velocity streams of solutions or vapors particularly when the high velocity stream contains solids or is turbulent or impinges on a surface cavitation is a particularly damaging form of erosion.

The best cure for cavitation erosion-corrosion is proper design, since design improvement is often impossible, substitution of more corrosion resistant and harder steels is necessary. One economical answer is the use of precipitation hardening steels, such as 17-4 PH. 17-4 PH is between T-304 and T-316 in corrosion resistance, but may be hardened to above 400BHN.

The above has been a brief review of some of the most common causes of corrosion in stainless steel.

SOME OF THE CORROSION PROBLEMS THAT ARE ENCOUNTERED IN PULP AND PAPER INDUSTRY

In Pulp and Paper Industry, the corrosion is predominant in sections like digester house, bleach plant, evaporators, recovery boiler, causticizing, loading and sizing chemicals handling etc. While the effect of corrosion can not be neglected in other sections like blow-heat recovery, brown stock washing, screening, black liquor oxidation, boiler house, paper machine head boxes, stock preparation sections etc.

DIGESTER HOUSE

Cooking of chips with white liquor containing chemicals like sodium hydroxide and sodium

sulfide as active alkali in digesters (Pressure vessels) takes place at elevated temperatures as high as 165°-175°C, and as such digesters are subjected to corrosion accelerated by the elevated temperatures.

Temperature has a marked effect on corrosion with rate of corrosion increasing with rise in temperature. The temp. effect on rate of corrosion can be expressed in terms of simple Arrhenius equation.

$$\text{Log } K = A + \frac{B}{T}$$

Where 'K' = the rate of corrosion
'T' = absolute temperature

A and B are constants.

Like most of the chemical reactions, two to three fold rate enhancement for every 10°C rise in temperature is observed in corrosion reaction also.

It is interesting to note that shell wall thickness of all digesters were measured in APPM it was found that two digesters after in operation for about 10 years, are found with reduced shell wall thickness to 18 mm from original 25 mm at the bottom cone portion of the digesters. This type of metal wall loss is also experienced by other mills. This leads to think for higher metal thickness of digester shell probably for hardwood cooking, where higher cooking temperature and sulphidity would be required.

BLEACH PLANT

In most of the Indian Paper Mills, bleaching sequence followed is CEHH with 'C' for Chlorination, 'E' for Extraction with alkali and 'HH' for Hypo Oxidation spread over two stages. Out of the four stages of bleaching, it is observed that chlorination stage is posing more corrosion problems with even SS-304 for pump impellers, agitators etc. SS-316&317 for pipe lines, fittings etc., and even rubberlined surfaces for chlorine mixers etc., are subjected to severe corrosion. This experience made it imperative in APPM to go for sound alternative material of construction like FRP (Fibreglass Reinforced Plastics) in its new bleach plant of 150 TPD, which was installed and commissioned two years back.

It is worth mentioning that how the problems arising out of FRP Piping are encountered in APPM. Though the FRP piping posed no corrosion problems some of the pipe lines were found to have collapsed in not withstanding even slight surges of vacuum caused by syphoning action due to failure of stock pumps. With the result, some of the FRP Pipelines which are critical for running of the plant had to be replaced by SS Piping. However, credibility of FRP as a competitive and competent anti-corrosion materials of construction remains unquestionable, but in the light of the above experience, this can be stated that if proper care is taken in the design of FRP Pipe line to withstand vacuum stresses, FRP would stand far superior to SS of all grades and its encroachment in pulp and paper industry in particular and process industry in general world go unmatched.

EVAPORATORS

In this section it is observed that barometric condenser shell and barometric legs which are of MS Construction are getting corroded with pittings. This may be attributed to incomplete evacuation of non condensible gases of corrosive nature from the vapours of evaporators. This problem can be mitigated if barometric condenser shell and legs are replaced with FRP and designed properly to withstand high vacuum as high as 26" HG.

RECOVERY BOILER

In this section it is found that flue gas ductings of MS are getting corroded, so also E.S.P. (Electrostatic Precipitator) discharge handling system consisting of screw conveyor, distributor and discharge chute. It is also observed that the air heaters installed at recovery boiler are affected by corrosion with both shell and coils getting corroded with number of pittings.

CAUSTICIZING SECTION

It is one of the major problems that paper industry facing in causticizing section, that causticizer overflow lines of M.S. Construction are getting corroded with pittings and thus calling for frequent repairs/replacements.

In clarifiers and mud washing system O.D.S. Pump delivery lines which are of MS Material are getting subjected to severe corrosion. Here, with the experience gained in APPM cast iron proved better than MS.

Most of the plug valves that are used in causticizing section are affected by corrosion with pittings and causing frequent leakages. When this matter has been referred to the manufacturers of valves, they are recommending Alloy plug valves which are being tried.

HYPOCHLORITE PREPARATION PLANT

In this section M.O.L. (Milk of Lime) tank piping of M.S. is subjected to corrosion due to presence of wet chlorine in MOL Tank, whenever chlorine from lines is vented (drained) into the tank. Here M.S. piping can be replaced with FRP. APPM has taken timely care in going for FRP reactors for hypochlorite preparation where the corrosion is prohibitive.

SULPHURIC ACID HANDLING

Sulphuric acid pumps: In this section, alarming problem that has been faced is on sulphuric acid pumps which are often affected, despite the material of construction SS 317. Now this problem is sought to be overcome by going in for compressed air pumping system in APPM.

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