

A Brief Discussion on Corrosion Fundamentals and Review of Corrosion Problems in World Paper Industry

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SUMMARY

Corrosion is one of the responsible factors for equipment failure. The paper briefly touches on factors controlling corrosion, types of corrosion, the chemical composition of some important alloys used in industry for corrosion resistance, chemical properties of FRP, properties of corrosion resistant refractory concretes and laboratory and field tests on corrosion.

The paper also discusses corrosion aspects of specific areas in pulp and paper industry, viz. digesters, bleach plant, evaporators, recovery boiler, paper machine and effluent treatment.

INTRODUCTION

Corrosion may broadly be defined as destruction of a metal by electro-chemical or chemical action of its environment. Under ordinary conditions of exposure the corrosion products comprise mainly oxides (more or less hydrated), carbonates and sulfides.

Some established facts regarding corrosion are :

(a) both moisture and oxygen are necessary for corrosion in most cases, (b) the initial rate of corrosion is rapid, slowing as a protective film forms, (c) increased rate of motion increases corrosion in water upto a certain velocity, the rate however dropping when strong protective films are formed, (d) dissimilar metals in electric contact accelerate corrosion of the anodic metal, (e) the composition of ordinary iron and steel has little or no effect on their relative rates of corrosion under water. Under these conditions the particular ferrous metal usually is not so important as environment, (f) variation in the concentration or composition of a solution in contact with a metal tends to localize corrosion and (g) surface films are important in controlling the rate and distribution of corrosion.

FACTORS CONTROLLING CORROSION

The primary factors having to do with the metal itself are : (1) Effective electrode potential of the metal in solution, (2) Chemical and physical homogeneity and texture of the metal's surface, (3) The metal's inherent ability to form an insoluble protective

film and (4) Overvoltage of hydrogen on the metal surface.

The secondary factors, usually more important than the primary factors, are : (1) hydrogen ion activity (pH) in the solution, (2) effective supply of oxygen in the solution adjacent to the metal, (3) distribution of available oxygen on the metal surface, (4) specific nature, concentration and distribution of other ions in the solution, (5) effective flow rate of the fluid past the metal surface, (6) presence of solid particles (dirt), or a coating of any kind, as mill scale, on the metal surface, or contact with other conducting material in the presence of an electrolyte, (7) temperature, (8) whether the metal is under static stress or cycles of alternating stress (the so-called corrosion fatigue), (9) the ability of the environment to build up protective films on the metal, (10) biological influences and (11) restraining or preventing of corrosion reaction by inhibitors such as chromates, silicates and carbonates in water.

While all the above factors are important under some conditions, the usually dominating factors are moisture in air and dissolved oxygen in water.

TYPES OF CORROSION

It is important to recognise the various forms of corrosion in order that the available information can be applied effectively to overcome corrosion problems. The usual types of corrosion are (a) General corrosion (which causes the greatest amount of damage to metals), (b) Localised corrosion (pitting and crevice corrosion come under this category), (c) Stress corrosion cracking (corrosion fatigue is a type of stress corrosion), (d) Hydrogen blistering and cracking (experienced in steel equipment handling solutions containing hydrogen sulphide), (e) Intergranular

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corrosion (due to precipitation of chromium carbide on austenitic stainless steels), (f) Galvanic corrosion based on the difference in the e.m.f. of the metals), (g) Erosion corrosion (occurring in liquor streams containing solids), (h) High temperature corrosion (due to oxidation and sulphidation) and (i) Biological corrosion (caused by anerobic sulphate reducing bacteria).

LABORATORY AND PLANT CORROSION TESTS

In the selection of material for the construction of a chemical plant, resistance to the corroding medium is usually the determining factor because the choice would otherwise fall automatically on the cheapest material mechanically available. In this context, laboratory tests help in arriving at the quickest and satisfactory means of arriving at a preliminary selection of the most suitable materials to use. However, the laboratory tests are of limited value in as much as these tests do not reproduce the actual conditions of service. Hence, the need for field tests in plant atmosphere.

MEANS OF COMBATING CORROSION

The usual means to combat corrosion are: (1) selection of proper material, (2) proper design considerations, (3) alteration of environment, (4) use of inhibitors, (5) cathodic protection and (6) the application of non-metallic coatings and linings.

CORROSION IN PULP & PAPER INDUSTRY

Corrosion problems experienced in digesters, evaporators, recovery boiler, bleach plant, paper machine headbox, suction press roll and environmental control in pulp and paper industry, are discussed separately.

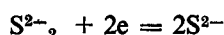
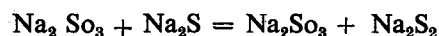
DIGESTERS

Traditionally kraft digesters were constructed of carbon steel plate containing a minimum of silica. For effective corrosion resistance, pulp mills are now turning to clad plate with a lining of Type 304 stainless steel.

Heat-exchanger tubes were previously of Ferritic 13 per cent chromium steel, type 410. However, with the use of higher sulphidity liquors, there has been a shift to use 304 steel. However, austenitic 304 steel cannot effectively resist chloride attack. Stress corrosion appears in these steels under tensile stress when in contact with a solution containing chlorides at temperatures above 100° F. This problem is solved by 3RE60 whose high molybdenum content, increased silicon and low carbon provide high resistance to general corrosion, pitting, and intergranular corrosion. The composition of 3RE60 is given in Table 1.

It is reported that thiosulphate (4) in the cooking liquor considerably accelerates corrosion, probably

due to the following reactions:



The corrosion of steel in white liquor appears to consist of an anodic dissolution of ferrous ions, which are precipitated in the solution as ferrous sulphide, while an equipment amount of polysulphide ions reacts with the excess electrons on the corroding steel surface. Yet, polysulphide in high concentration rather inhibits the corrosion probably by anodic polarisation (passivation). The digester corrosion is virtually absent above 120°C, possibly because of the decomposition of polysulphides at higher temperatures. Normal rates of corrosion are 0.3-0.6 mm per thousand cooks (less than 1 mm/year) but rates as high as 1-3 mm/1000 cooks or upto 7 mm/year were also reported.

It is found that the necessary current required to achieve passivation in kraft digesters (anodic protection) is strongly reduced by (a) increasing the proportion of black liquor (b) change from indirect to direct steam (c) change from non-oxidised to oxidised black liquor and (d) reduction of the concentration of non-hydrolysed sodium sulphide.

EVAPORATORS

Choice of steel for the tubes of multiple effect evaporators depends on sulphur content, black liquor velocity, viscosity, etc. and other operating conditions. Experience shows that stainless steel is generally to be preferred to carbon steel. At moderate sulphur concentrations, type 410 gives good service. However, at the present high level of sulphidities, stainless steel type 304 or 304L is recommended, particularly for the effects working with the heaviest liquor. Condensate condensers of 304 stainless hold up well.

RECOVERY BOILER CORROSION

Alarming reports of severe gas side corrosion were received in Scandinavia, which might have been due to higher sulphidity levels in Scandinavia than in North America. To minimise corrosion, the furnace tubes in the lower part of the furnace were flame sprayed or clad welded. The flame spraying was made with aluminium or stainless steel. The clad welding of carbon steel tubes has been successfully applied in some boilers in Finland. The method is usable for shop welded tubes and to ensure that the analysis of the clad welded material is of 18 cr-8 Ni type, one has to use over alloyed electrodes and a careful welding procedure.

If the corrosion rate for certain alloyed steels is less than 0.1 mm/year, a thickness of the alloyed steel of 1.5 mm outside the carbon steel tube would be sufficient to protect a recovery boiler during fifteen years of operational life. This will hold true at the present drum pressure of 1000-1300 PSI and 30-35% levels of sulphidity. Laboratory tests have

shown that superheated steam temperature could be raised to 500–520°C, using chromium alloyed steels, from the present levels of 450–480°C.

At temperatures less than 400°F, the effluent gases from the recovery furnace are quite aggressive and corrode cut the induced draft fans about every two years, despite the application of organic coatings and other protective measures. Corrosion of the heavy, high speed fan components created a number of problems. For example, uneven loss of metal from blades unbalanced the rotating assemblies and caused heavy vibration in the fans. Various metals, plastics and refractories were tried to replace carbon steel. Only Hastelloy alloy C-276 and titanium stood in the environment. Titanium was eliminated due to the problems of welding to carbon steel. Also, Hastelloy alloy C-276 offered higher impact strength. The rotor and shaft were clad with 0.044 inch Hastelloy alloy C-276 sheet. After its installation, for the last six years, the rotor required neither cleaning nor balancing.

BLEACH PLANT

Corrosion is most severe in chlorine and chlorine dioxide towers and in washers and other equipment handling the highly acid materials and effluent from the towers.

At the inlet to the mixer where gas and pulp are mixed, the pipe carrying chlorine should be of lead or abonite. Pipe carrying chlorine dioxide into the mixer may be of titanium or of an approximate plastic. For the mixer housings and blades, 317L, Hastelloy C, titanium, or 2RN65 are recommended. The top cover and top scraper of the towers are usually of steel clad with titanium. After treatment or between treatments, the pulp is carried to washers in piping of 316 or 317 or glass fiber reinforced plastic.

Use of type 316L or type 317L stainless steel for the washer cylinder and wire cloth has not been entirely satisfactory. Corrosion is particularly severe where the pH is below 3.1. But even at higher pH values, pitting, crevice and stress corrosion are quite common. As a result there is premature failure of the screen backing wire, washer drums and screen banding.

Recent developments in bleaching technology resulted in an effluent of only 1600 US gallons/ODT of pulp in bleach plant. However, in reducing the volume of water, the chloride ion concentration rises from 1,000 to 11,000 ppm and pH falls from 1.9 to 0.8. In these highly corrosive solutions, the bare minimum quality of steel that may be used throughout the pulp washing system will be type 317-ELC with molybdenum concentration greater than 3.9%. The use of more highly resistant stainless steels of the 17 cr. 24 Ni and 4.7 Mo low carbon type will increase. The introduction of titanium and plastics will be the answer for some equipment.

PAPER MACHINE

Based on an exhaustive study of paper machine

headboxes, the following recommendations were made to minimise headbox corrosion :

- 1) The growth of slime and the accumulation of deposits must be properly controlled, e.g. by using slime killers efficiently and by maintaining the headbox showers in good condition.
- 2) After any repairs done by welding within the headboxes, the repaired area must be ground and polished.
- 3) Passivation must be done before initial start-up, after repairing and whenever there is reason to assume that there might be local activation of stainless steels.
- 4) Rectifier drive motors must be properly separated and insulated from the headboxes to prevent stray currents from entering the headboxes.
- 5) The temperature of the stock should be lowered to 110°F side and pH raised to 5.0, if it is compatible with operation.
- 6) The chloride and sulphate contents should be lowered as far as possible.
- 7) In case of relining, 316L stainless steel is recommended in place of 304 or 304L.
- 8) Cathodic protection is possible and would require little current to obtain a cathodic polarisation of 0.1–0.2 V.

SUCTION ROLLS

The most desirable characteristics of a suction roll material are considered to be high corrosion fatigue strength and high structural stability. 3 RE60 is a ferritic austenitic stainless steel which in rolled and welded condition gives very suitable properties for this application.

Suction holes must be kept open to prevent a build up of fibers and eventual plugging. This condition can lead to crevice corrosion, loss of bond and inception of cracks in the metal.

Service life evaluation of suction rolls depends on the proper correlation of calculated alternating stress values with the available corrosion fatigue data. The corrosive nature of the particular operating environment, the probabilistic nature of fatigue data, uneven loading, increases in stress concentration due to notch effects, and residual stresses arising from the fabrication process must be considered.

Alkaline felt cleaners have much less effect on the failure of suction press rolls than do the acid felt cleaners. Also, making the inner surfaces of suction roll holes smoother by gun drilling or the new Sandh-usky SDH method reduces the chances of getting corrosion fatigue cracks.

POLLUTION ABATEMENT (CLOSED LOOP MILL)

With the tendency to close white water systems, there is a continuous build up of solids, especially the chlorides. In view of this, in kraft mills using displacement bleaching and closed white water systems high molybdenum containing steel should be used

in washing and screening departments to reduce the risk of pitting by chlorides.

The most severe conditions occur in the bleach plant where, due to the extensive use of chlorine dioxide and the high concentration of filtrates even high alloy stainless steel will be severely attacked. In the displacement bleaching tower, it is therefore customary to use 100 percent titanium for the upper part of the central shaft and the diffusers. Hastelloy 'C' is used for the lower part of the shaft, tower pockets and distribution nozzles. Tanks and piping are made of special fibreglass reinforced plastics, or are lined with these materials.

In sulphite mills and soda-oxygen pulping operations where no chlorides are expected to enter the cooking liquor circuit, the usual conventional alloy steels can be used.

CRITICAL CONCENTRATION:

The chlorides being introduced into the kraft black liquor in the close cycle kraft pulp mill reach a critical concentration above which the corrosion increases rapidly. It is therefore advisable to keep the chloride input as low as possible. Fortunately, at the high pH in spent kraft liquor, the corrosive attack by chlorides is moderate. It is therefore possible to cope with the problem by using higher alloy steel only in the evaporator tubes.

The risk of corrosion is far greater, where organic or inorganic deposits can build up. Underneath the deposits the corrosion attack could be serious.

When evaporating spent sulphite bleach plant filtrates as proposed earlier, the low pH-range together with small amounts of chlorides suggests the application of high alloy steels. The first evaporator plant installed for this purpose in a German sulphite pulp mill has been built entirely of titanium in order to avoid the corrosion risk.

Several investigations have been carried out recently to define the corrosion to be expected in the recovery boiler. Laboratory tests show that in the reducing zone of the furnace the effect of chlorides on alloy steel (18 Cr 8 Ni) is very small. Even under superheater conditions the presence of sodium chloride in flue gas resulted in only moderate corrosion of carbon and alloyed steels. Normal carbon steel shows about the same rate of corrosion as the stain-

less steel when exposed to boiler atmosphere containing chlorides.

Very severe corrosion problems are to be expected in the flue gas scrubber at the exit of the recovery boiler. In this scrubber hydrochloric acid, sulphuric acid and sulphur dioxide are present and plastics or titanium are the preferred materials of construction.

In sulphite recovery boilers and in the boilers burning the spent liquors from the soda-oxygen process the conventional materials of construction could be used, because no chloride would be introduced from the bleach plant.

In general higher concentration of corrosive solutions are to be expected in effluent-free pulp mill operations. Corrosive ions such as chlorides are introduced into the system with fibrous raw materials, chemicals and water and in the course of recycling will rise in concentration until a steady state is reached (that is, when the input balances the system losses). This fact demands the use of much higher alloy steels than hitherto used. By the proper application of these materials the corrosion problems can be solved, but at a price.

CORROSION RESISTANCE OF REINFORCED PLASTICS

More than 90% of reinforced plastics are thermosets and more than 90% of these are polyesters. Table 2 lists the chemical properties of FRP to weak and strong acids, weak and strong alkalies and organic solvents. Reinforced plastics offer properties of corrosion resistance and strength and competitive in cost. These could be advantageously used at several locations in pulp and paper industry.

CORROSION RESISTANT REFRACTORY CONCRETES

Corrosion resistant refractory monolithic linings are now available for both new and existing installations for separators, precipitators, lime kiln scrubbers, chlorine scrubbers, etc. Table 3 compares three typical corrosion resistant refractory concretes. These products are of new generation taking the place of acid proof brick and tile which have been the standard materials for corrosion protection. These refractory concretes are now available over a pH range of 0 to 9 and withstand temperatures upto 955° C.

TABLE-1
CHEMICAL COMPOSITIONS (NOMINAL) OF SOME IMPORTANT MATERIALS (%)

AISI/SANDVIK	C	Mn	Si	Ni	Cr	Mo	Cu
	max						
304	0.08	2.0	1.0	8.0-10.5	18.0-20.0	—	—
304L	0.030	2.0	1.0	8.0-12.0	18.0-20.0	—	—
316	0.8	2.0	1.0	10.0-14.0	16.0-18.0	2.0-3.0	—
316L	0.030	2.0	1.0	10.0-14.0	16.0-18.0	2.0-3.0	—
3R64 (317L)	0.030	1.75	0.45	14.5	18.5	3.5	—
2RN65	0.020	1.75	0.45	24	17.5	4.7	—
2RK65	0.020	1.75	0.45	25	19.5	4.5	1.5
3RE60	0.030	1.5	1.65	14.7	18.5	2.7	—

TABLE—2
CHEMICAL PROPERTIES OF FRP

Resin system	Weak acids	Strong acids	Weak alkalis	Strong alkalis	Organic solvents
THERMOSETS					
SMC (polyester)	G-E	F	F	P	G-E
BMC (polyester)	G-E	F	F	P	G-E
Phenolic	F	P	F	P	F
Diallyl phthalate	G-E	F	G	F	G-E
Melamine	G-E	P	G-E	E-F	G-E
THERMOPLASTICS					
Acetal	F	P	F	P	E
Nylon	G	P	E	F	G
Polycarbonate	E	G ¹	G	F	P ³
Polyethylene (HD)	E	G ¹	E	E	G ⁵
Polypropylene	E	G ¹	E	E	P ³
Polystyrene	E	G ¹	G	G	P ³
Polysulfone	E	E	E	E	G
PPO (modified)	E	E	E	E	G ⁶
ABS	E	G ¹	E	E	P ⁴
SAN	G	G ²	G	G	P ⁴
Polyester (thermoplastic)	F	P	P	P	G-E
Polyphenylene sulfide	E	E	E	E	
Polyvinyl chloride	E	E	E	E	G-E
Urethane elastomer (Thermoplastic)	F-P	P	F-P	P	G-E

Notes on chemical properties :

E = Excellent P = Poor G = Good F = Fair

- (1) Attacked by oxidizing acids
- (2) Disintegrates in sulfuric acid
- (3) Soluble in aromatic and chlorinated hydrocarbons
- (4) Soluble in ketones and esters, aromatic and chlorinated hydrocarbons
- (5) Below 176° F (80° C)
- (6) Softens in some aromatic and chlorinated aliphatics. Resistant to alcohol.

TABLE—3
COMPARISON OF TYPICAL CORROSION-RESISTANT REFRACTORY CONCRETES

Property		Acidproof concrete	Modified silicate	Light weight
Compressive strength (7 days), (ASTM C-396)	psi	1800-3000	3500-4000	2800-3200
Tensile strength (7 days), (ASTM C-307)	psi	420-450	300	400-450
Flexural strength (7 days), (ASTM C-580)	psi	450	1360	550
Modulus of elasticity, (ASTM C-580)	psi	2.32×10^6	1.4×10^6	1.06×10^6
Co. ef. of thermal expansion, in./in./°F (ASTM C-228)		7.1×10^{-6}	7.5×10^{-6}	7.1×10^{-6}
K factor, Btu/ft ² /in./in./°F (ASTM C-177)		10.56	8.3	4.9
Water absorption, (ASTM C-413)	%	6.3	1.25	1.25
Shrinkage, % (ASTM C-531)		0.4	0.75	0.36
Density,	lb/ft ³	168	135	98