Corrosion Failures in Industries: Some Case Studies

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One of the major obstacles in industries is premature failure of an important metal component due to corrosion. The environmental conditions encountered in an industry are often quite complex and the causes for failure of metal components deserves a thorough investigation, the results of which greatly helps in prolonging its life, or in selection of a more suitable material of construction.

Corrosion and selection of materials of construction plays a vital role in the ultimate production rates in various industries such as fertilizers, chemical, petrochemical, and power plants. Considerable time and energy can be saved if every case of a premature failure is thoroughly investigated by the corrosion engineers and a proper remedy suggested.

Among the various methods generally employed for corrosion prevention in the industries are : (i) Selection of the correct material of construction, keeping in view the environmental conditions and other chemical and physical properties. (ii) Protection by a metallic or non-metallic anti-corrosion coating. (iii) Cathodic or anodic protection. (iv) Use of non-metals such as plastics, glass, and ceramics. (v) Proper design of the equipment.

Some of the corrosion failures referred by the industries and investigated in the National Metallurgical Laboratory, are discussed here.

I. Corrosion Problems from Casustic Soda Industry

(1) Corrosion of Nickel Tubes

Nickel tubes were used for concentrating 45% caustic soda solution and were heated externally by steam. The tubes started corroding from the steam side and developed leaks within 2 to 3 years (Fig. 1). The evaporators were of multiple effect type and the tubes corroded mostly in the first effect and to a slight extent in the second. The nature of corrosion was localised and pitting type.

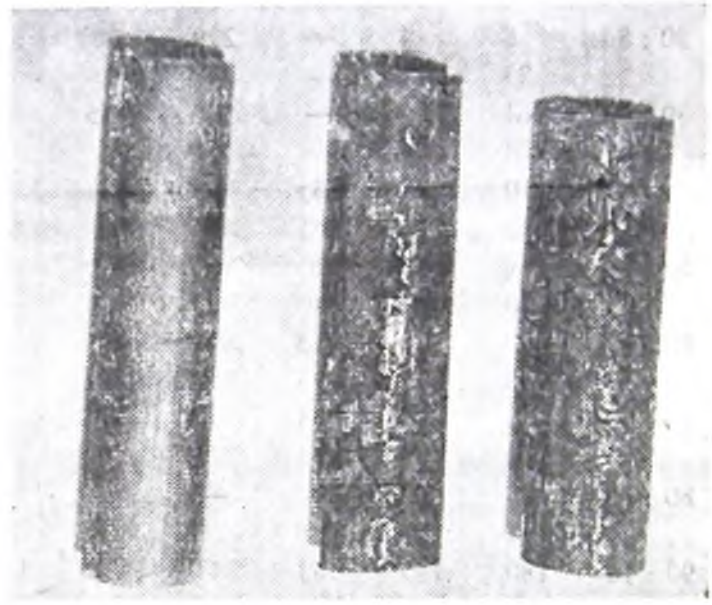


Fig. 1 : Corroded nickel tubes in the steam chest in caustic soda evaporators.

Nickel is a resistant material to pure steam even at higher pressures and temperatures, but the presence of impurities such as carbon dioxide and oxygen can promote attack. Laboratory tests conducted on nickel confirmed that mixtures of carbon dioxide and air/oxygen in distilled water or steam were corrosive to nickel. It was more so when the ratio of CO_2 to O_2 was about 63 : 40 (see Tables I and II). These tests indicated that steam contaminated with carbon dioxide and oxygen was severely corrosive to nickel at such high pressures and temperatures

It was recommended in this case that contamination of steam with carbon dioxide and air should be avoided.

(2) Corrosion of Cast Iron Pots

Cast iron pots are generally used for heating the 50% caustic soda solution and subsequent fusion of

caustic soda up to 500°C. Grey cast iron has moderate resistance to caustic soda and is still being used on account of low cost and easy availability.

Table I Corrosion of Nickel in Distilled Water, Saturated with CO_2 and air.

Test soln CO_2 : air	7 days tests Corrosion rates in mg/dm²		15 days tests Corrosion rates in mg/dm²		30 days tests Corrosion rates in mg/dm²	
	1st set	2nd set	1st set	2nd set	1st set	2nd set
20 : 80	8	4	—	299	28	
	23	—	—			
30 : 70	Nil	14.4	—	200	85	
	Nil	45.8	—			
40 : 60	210	238	483	705		
	225	210	465	608		
50 : 50	200	213	465	985		
	190	260	440	620		
60 : 40	200	190	415	890		
	218	183	393	860		
70 : 30	180	148	368	735		
	180	155	365	775		
80 : 20	178	—	—	—		
	193					
90 : 10	180	115	363	347	434	419
	180	110	367	334	523	381
100 : 0	152	112	—	—	—	—
	142	206				

Table II Corrosion of Nickel Tubes by Steam Condensate

Medium	Loss in wt. (gms.)
1. CO_2 + air	0.2162
2. CO_2 only	0.1300
3. Only air	Negligible
4. Steel plate in direct contact with Ni tube (CO_2 + air)	0.1675
5. Steel plate without touching Ni-tube (CO_2 + air)	0.1028

In one case, these crucibles started cracking within a short period. Laboratory examination of the failed pieces revealed that the attack penetrated more are less perpendicular to the surface and also followed the graphite flakes (Fig. 2). It is known that at higher temperatures, concentrated caustic soda can attack cast iron. Graphite distributed in the cast iron in flaky form appeared to have promoted the attack by absorbing caustic soda along the flakes/metal interface. Morever, there is the possibility of graphite reacting with caustic soda above 500°C which can further accelerate the attack. The penetration of attack at right angles to the surface occurred due to the alternate and uneven heating of the pots. Sulphur which is generally added to caustic soda to improve the appearance had an effect of promoting corrosion. Sodium nitrite which is also added for the same reason showed no effect. It was suggested in this case that uneven and alternate heating and cooling should be avoided to eliminate the attack. The presence of graphite in cast iron in the form of flakes was considered undesirable in this respect. Nickel cast irons have considerable resistance to caustic soda at such high concentration and temperatures and should be adopted if long life is to be expected.



Fig. 2 : Microstructure of corroded cast iron in fused caustic soda showing attacked graphite flakes. × 100.

II. Soda Ash Manufacture

Corrosion of Cast Iron Spun Pipes :

Cast iron pipes are used to cool ammonia from 70° to 60°C by passing sea water through the pipes in soda ash manufacture. It was reported that the cast iron pipes from one lot lasted for 5 years while from the

other lot the pipes corroded heavily within two years mainly due to attack from see water side.

Table III Corrosion of Cast Iron in Fused Caustic Soda

	Loss in wt. gm/dm²			
	Up to 200°C for 5 mins.	Up to 360°C for 15 mins.	Up to 520°C for 15 mins.	Uu to 520°C for 4 hrs.
Caustic Soda	Nil	0.25	0.28	0.56
Caustic Soda (with 1% sulphur)	Nil	0.9	1.15	1.7
Caustic Soda (with 1% $NaNO_3$)	Nil	0.32	0.32	0.52

Microstructure studies showed that in one case the carbon was evenly distributed and in the other it was massive and rossette form (Fig. 3). The difference in corrosion behaviour was due to the fact that carbon in massive form provided greater surface activity and resulted in intensification of attack. Uniform distribution of carbon on the other had helped in preventing such graphitic corrosion and the pipes lasted longer. It was recommended that cast iron in which carbon was uniformly distributed, may help in increasing the normal life of pipes.

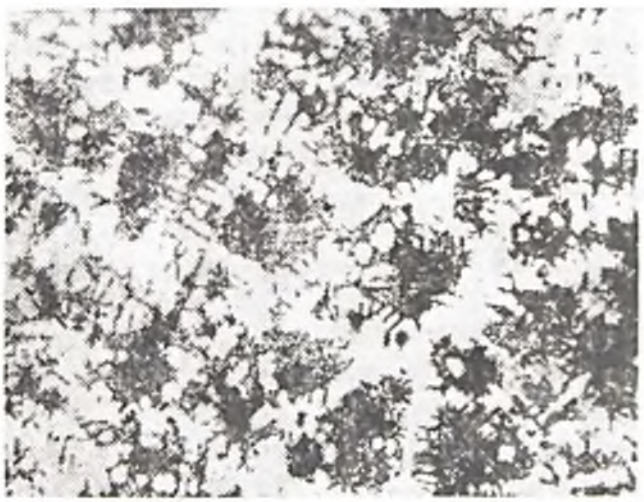


Fig. 3 : Microstructure of corroded cast iron in sodo ash manufacture showing distribution of carbon in massive rossette form. ×100

III. Sulphuric Acid

(1) Corrosion of Cast Iron Pipes

This is yet another corrosion problems concerning cast iron pipes. The pipes transporting the hot acid were cooled from 100° to 50°C by spraying water over them. Examination of corroded pipes indicated that internal surfaces in contact with the acid were practically in tact, but corrosion occurred on the outer surface in contact with the cooling water. Pit formation also was observed. It was informed that the impure water used for cooling, contained small amounts of chlorides, sulphates, etc. As air also was freely available under sprayed conditions, corrosion was favoured.

As a remedial measure, it was suggested that water used for spraying requires purification and control in respect of chlorides, sulphates and pH.

(2) DDT Manufacture

During the manufacture of DDT it was reported that severe corrosion troubles were experienced in the chlorination chamber, accessory equipment and heat exchangers necessitating frequent replacement of pipe valves, pumps, heat exchanger tubes etc. The lead lining in DDT Section also required frequent replacement.

Laboratory investigations and an on-the-spot survey showed that the condensate and the circulating water were corrosive to mild steel. Even though chromates and phosphates were used as inhibitors in the circulating water, corrosion took place due to inadequate replenishment of the inhibitors. The presence of moisture and hydrochloric acid vapours in the mixed vapours of benzene and mono-chlorobenzene was found to be an important factor responsible for increased corrosion rate.

The corrosion of lead lining of the DDT wash tank appeared to be due to the mechanical damage caused to the protective lead sulphate films by DDT crystals.

IV. Caustic Potash Electrolysis : Failure of Stainless Steel Bolts

The investigation relates to corrosion of stainless steel bolts of the composition shown below in fastening mild steel anodes and cathodes in a cell containing 20% KOH solution.

	Cr	Ni	Ti	C
Indigenous	18.5	9.0	0.2	0.07
Imported	18.0	12.25	0.15	0 05

It was reported that indigenous bolts failed after a period of one year while the imported ones lasted for more than four years The attack was mostly near the bolt heads. The laboratory investigation revealed that the indigenous bolts were magnetic, and imported ones were non-magnetic, indicating the fact that the indigenous bolts were of duplex structure, i.e. ferrite and austenite (see Fig. 4). The attack was intergranular. Hardness values indicated higher amounts of internal stress in indigenous bolts due to insufficient annealing treatment after the drawing operation. Absence of attack at places other than the bolt heads showed that the failure was due to combined effect of stress and corrosion taking place near the head due to accumulation of high alkali concentration at the annular spaces between the bolt and the body.

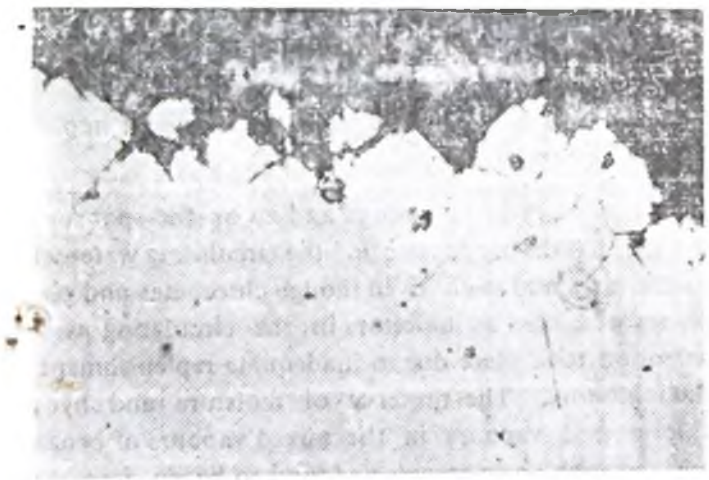


Fig. 4 : Microstructure of corroded S.S.bolt (indigenouc). ×60

V. Power Plant Corrosion Problems

(1) Failure of Super-heater Tubes

The present investigation relates to failure of super-heater tubes in a power plant. The boiler was radiant heat water tube type and the fuel was pulverized coal. It was reported that in the secondary section the tubes failed (Fig. 5) by cracking and general corrosion. The operating pressure and temperatures were 36 kg/cm² and 450°C respectively.

No abnormality was noticed in the boiler feed water and the analysis. The composition of the tube material showed that it contained 0.22% Cr and 0.21% Mo.

The outer surface of the tubes showed slight bulging at the site of cracks. There was also considerable oxide build-up in the tubes particularly at the site of cracks, and below the oxide layer the tube surface was quite rough. Microscopic examination showed that there was to some extent grain boundary attack. There was indication of over-heating also

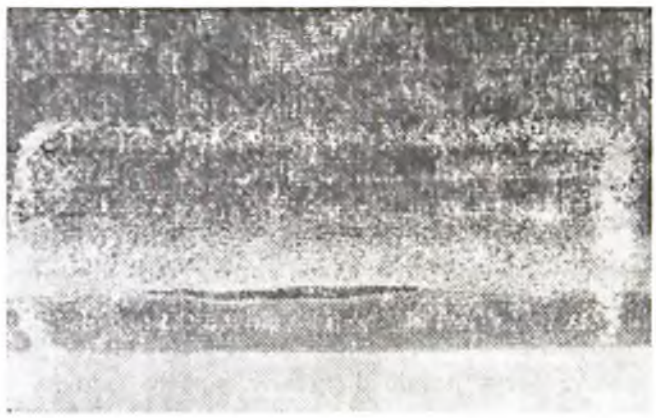


Fig. 5 : Failed super-heater tube showing the cracking and bulging.

It was also considered that the heavy build-up of oxide layer (from the steam side) had interfered with the efficient heat transfer, which in turn occurred due to local over-heating of the tubes. As overheating of the tubes is considered as one of the important factors for similar nature of failures, the important causes for the same are mentioned below : 1. Poor heat transfer because of build-up of heavy oxide scale, coke ash or corrosion products. 2. Bad deposition of the fuel. 3. Loss of circulation. 4. Faulty design. 5. Increased through-put. 6. Putting the boiler on line too quickly.

It was recommended that tube material containing at least 0.5% Mo, and 2% Cr, which has both high temperature oxidation and creep resistance be used for better performance. The operating conditions also need strict supervision.

(2) Corrosion of Economiser Tubes from the Water Side

It was reported in this case that the economiser tubes were frequently failing particularly at bends from the

water side. The operating pressure was 15–17 kg/mm², and flow rate 27 m³/hour. Feed water inlet temperature was 102°C and that of outlet 190° – 194°C. Fig. 6 shows the type of attack encountered.

Visual examination of the inside of the sectioned tubes near bends showed full of streaks of corrosion grooving along the direction of flow of water, and deep pits leading to perforation. The pit developed was an elongated one and showed the directional effect of flow. It was also noted that the grooves and the corrosion pits were free from rusting.

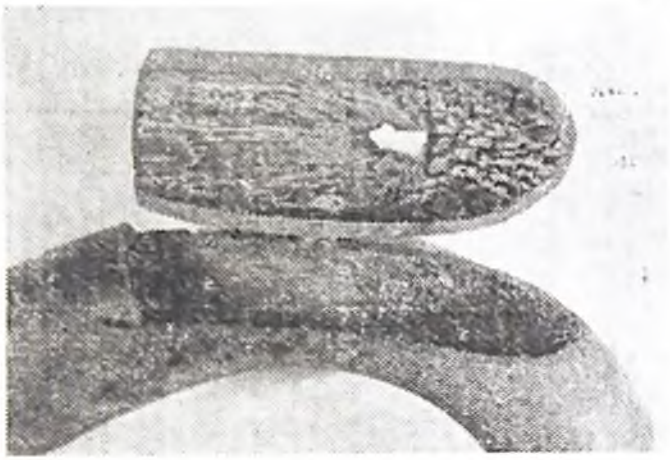
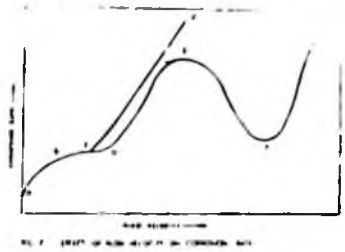


Fig. 6 : Failure of economiser tube at a bend showing perforation and grooving from inside.

Under the operating conditions as mentioned above the general trend of corrosion attack with increased flow of water is shown in Fig. 7. It can be seen that at high velocities the protective film is likely to be damaged and the corrosion rate becomes high. For water corrosion in flowing systems, the relative motion between the metal and water is very important. When the flow rate exceeds a critical value turbulence is expected. For water flow in tubes, the critical velocity is so low that in most cases the flow is turbulent. Turbulance is further increased when the direction of flow sharply changes as in the case of bend. This effect is likely to damage the protective film and the metal exposed is subjected to attack. In addition to the above, any aggressive constituents in the water specially chlorides, oxygen, etc. will increase the rate of perforation. It is also to be noted that the protective magnetite film when cracked due to thermal or mechanical shocks, may also lead to ultimate perforation and leaking of the tubes.



As a remedial measure it was suggested to avoid turbulance effect, either by modified design, or by removal of deposits at the bends. It was also suggested that the corrosive constituents should be removed from the feed water.

VI. Corrosion of Stainless Steel Valve in Pharmaceutical Industry

It was reported from a pharmaceutical industry that a stainless steel valve (18 : 8) used for handling mixtures of water containing small amounts of chloride and sulphate salts and solvents such as butanol or butyl acetate, developed localised corrosion and rust spots. As the corrosion products contaminate the end products the problem was considered to be serious. Chemical analysis of the material showed that it was plain 18 : 8 stainless steel. Microscopic examination of the polished and unetched specimen cut from the valve showed presence of considerable amounts of non-metallic inclusions. The inclusions (Fig. 8) which were concentrated more near the surface of the castings, were found to be of oxides, sulphides and silicates. There was also clear evidence of rust being initiated near the inclusions.

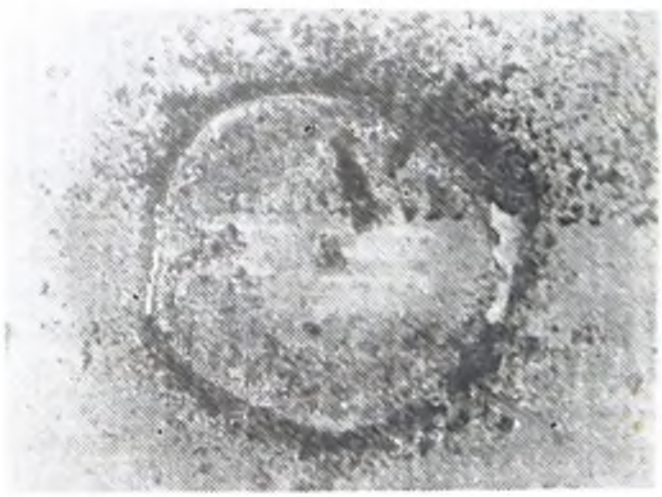


Fig. 8 : Initial corrosion around inclusion in stainless steel valve. × 10



Fig. 9 : Attack of supercheater tubes from the steam side showing damage to the magnetite film.

It is known that the high corrosion resistance of stainless steel is due to the passive film which has a self-healing property even if a break occurs. The repair of the film is favoured in presence of oxygen, but in presence of chlorides the stainless steel is liable to be attacked, giving rise to pitting nature of corrosion. The observations made in the above case showed that the passive film on the surface was found discontinuous because of the presence of non-metallic inclusions, oxides, sulphides, and silicates.

It was recommended to remove the scale and surface inclusions by pickling or any other suitable mechanical process. It was also suggested that stainless steels free from such inclusions should be used.

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