Kraft Liquor Recovery Boiler Corrosion

VERMA, V. K. and ELANCHEZHIAN P. K.*

SUMMARY

The article gives wny corrosion takes place in recovery boilers of Kraft paper mills. Factors which influence corrosion and methods which can be used for protection from corrosion have been delt in details.

INTRODUCTION

The technical advancements and the economics electrical power have made the pulp and paper industry to go in for higher pressure levels of steam cycle for their captive power generation. With the operation of these high pressure recovery boilers severe gas side corrosion has been experienced in the water-walls and to some extent on the superheaters. This necessitated some preventive action if expensive repairs of the boilers and serious accidents were to be avoided. A lot of research work has been done in this field and this paper draws conclusions from such reports.

CORROSION PHENOMENON

The main corrosion product is FeS, identified by a hard black scale, (with bright blue colour frequently observed underneath) which is tightly bonded to the tube surface. The elemental sulfur formed by the reaction of furnace gases with the frozen smelt on water wall tube surfaces, corrode the tubes forming Fe.S There are only a few reactions which yield elemental sulfur :

$$Na_2S+2\,CO_2 = Na_2CO_3+S+CO \qquad (1)$$

$$2\,Na_2S+3SO_2 = 2\,Na_2SO_3+3S \qquad (2)$$

$$H_2S+1/2\,O_2 = H_2O+S \qquad (3)$$

Laboratory tests have proved that all the above reactions cause severe corrosion. The reaction (1) is predominant at temperatures above 370°C. The reaction (3) is very much dependent on the temperature. The hydrogen sulphide-oxygen corrosion is low below 300°C but increases rapidly above this temperature. Laboratory investigations show that maximum corrosion occured if the ratio between hydrogen sulphide and oxygen in the gas phase was about 1:1. The above temperature limits also explain the reason for high pressure units (with high water wall temperatures) subjected to significant corrosion.

FIELD EXPERIENCE

Most of the recovery boiler corrosion has occured in the lower part of the furnace before the full amount of combustion air has been supplied. The areas of attack have been below primary air poits, black liquor spray openings and secondary air openings. The extent of metal wastage ieported is maximum below the primary air level and ranges from 0.75 to 1.25 mm per year.

FACTORS INFLUENCING CORROSION

Most of the corrosion occur in the reduction zone of the furnace. It is very difficult to predict the flue gas composition in this zone. The combustion characteristic of the flue gas with reference to hydrozen sulphide (H_2S) and sulpher dioxide (SO_2) content change with increasing loads. The

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*Bharat Heavy Electricals Ltd., Tiruchirapalli.

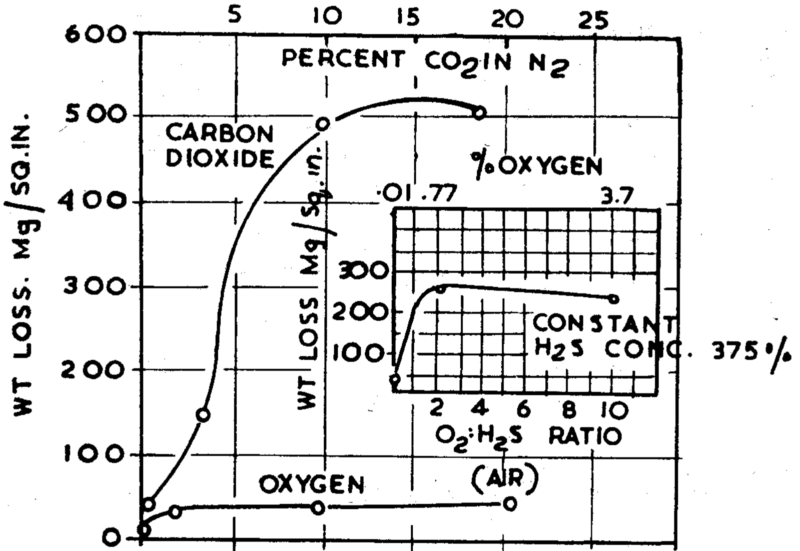

FIG. 1

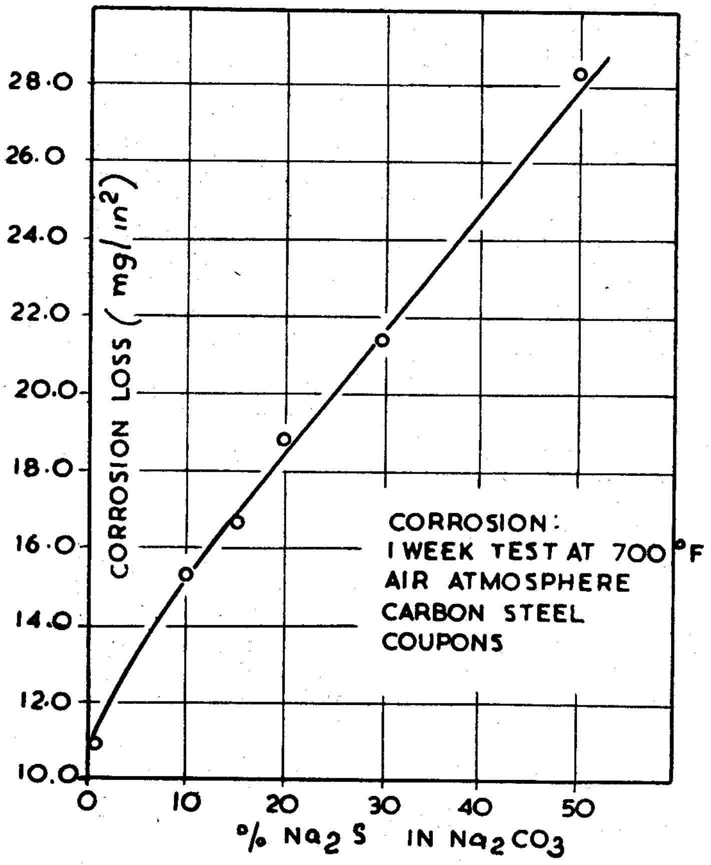

FIG. 2

hydrogen sulphide content increases with load while the SO_2 decreases and only on some occassions the SO_2 content could be found at very high loads. The H_2S is generated during the combustion in the hearth bed and during the combustion of liquor droplets carried over with the flue gas which burn in suspension.

The major factors which influence corrosion are :

1. Gas Composition
2. Smelt Composition
3. Physical state of the deposits
4. Metal surface temperature.

1. GAS COMPOSITION

The effect of various constituents of flue gas on corrosion are given below :

SULFURDIXIDE–The effect of sulfurdioxide seems to be negligible. However the corrosion rate is higher with higher water content.

HYDROGEN–As the hydrogen content increases the rate of corrosion increases except at the highest water vapour content where the hydrogen does not have any influence. The corrosion rate is increased if hydrogen is present in the temperature range of 330°C to 480°C.

CARBON MONOXIDE— The influence of carbon monoxide seems to be very little. The corrosion is more with low concentrations.

CARBON DIOXIDE—The effect of CO_2 concentration on the corrosion rate is shown in Figure 1. Increased corrosion in the presence of CO_2 has been reported as one of the several significant reactions in the reports submitted by the Finnish and Swedish corrosion committees.

HYDROGEN SULPHIDE / OXYGEN RATIO—The corrosion rate is affected to the greatest extent by the H_2S/O_2 ratio. A large increase in the corrosion rate will occur at low concentrations of oxygen and hydrogen sulphide. At higher contents, the corrosion will be less.

2. SMELT COMPOSITION

SMELT SULPHIDITY.—High sulphidity of the pulping process contribute to higher rates of corrosion. The maximum corrosion occurs where the concentration of Na_2S in the wall deposit is highest and where there is maximum oxygen supply. This is the area just below the primary air points. The concentration of Na_2S in furnace deposits decreases with increased elevation of the furnace. Figure 2 shows the effect of Na_2S concentration on corrosion. The effect of high sulphidity on corrosion has been shown in Figure 3 and 4.

MELTING POINT OF SMELT.—It has been found that frozen smelt layer protects against corrosion. The degree of protection depends on the thickness of the smelt layer. This obviously depends on the melting point of smelt and the temperatures prevailing. Due to environmental reasons, waste acid from the bleaching plant may be recycled. In such cases the NaCl content of smelt will increase. This effects the melting point of smelt, the thickness of smelt layer and indirectly affect the corrosion protection.

EFFECT OF SODIUM CHLORIDE.—The effect of sodium chloride in the performance of a recovery unit is of importance to many operators. The major effect of chloride corrosion potential in recovery units is the lowering of the melting point of smelt. This occurs because of the eutectic formation of NaCl with smelt. Waterwall wastage occurs as a result of the reaction of newly formed elemental sulfur with iron oxides or iron metal or carbon steel tube surfaces. The sulphur is formed as a result of furnace gases reacting with the smelt normally covering the water walls. The frozen smelt tends to protect the tubes from attack however increased furnace operating temperatures or decreased smelt melting temperature will result in a decrease in the thickness and hence the protective ability of the frozen smelt.

Many mills have operated with an NaCl content less than 5% in the smelt without any abnormal metal wastage. The melting point of smelt is not affected until the NaCl content exceeds 7% and wastage rate has been observed to double when the NaCl content was 22%. The Finnish experience with NaCl is that corrosion increases with increasing NaCl content up to 10-12% but no further increase in wastage was observed beyond this point. Table 1 gives the relative corrosion of recovery units operating at various parameters for different NaCl content.

TABLE 1

Operating Pr/Temp.		NaCl content in strong BL gm/liter	Intensity of corrosion
85 Kg/cm^2	480°C	50	Extremely severe
65 Kg/cm^2	450°C	10	Severe
42 Kg/cm^2	400°C	50	Little

3. PHYSICAL STATE OF THE DEPOSITS

During the recovery boiler operation the tubes are covered with a sheet of frozen smelt in the lower furnace. This deposit is generally separated from the tube surface by a thin layer of irregularly spaced porous material, probably dried black liquor as shown in Figure 5. This provides a space of about 1 mm which may serve as a passage way for corrosive gases. On the outer surface of the wall deposit there is a pulsating flow of molten smelt. Depending on the ash bed configuation, this molten outer layer may be in contact with the glowing ash bed and/or bathed in a gaseous stream of widely varying concentrations of primary air and combustion products.

4. METAL SURFACE TEMPERATURE

At the temperatures normally prevailing in the medium pressure recovery boiler tube surface negligible corrosion is caused by the smelt. However the corrosion increases above 300°C especially at a low oxygen content. The region of lower furnace, about 0.5 meters above the primary airport to the surface of the smelt is the zone of high heat release. The heat absorption rate is nearly twice as high as the average rate for the furnace. Only this zone has the greatest extent of tube wastage. Fast temperature changes can also increase the corrosion by cracking the layer of corrosion products.

PROTECTION FROM CORROSION

A number of methods of protection against recovery boiler corrosion have been experimented and tried in operation. Some important methods are as follows :

1. Studs and refractory
2. Diffusion coating
3. Clad welding
4. Metallizing
5. Compound tubes.

Before deciding on any corrosion protection method a thorough inspection of the various areas that are likely to corrode shall be made.

RECOVERY BOILER WATERWALL INSPECTION PROCEDURE

A. Examine the unit before it is cleaned and sand blasted, if possible.

B. Look for a blue colour underneath any deposit. The location of this area should be noted so that ultrasonic wall thickness measurements can be made, following the removal of adherent smelt. Clean adherent smelt from walls by water wash or sand blasting.

C. A preliminary visual inspection of the metallized coating should be conducted. This will show where any spalling has occurred. A magnetic thickness gage may be utilized to determine remaining thickness of coating in regions susceptible to wastage. Careful ultrasonic wall thickness measurements should be taken in these areas.

D. Grit-blast the unit in preparation for respraying.

E. A fixed increment of the tube elevation should be established where measurements will be taken. Measurements at elevations below the primary air ports at about 150 mm intervals from the centerline of the airports to the bed should be made. Additional measurements are recommended at elevations 0.3, 0.6, 3, and 6 meters above the centerline of the primary air ports. Each area should be wire-brushed to insure an adequate surface. The lubricant is applied just prior to measurement.

NOTE : A multiplicity of readings is recommended to provide a firm basis for establishing the rate of wastage so that severe tube metal losses will not be "discovered" unexpectedly and result prolonged down-time for major repairs.

F. Measurements should normally be made on the fireside crown of each tube. If thinning is detected at any elevation, then additional read-

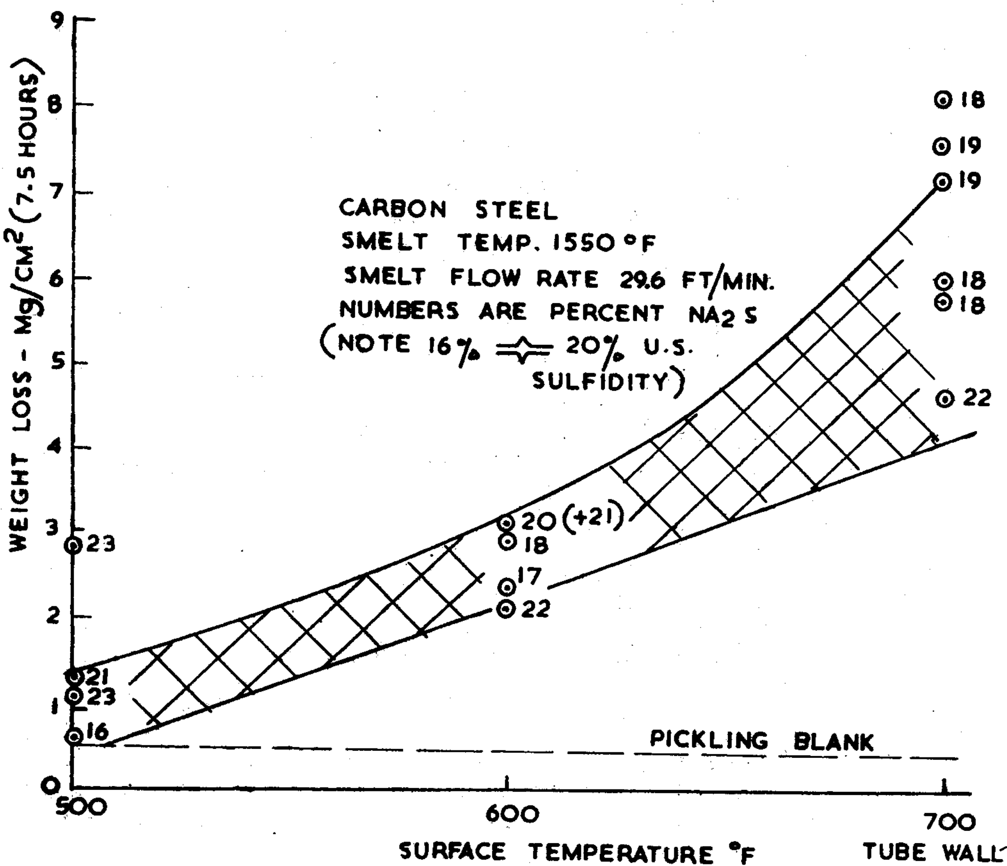

FIG: 3

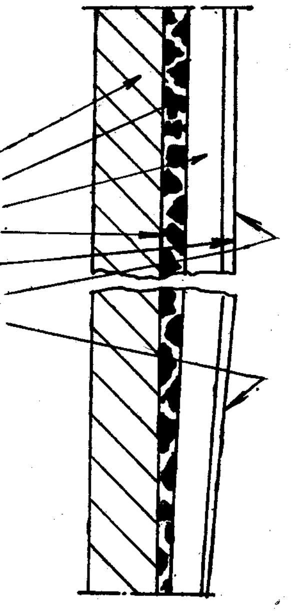
TUBE WALL
POROUS LAYER
FROZEN SMELT
ADHERENT LAYER
MOLTEN FLOWING SMELT
UPPER WALL AREA
REGION NEAR PRIMARY AIR PORTS

FIG: 5

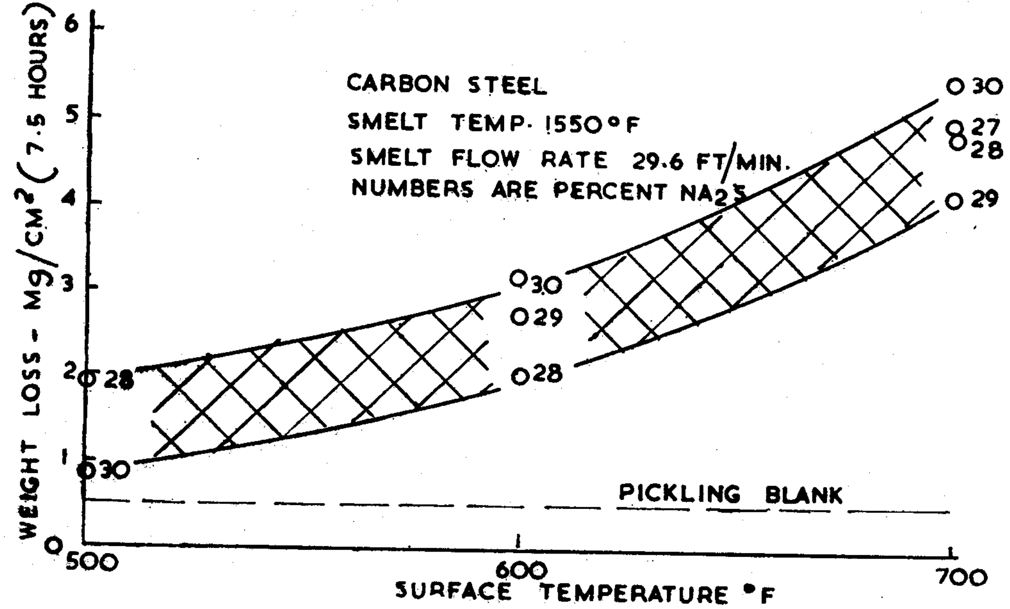

FIG: 4

ings should be taken to determine any directional character of the wastage.

G. Tubes in the region of starting gun ports and auxiliary fuel ports should be measured at 50 mm intervals.

H. An attempt should be made to spot check the tubes in the vicinity of the liquor gun ports and secondary air zone. This is another area where wastage has occurred in the past. Measurements of one or two tubes in each wall at 300 mm intervals from primary air port to secondary air port elevations will provide an indication of any unexpected or unusual wastage zones.

I. At approximately five year intervals, a few floor tubes should be checked. When removing smelt from the floor, extreme caution must be exercised in order to avoid damage to the tubes.

J. Periodically the superheater and screen tubes should be examined; if a metallizng program is established, then measurement of the same areas is recommended.

K. As these measurements are being taken, any tube wall thickness less than 3.8 mm should be marked. These tubes should be re-examined. Tubes with significant wastage (wall thickness less than 3.43 mm) should be repaired or replaced.
NOTE : These thicknesses are approximate and each case must be reviewed by the owner's insurer.

L. Measurements should be made at each annual outage to insure integrity of measurements and effectiveness of protective coatings.

1. STUDS AND REFRACTORY

The studded tubing provided in recovery boilers has required extensive repairs and replacement after five to seven years of operation. With this construction monitoring of wall thickness is very difficult. The manufacturing cost is also very high.

2. DIFFUSION COATING

Diffusion coating of chromium and aluminium chromium have been tried with no measurable loss in water wall thickness. Manufacturing problems associated with this process is being resolved.

3. CLAD WELDING

Metal clading of austentic alloys containing 18% Cr or more have been provided in the lower 2 to 3 meters of recovery furnaces operating at high pressures. There is quite a good amount of manual labour involved though this method has proved satisfactory corrosion protection. Tube replacement is very difficult in this method although surface repair can be done very easily.

TABLE II.

Typical Weld Metal Composition

Cr	Ni	C	Mo	Mn	Nb
21.9	14.8	0.04	2.6	—	—
17.9	—	0.09	—	0.3	0.8
18.0	9.4	0.04	2.5	0.7	—
24	15	0.06	—	—	—

4. METALLIZING

Multi-coating metallizing of nickel aluminide, stainless steel and aluminium has proved very successful in many recovery units. This process has been explained below in detail.

A. SURFACE PREPARATION—The most important aspect of flame or plasma spray metallizing is that the tube surface be absoultely clean and dry. The tubes should be cleaned by steel shot or grit blasting (0.13 mm size) and flame spraying should follow immediately. Sand blasting is not recommended because of dust residue left on tubes. More than one blast-cleaning operation may be necessary.

B. REVISED MULTI-COAT FLAME SPRAYING
Undercoat ayer 0.05 to 0.13 mm of "Metco 405" nickel alumi- nide ro "Exotherm" nickel titanide adjacent to the grit blasted tube surface.

Middle layer 0.08 to 0.10 mm of "Metco#1" (300 series stainless).

Outer layer 0.08 to 0.10 mm of "Metco Superfine" (aluminium).

A layer of Metco SA silicate-aluminium sealer is sprayed or painted on to fill up the naturally occuring pores in the metallized coating.

Multi-coat layers used originally consisted of 0.2 mm of 300 series stainless adjacent to the cleaned tube surface followed by 0.1 mm of alumnium followed by a layer of silicate-aluminium sealer.

The multi-coat flame spraying has successfully prevented additional wastage in several units for more than five years with only annual touch-up maintenance.

C. CHROMIUM-NICKEL TITANIDE PLASMA SPRAY COATING—An alternate metallizing procedure of plasma sprayed multi-coat layers consists of 0.13 mm of Exotherm, an exothermic nickel-titanium compound, adjacent to the cleaned tube surface followed by 0.25 mm of chromium.

The plasma sprayed chromium/nickel-titanide coating is expected to provide protection with maintenance required at two or three year intervals.

Corrosion protection has been achieved in full scale units in western Canada using both stainless plus aluminium and chromium over nickel aluminide. Both coatings can be applied as *flame* spray powders, but the plasma spraying assures unoxidized metal coatings for maximum protection.

5. COMPOUND TUBES

Composite tubes are produced by the co-extension process in which austentic steel (TP304) and carbon (SA 210 GrA$_1$) billets are fitted together and then coextended. A metallergical bond is obtained during this process. This bond remains unchanged under service conditions of boilers operating at 85 kg/cm^2 steam pressure. The compound tube used for this application may have approximately 6.3 mm thick carbon steel core tube for the water side and 1.6 mm thick coating of 304 material outside This tube is supposed to give a ten fold increase in life since corrosion resistant 304 material would be exposed to the gas side. This tube may also have an advantage of avoiding water side stress corrosion internally by chlorides or caustic attack because of the carbon steel lining as compared to using an alloy steel tube. The only prohibitive factor for these tubes is almost ten times the cost of carbon steel tubes. However a few high pressure (85 Kg/cm^2) recovery units in Sweden and Finland are in operation with these tubes.

CONCLUSION

Extensive corrosion of the furnace tubes have been found in the surroundings of primary, black liquor spray and smelt openings. Recovery boilers with tangent tube construction of furnace walls may be subjected to external corrosion due to diffusion of gases and salts between the tubes and condensing on the other cooler surface. This external corrosion is avoided by having fusion welded wall construction.

Hydrogen sulphide generated as reduction product and by suspension burning of black liquor mainly contributes to the corrosion. This corrosion rate increases in the presence of oxygen and reaches a maximum when molar ratio of H_2S/O_2 is one. Unfortunately the H_2S/O_2 ratio less than unity is a requirement of kraft process since the saltcake (Na_2SO_4) must be reduced to Na_2S. Therefore it is desirable to have protection against H_2S attack in the recovery boilers. However at temperatures below 300°C this corrosion is very low (especially at low oxygen content). At higher oxygen levels the corrosion rate decreases due to suppression of FeS formation caused by the formation of magnetite (Fe_3O_4). Magnetite forms a tight scale on the tube surface and offers reasonable protection for carbon steel tubes. The increased corrosion rate at higher temperatures is due to the higher diffusion rate of H_2S through the magnetite layer. Tube hot spots occuring due to internal deposits will also be subjected to higher metal wastages.

Not much has been dealt so far on superheater corrosion. This is because the superheater corrosion rate is very insignificant in the tube metal temperature levels presently practised. The normal maximum superheater temp. used is 450°C with occasional values of 480°C. However laboratory tests indicate that the steam temperature could possibly be raised further to 500 to 520°C using chromium alloyed steels. Corrosion occurs where the concentration of Na_2S is high and where oxygen is high. This is the reason for superheater corrosion. Under oxidising superheater conditions the gas composition has only a little ifluence on the corrosion rate. Generally sulphide is found on superheater tubes except at the bends where there is usually about 1 to 3% Na_2S. It is only at the bends superheater corrosion has been experienced even at very high metal temperatures.

The presence of sodium chloride in the smelt will change the composition regarding Na_2S and $Na_2S_2O_3$ considerably. This may also change the equilibrium between the gas phase and the smelt and the H_2S/O_2 ratio where the maximum corrosion rate is to be expected. NaCl content upto 3% in kraft liquor smelt will not have significant operating problem. Increasing NaCl content up to about 10-12% increases corrosion but no further increase is observed beyond this point.

Another operating variable that could strongly affect corrosion rate is the sulphidity. Increased smelt sulphidity increases the corrosion rate sharply. A sulphidity level of 27.5% can be considered as maximum allowable without significant corrosion rate. In this context it may be noted that strong black liquor oxidation increases the sulphidity of white liquor could strongly affect corrosion.

The multicoat metallizing process has been success fully tried in many high pressure boilers. It is a good practice to go for corrosion protection whenever the recovery boilers have an operating pressure of 65 Kg/cm^2 and above at the superheater outlet. The procedure has been clearly explained. The metallizing shall be done for a height of 3 to 4 meters from the bottom tube level. In the case of recovery units with 85 kg/cm^2 pressure and aobve at superheater outlet the metallizing height should be increased to about 1 metre above the top level of air admission. An alternative for such very high pressure units would be to monitor the tube wall thickness closely to determine whether additional coating is required. Proper surface preparation and application of the coating together with annual inspection and touch up maintenance should provide corrosion protection with no significant loss of base metal.

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