Corrosion in hardwood stationary digester : a case study

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ABSTRACT

Within five years of operation, unusual it may be seen, both the Hardwood stationary digesters at TNPL experienced severe corrosion and required replacement of the affected bottom conical portion. Investigations to know the cause of the corrosion revealed presence of thiosulphate in the mill White liquor, which triggered metal loss This article traces the case study of what happened to these pressure vessels, which should, under normal circumstances, have a service life of about 25 years.

The Corrosion problems occuring at TNPL are typical for a bagasse based paper mill and were dealt with in the article "Corrosion problems in a bagasse based Paper Mill", published in IPPTA, September 1987. The most severe among them is the corrosion that occurred in the Hardwood stationary digesters.

TNPL employs kraft process for chemical cooking of bagasse and Hardwood. The chemical wood street comprises of two stationary digesters of 80 Cu m. capacity each, used for cooking hardwood chips. Two rapid continuous digesters of 125 TPD capacity each, cook depithed bagasse for production of chemical bagasse pulp.

The design specifications of the digesters, cooking conditions, white liquor composition etc., are given below.

A. Hardwood Street

STATIONARY DIGESTER

Capacity	: 80 Cu.M
Type	: STATIONARY BATCH
Make	: Utkal Machinery Pvt. Ltd. Orissa
Shell thicknass	: 25 mm
Material of construction	: SA 515 GR 60
Design pressure	: 10 5Kg/Sq. cm.
Bath ratio	: 2 8

COOKING CONDITIONS

Active alkali charged	: 14% on BD chips
Cooking temperature	: 170 Deg C
Pressure	: 7.5 Kg/Sq. cm
Cooking time	: 1 hour 30 mts

B. Chemical Bagasse Street

CONTINUOUS DIGESTER

Capacity	: 125 BDTPD
Type	: Horizontal, Twin tube continuous
Make	: Sunds Defibrator, USA
Material of construction	: SA 285 GR C
Shell thickness	: 16 mm
Design pressure	: 10.5 Kg/Sq. cm

COOKING CONDITIONS

Active alkali charged	: 12-13% on BD bagasse
Residence time	: 14 minutes
Temperature	: 170 Deg C.
Pressure	: 7.5 Kg/Sq. cm

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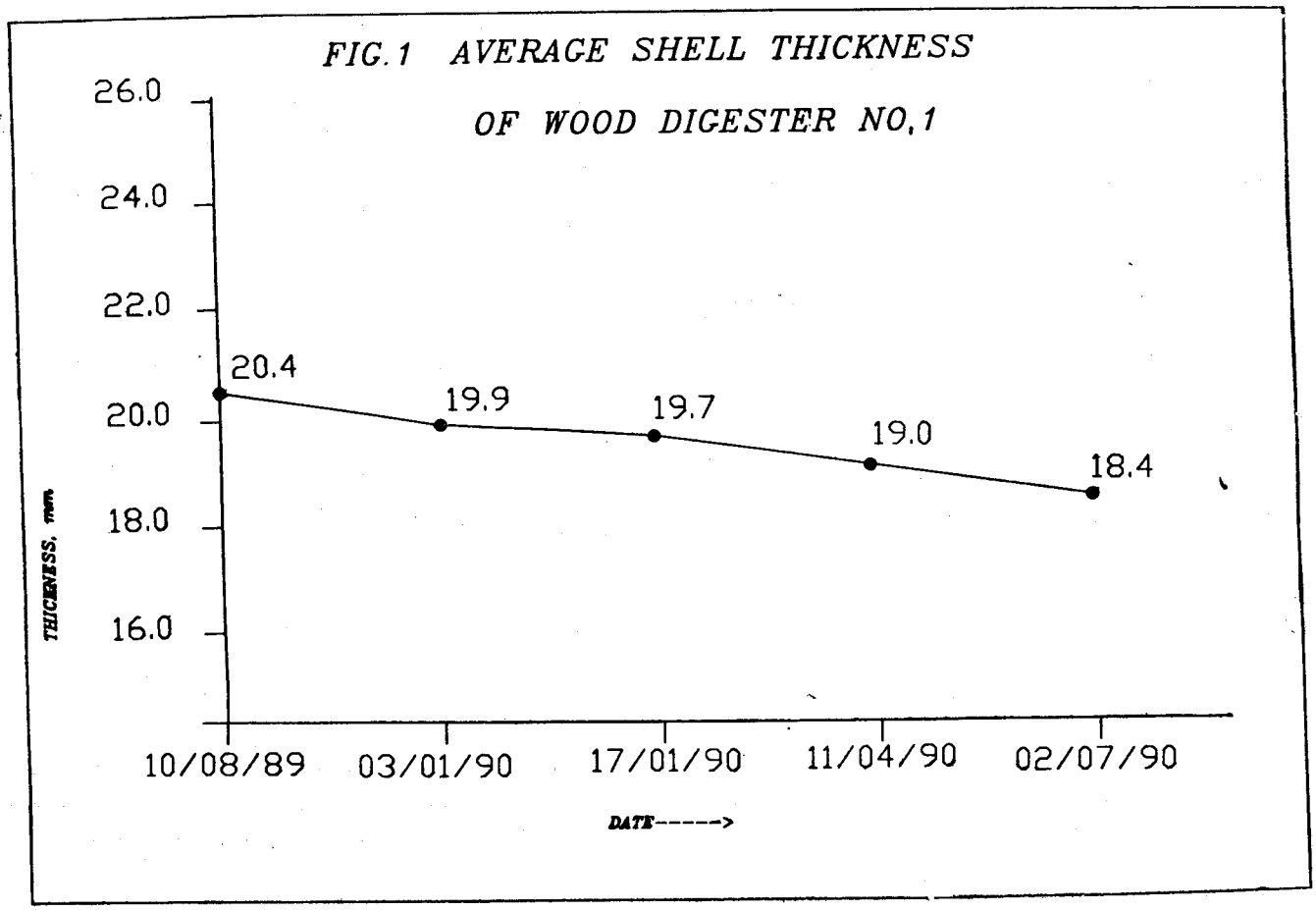
C. White Liquor Characteristics

TTA as Na_2O	: 90.8 gpl
TAA as Na_2O	: 82.4 gpl
NaOH as Na_2O	: 65.3 gpl
Na_2S as Na_2O	: 17.1 gpl
Na_2CO_3 as Na_2O	: 8.4 gpl
Sulphidity	: 20.7%

CORROSION IN THE STATIONARY DIGESTER :

The corrosion in the stationary digesters came to light in August 1989 i.e. after 4 years of operation, when leakage of Black liquor was noticed from the bottom conical portion of one of the digesters under pressure. On examination, the thickness of the shell was found reduced to 14-16mm at several places from the initial value of 25mm. The shell thickness of both digesters was then monitored at regular intervals using ultrasonic thickness tester. Figure 1 shows the average shell thickness measurements of Digester No. 1 taken over a period of 8 months. As seen, the corrosion is occurring at the rate of about 2mm per year. Also steps have been taken to replace the affected portion of the digesters by taking a prolonged shut of 3 weeks. It must be mentioned here that the first signs of this cooking liquor related corrosion were noticed in the white liquor lines (carbon steel) both in Pulp Mill and Recovery, where repeated failures occured within 2 years of operation. These lines were then replaced with SS 304 piping in a phased manner. Corrosion was also observed in the causticizing plant drum slaker, evaporator tubes etc. The corrosion of the digester shell is however unique considering the following :



— Raw material i.e. hardwood chips, cooking, conditions, the white liquor characteristics, sulfidity etc. are in line with the prevailing standards maintained in the industry.

— Though corrosion is not an uncommon phenomenon in the carbon steel digesters, the rate at which it occurred was alarming. The normal life of the digester is expected to be around 20-25 years.

— No signs of corrosion were noticed in the Bagasse continuous digesters though the same White liquor is used for cooking bagasse, as well.

FINDINGS AND RECOMMENDATIONS OF CECRI :

The corrosion problem was sponsored in April 90 as a special project to Central Electro Chemical Research Institute, Karaikudi for detailed investigation by them. CECRI has since submitted the final report based on which the following conclusions could be drawn.

a. The White liquor analysis showed presence of thiosulfate of 3 gpl which accelerated corrosion.

b. The concentration of thiosulfate in white liquor is however fluctuating. It varied from 2.5 gpl to 7 9 gpl.

(c) The chemical composition of the digester shell material conforms to SA 515 Gr. 60. (Carbon—0.17%, Silicon—0.22%, Manganeese—0.77%, Sulphur—0.013%, Phosphorus—0.012%. Copper —0.011%).

(d) Addition of elemental sulphur to White liquor at concentrations greater than 7 gpl has decreased the corrosion rate significantly. To ascertain the effectiveness, it is suggested that the mill should incorporate carbon steel coupons (2cm × 5 cm) in the process line and collect corrosion data periodically.

(e) Anodic protection of carbon steel in White liquor is not feasible since no passive range is observed on anodic polarisation.

While the Mill is examining the techno-economic feasibility of implementing the recommendation of CECRI, an attempt is made to relate the above findings to the mill wide cooking liquor related corrosion problems that have occurred.

GENESIS OF CORROSION :

The mills Recovery Boiler operates on mixed Black Liquor feed originating from chemical hardwood streets which employ different cooking conditions as detailed earlier. Though a 4 stage screening and cleaning is employed in the chemical bagasse pulping street, the efficient operation of this section is often affected by the presence of silica leading to frequent plugging of centricleaners. The resultant pulp contained shives/specks affecting the quality of bleached pulp made. In order to keep the shive content low, the cooking chemical for bagasse is charged at the rate of about 13% on B.D. raw material which is almost on par with wood cooking. Considering the openness of bagasse fibre, the chemicals charged is on higher side with Kappa No. around 10-11 as against 16-18 maintained for similar applications.

With moderate cooking conditions employed in the rapid continuous digester, such high chemical dosages result in excess residual active alkali in the black liquor. This is confirmed from the higher RAA content of bagasse Weak Black liquor as compared to Wood liquor as shown below :

Average RAA of bagasse WBL	: 6-7 gpl as Na_2O
Average RAA of wood WBL	: 2.3 gpl as Na_2O

The residual active alkali when computed on per day basis presents a clearer picture on the amounts of RAA recycled to the recovery as given below :

	During News print run	During Paper Writing & Printing run
Chemical bagasse pulp production (tpd)	110	180
Quantity of weak black liquor from chemical bagasse street (Cu.M)	1100	1800
RAA recycled to Soda Recovery boiler (tonnes)	7.15	11.7
RAA per ton of chemical bagasse pulp (Kgs)	65	65
Chemical hardwood pulp production (tpd)	55	60
Quantity of weak black liquor from hard wood street (Cu. M)	495	540
RAA recycled to soda Recovery boiler (tonnes)	1.24	1.35
RAA per ton of chemical wood pulp (Rgs)	22.5	22 5

As seen above, the quantity of RAA recycled to recovery from Chemical bagasse street is different during NP and PWP runs and is several times higher than RAA originating from hardwood street.

In the Recovery system, the high residual sulphide forms sodium thiosulphate when comes into contact with air in the furnace.

$$2\ Na_2S + 2\ O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2\ NaOH$$

It is reported that presence of thiosulphate in the cooking liquor even in very low concentration considerably accelerates corrosion. It is realised that formation of polysulfide in equilibrium with sulfite, thiosulphate and sulfide according to the reaction.

$$Na_2S_2O_3 + Na_2S \longrightarrow Na_2SO_3 + Na_2S_2$$

will drastically reduce the cathodic polarization of the carbon steel by reacting with electrons to the form ferrous sulfide.

$$S_2^{2-} + 2e \longrightarrow 2\ S^{2-}$$

The corrosion of steel in white liquor appears to consists of an anodic disssolution of ferrous ions, which are precipitated in the solution as ferrous sulfide, while an equivalent amount of polysulfide ions reacts with the excess electrons on the corroding steel surface.

EFFECT OF TEMPERATURE

It is known that polysulfides decompose at temperatures exceeding 120 Deg C causing no harm to the digester shell. It is thus possible to conclude that what ever corrosion that is taking place in the digester is limited to initial steaming and first stage cooking period at 120 Deg. C. This also explains the absence of corrosion in bagasse continuous digesters which are always maintained at 170 Deg. C. The corrosion occuring in various white liquor lines where the temperatures are limited to 70—80 Deg. C is also attirbutable to the presence of polysulfides.

EFFECT OF CONCENTRATION :

The concentration of polysulfides in white liquor again plays an importance role in establishing the corrosion rate. It is reported that the corrosion rate increases with increase in polysulfide concentrations upto 2 5 gpl. and shows declining trend there after. The corrosion rate drops to permissible levels at concentrations above 5 gpl. Polysulfides in high concentration is know to inhibit the corrosion by passivating the steel probably by anodic polarisation.

CORROSION CONTROLLING STRATEGY :

With the digesters corrosion occuring at the rate of 2-3 mm per year it is unlikely the existing digesters would last for longer period. In order to extrct the maximum life of the digesters the following action plan has been recommended for review and implementation.

— To carry out periodic measurements of thiosulphate concentration in the white liquor to monitor corrosion in the digester.

— To add elemental sulfur to the white liquor charged to the digester to keep its concentration above 7 gpl.

— To effect modification in the screening and cleaning plant of chemical bagasse pulp so that the pulp could be cooked to higher kappa number. The RAA in the black liquor recycled to recovery could be reduced.

— To resort to single stage cooking of wood chips as the corrosion seems to be predominant during the first stage cooking time (30 minutes) at 120 Deg C.

CONCLUSIONS :

The hardwood stationary digesters of the Mill are experiencing corrosion at rapid rates. Investigations revealed presence of thiosulphate in the cooking liquor. The origin could be traced to the operating strategy of the Pulp Mill. Addition of elemental sulphur to the white liquor reduced corrosion rate markedly. After studying the technoeconimics, the appropriate strategy for controlling the corrosion will be evolved for implementation.

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REFERENCE ;

Report on "Studies on corrosion of Digester material in White liquor", by CECRI, Karaikudi, Jan 1991.