Studies On Polysulphide Cooking For Improving Pulp Yield And Pulp Strength And Impeding Digester Corrosion

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ABSTRACT

It has been observed that the batch digester at Star Paper Mills Ltd. Saharanpur were effected with severe corrosion within ten years of operation. Laboratory investigations were made to know the cause for corrosion. Corrosion rates of mild steel by weight loss method under different polysulphide concentrations in white liquor of normal and diluted strength were also studied. It was observed that the corrosion rate varies with polysulphide content in the cooking liquor, being higher at low concentration of polysulphide (1.5-2.5 g/l, as sulphur). At the polysulphide concentration above 19 g/l, as sulphur, it becomes constant; this infers the safe range of polysulphide content from the point of view of corrosion of digester. When sulphur is added in white liquor to get a polysulphide concentration of 19 g/l ,the dead load of sodium thiosulphate on recovery furnace increases. The polysulphide concentration of 19 g/l from white liquor is formed by catalytic oxidation of the sodium sulphide normally present. Under this condition not only digester corosion is prevented but pulp yield, having low kappa number, and strength also increases. Pulping results with oxidised white liquor shows an increase in pulp yield by 2.7% (based on o.d. wood basis), burst factor by 2.7%, breaking length by 10.1% and decrease in tear index by 1.5% as compared to kraft pulping.

INTRODUCTION

In 1879, a German chemist C.F. Dahl incidently discovered Kraft process, when he replaced Na_2CO_3 by Na_2SO_4. The Kraft process has several advantages such as enhanced delignification rate and higher pulp yield of superior quality. In 1960 A. Kibrick and his co-workers found that pulp yield could considerably be increased by using liquors with higher polysulphide content. In a Kraft process not only the malodorous gases are evolved that effects the eco-balance greatly but also causes rapid corrosion of digester thereby affecting the economy of the process.

Laboratory studies as well as the practical experiences with corrosion of Kraft digester (1-7) have indicated that composition and concentration of cooking liquor is the most important for the same. The basic factors responsible for the digester corrosion are the presence of Sodium hydroxide, Sodium sulphide, Polysulphide, Sodium thiosulphate and sodium thiosulphonate contents in the cooking liquor for the Kraft cooking. The rate of corrosion increases with increased concentration of white liquor.

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Haegland and Roald (8) have reported that the polysulphide ions act as cathodic depolarizers and cause severe corrosion of steel in cooking liquor. Sodium thiosulphate in the cooking liquor considerably accelerates corrosion. Polysulphide in equilibrium with sulphite, thiosulphate and sulphide exists as:-

$$Na_2S_2O_3 + Na_2S_2 \rightleftharpoons Na_2SO_3 + Na_2S_3$$

It will drastically reduce the protecting cathodic polarization of the steel by reacting with electrons to form sulphide:

$$S^{-} + +2e^{-} \text{------------->} 2S^{--}$$

The corrosion of steel in white liquor appears to consist of an anodic dissolution of ferrous ions, which are precipitated from the solution as ferrous sulphide, while an equivalent amount of polysulphide reacts with the excess electrons on the corroding steel surface.

$$Fe^{+++} \text{--------------->} Fe^{++} + e^{-}$$

$$Fe^{++} + S^{-} \text{--------------->} FeS$$

$$S^{-} \ +2e^{-} \text{--------------->} 2S^{--}$$

Besides this, design and circulation system in digester also affects the digester corrosion. The main reasons affect digester corrosion are nonuniformity of chips size, chip loading, chips packers, liquor volume, steam inlets and digester relief (9).

The composition of digester metal also affects corrosion. Digester scale, Calcium carbonate, if retained as a continuous film is beneficial in reducing corrosion of the carbon steel surface (10).

According to Uusitalo (11) passivation of steel can be affected by adding polysulphide with a sulphur content of 20-25 g/l of the white liquor. It is found that digester corrosion can be prevented by increasing polysulphide concentration upto 19 g/l, as sulphur, in white liquor. Addition of elemental sulphur in white liquor to get a polysulphide concentration of 19 g/l increases the dead load of sodium thiosulphate on recovery furnace (12)

The polysulphide is also formed by catalytic oxidation of sodium sulphide eliminating the need for additional sulphur. The Na_2S of Kraft white liquor is first oxidised to Na_2S_x (where x is 2-5) depending on equilibrium conditions and amount of Na_2S present. By using oxidised white liquor having polysulphide concentration 19 g/l, as sulphur, the digester corrosion can be prevented (13). The production of polysulphide liquor from kraft white liquor takes place as follows:-

$$2Na_2S + O_2 \text{------------->} S^0 + 4NaOH$$

$$xS^0 + Na_2S \text{------------>} Na_2S_x + 1$$

The sulphur emissions can be reduced because of the reduced amount of Na_2S (14 & 15). The use of polysulphide leads to increase in both pulp yield and strength.

EXPERIMENTAL

Analysis of white and green liquors

White and green liquor were collected from Pulp mill and Causticizing plant and analysed as per Tappi Test Method T 624 m-44 for one month. The results are reported in **Table-1.**

Preparation of different polysulphide concentrations from white liquor

By dissolving of elemental sulphur in white liquor

Elemental sulphur was added upto about 20 g/l polysulphide in white liquor at a temperature of 80 °C, 96-98% sulphur is converted into polysulphides by continous stirring on a water bath. The results of analysis of various polysulphide liquors are given in **Table-II.** This polysulphide liquor is not taken for conducting corrosion experiment due to rise in dead load of sodium thiosulphate.

By catalytic oxidation of sodium sulphide in white liquor

White liquors of different sulphidity were subjected to oxidation with compressed oxygen in presence of catalyst activated carbon partly coated with Teflon. The digester was filled with white liquor and heated to 120 °C. Oxygen gas at a pressure of 0.2 kpa was purged for oxidation of sodium sulphide. After 120 seconds 75% of the sodium suphide was converted into Na_2S_x. Oxidised white liquor of different concentrations were prepared for corrosion and cooking experiments.

Design of experiments

Corrosion experiments

Surface finished mild steel specimens of dimensions 31.5" x 14.5" x 2.4"mm were used for corrosion experiments. The percentage composition of mild steel was as follows:

Table-I

Analysis of White Liquor Collected from Causticizing Plant and Pulp Mill

	NaOH gpl	Na_2CO_3 gpl	Na_2S gpl	Na_2SO_3 gpl	$Na_2S_2O_3$ (%)	TTA (%)	Sulphidity (%)	Causticity (g/l)	SiO_2 (g/l)	Polysulphide g/l (as S)
Composition of White Liquor from Causticizing Plant										
Maximum	111.40	36.80	24.0	2.08	2.32	130.80	19.27	82.01	0.19	2.57
Minimum	83.20	20.00	20.8	0.95	2.21	130.40	15.90	74.82	0.17	0.70
Average	92.17	25.33	22.4	1.57	2.29	133.6	18.52	70.62	0.18	2.04
Composition of Green Liquor from Causticizing Plant										
Maximum	31.20	123.20	28.8	2.08	2.05	-	48.00	22.20	-	2.40
Minimum	24.20	85.60	17.6	1.89	1.58	-	42.00	20.00	-	1.10
Average	27.68	107.06	23.4	2.05	1.99	-	45.44	20.46	-	1.90
Composition of White Liquor from Pulp Mill										
Maximum	93.60	37.60	22.4	2.14	3.00	137.6	22.40	83.57	0.18	2.74
Minimum	77.60	18.4	19.2	1.39	1.90	120.0	17.91	67.36	0.15	1.71
Average	85.2	25.33	20.27	1.79	2.29	130.8	19.27	77.17	0.19	2.44

Table-2				
Preparation of polysulphide liquors of different concentrations viz. 0.0, 10.0, 15.0 and 20.0 g/l by addition of elemental sulphur in white liquor				
Particulars	**Sulphur addition, g/l**			
	0.0	**10.0**	**15.0**	**20.0**
NaOH, g/l (as Na_2O)	71.30	65.72	65.10	64.48
Na_2S "	12.40	13.64	13.64	13.64
Na_2CO_3 "	12.40	16.12	15.50	15.50
Na_2SO_3 "	1.70	0.44	0.06	0.06
$Na_2S_2O_3$ "	1.89	14.22	13.75	13.75
A. alkali "	83.70	79.36	78.74	78.12
E. alkali	77.50	72.54	71.92	71.30
Sulphidity, %	14.81	17.18	17.32	17.46

C	Si	Mn	P	S	Cr	Ni	Cu	N
0.16	0.14	0.54	0.015	0.017	0.05	0.04	0.12	0.04

The specimens were ground on SIC paper to remove sulphide layer after each experiment. The steel specimens were activated by rapid immersion in dilute hydrochloric acid; before each experiments. This was necessary to obtain the maximum reproducibility, also this has resulted in greater corrosion than regular practice. The sulphide layer that formed during corrosion experiment was removed by scrubbing before weighing. The weight loss of specimens was expressed in grams per square meter per experiment (cook).

The cooking experiments were carried out in electrically heated rotary digester of 0.02m³ capacity. The oxidised white liquor is preheated to about 100°C. Nitrogen gas was purged to prevent the oxidation of white liquor. The following cooking schedule was adopted; rising temperature from 90 °C to 165±2 °C, followed by two hours cooking at temperature of 165±2 °C for two hours.

For each polysulphide concentration six mild steel specimens were fixed with a rod at the bottom of digester in such a way that they could not come into contact with each other. At the end of cooking, the steel specimens were taken out and washed. The results of weight loss of specimens versus polysulphide concentrations in oxidised white liquor of normal and diluted strength are reported in Figure-III and IV.

Pulping experiments

The screened wood chips of Eucalyptus, Bamboo and Pine (80:15:5) were cooked with oxidised white liquor and white liquor having polysulphide concentrations 19 g/l, as sulphur. (The polysulphide concentration was selected on the basis of results reported in figure-III at which minimum digester corrosion was observed) and 0.0 g/l. The following cooking schedule was adopted for heating the digester:-

Time from room temperature to 105°C=45 minutes

Time from 105 °C to 165 °C = 45 minutes

Time at 165°C =180 minutes

At the end of cooking, the pulp was washed, screened and crumbled. The pulp yield, screening rejects and Permangnate number were determined. The results are reported in **Table-3.**

Pulp evaluation

Both the pulps were beaten to 40 °SR in valley beater and handsheets of 60 g/m² were prepared on British sheet former. The handsheets were evaluated as per Tappi method for various strength properties at a temperature of 27±2 °C and relative humidity of 65±2%. The results of pulp evaluation are compared in Table-3.

Results and Discussion

Table-1 shows that during causticizing reaction, the Sodium thiosulphate increases from 1.99 to

Table-3			
Comparison of kraft and polysulphide pulps of blend of Eucalyptus, Bamboo and Pine (80:15:5)			
Sl.no.	**Particulars**	**Kraft process**	**Polysulphide process**
1.	Screened pulp yield, %	48.5	50.2
2.	Rejects, %	1.20	2.1
3.	Total pulp yield, %	49.7	52.2
4.	K. number	18	21
5.	Burst Factor	45	46.5
6.	Tear Factor	82	80.5
7.	Breaking length, meter	5450	5998
8.	Bulk, cm^3/g	1.65	1.45
9.	Viscosity, cps	21.6	25.2
10.	Copper number	1.462	0.875

3.54 g/l and average polysulphide are found to 2.04 g/l, as sulphur. In white liquor collected from Causticizing plant, the sodium thiosulphate increases from 2.21 to 2.29 and average polysulphide are found to 2.32 g/l, as sulphur. The composition of white liquor from pulp mill shows great variations. The sodium thiosulphate increases from 1.90 to 3.00 and average polysulphide are found to 2.44 g/l, as sulphur. The above results can be explained on the basis of figure-III. The polysulphide concentrations are found in dangerous level at which maximum digester corrosion takes place.

Figure-I & II shows diagramatic presentation of cooking cycles in batch digester exhibiting corrosion prone area and cessation of corrosion. As the digester is filled with wood chips and white liquor, It starts to corrode. The rate of corrosion, when cooking has just begun, become very rapid. As temperature of digester reaches to around 120 °C, the cessation of corrosion takes place because at this stage the components of white liquor become unstable and consumed for chips impregnation. At this point corrosion diminishes rapidly.

Figure-III, Depicts the corrosion rate of mild steel under different polysulphide concentrations i.e. 0-20 g/l (calculated as sulphur) in oxidised white liquor of following compositions:

NaOH, g/l = 95.17

Na_2S, g/l = 23.40

$Na_2S_2O_3$, g/l = 2.83

Na_2SO_3, g/l = 1.80

SiO_2, g/l = 0.17

The corrosion of mild steel specimines increases very rapidly to a maximum at 2.0 to 2.5 polysulphide/litre (calculated as sulphur). On further increasing polysulphide dose, the curve declines sharply until it finally level-off. Beyond polysulphide concentration 2.5 g/l, the curve forms two sections in the same cooking experiment, one representing high corrosion zone while the other represent low corrosion zone. This is convincing evidence that polysulphide may exert a cathodic depolarizing action and an anodic passivation. The maximum corrosion is exerted by the upper part of curve i.e. activated curve. The corrosion by lower part of curve corresponds to passivated curve is approximately the same and at polysulphide concentrations of 19-20 g/l the corrosion becomes zero. The activated and passivated curves meet at a polysulphide concentration of 19 g/l and give a constant value of corrosion.

To study more closely the relationship between liquor concentration and corrosion, experiments were carried out with dilute oxidised white liquor having the following composition:

Polysulphides, g/l = 0.0-20 (calculated as sulphur)

NaOH, g/l = 74.20

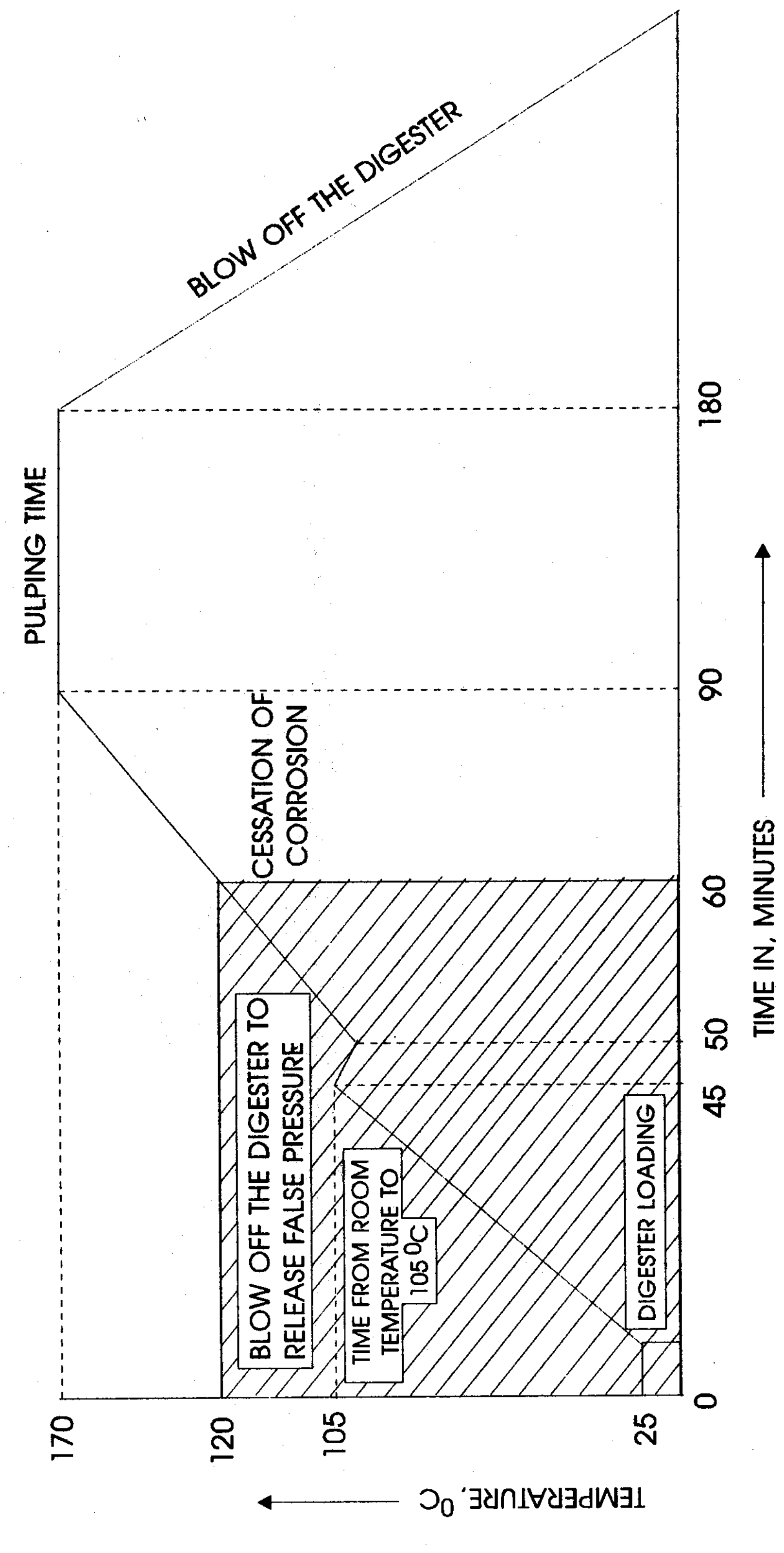

FIG.-1. PLOTS OF TIME (IN MINUTES) Vs TEMPERATURE (0C) OF A NORMAL COOKING CYCLE SHOWING CORROSION OF SULPHATE DIGESTER DURING COOKING OPERATION.

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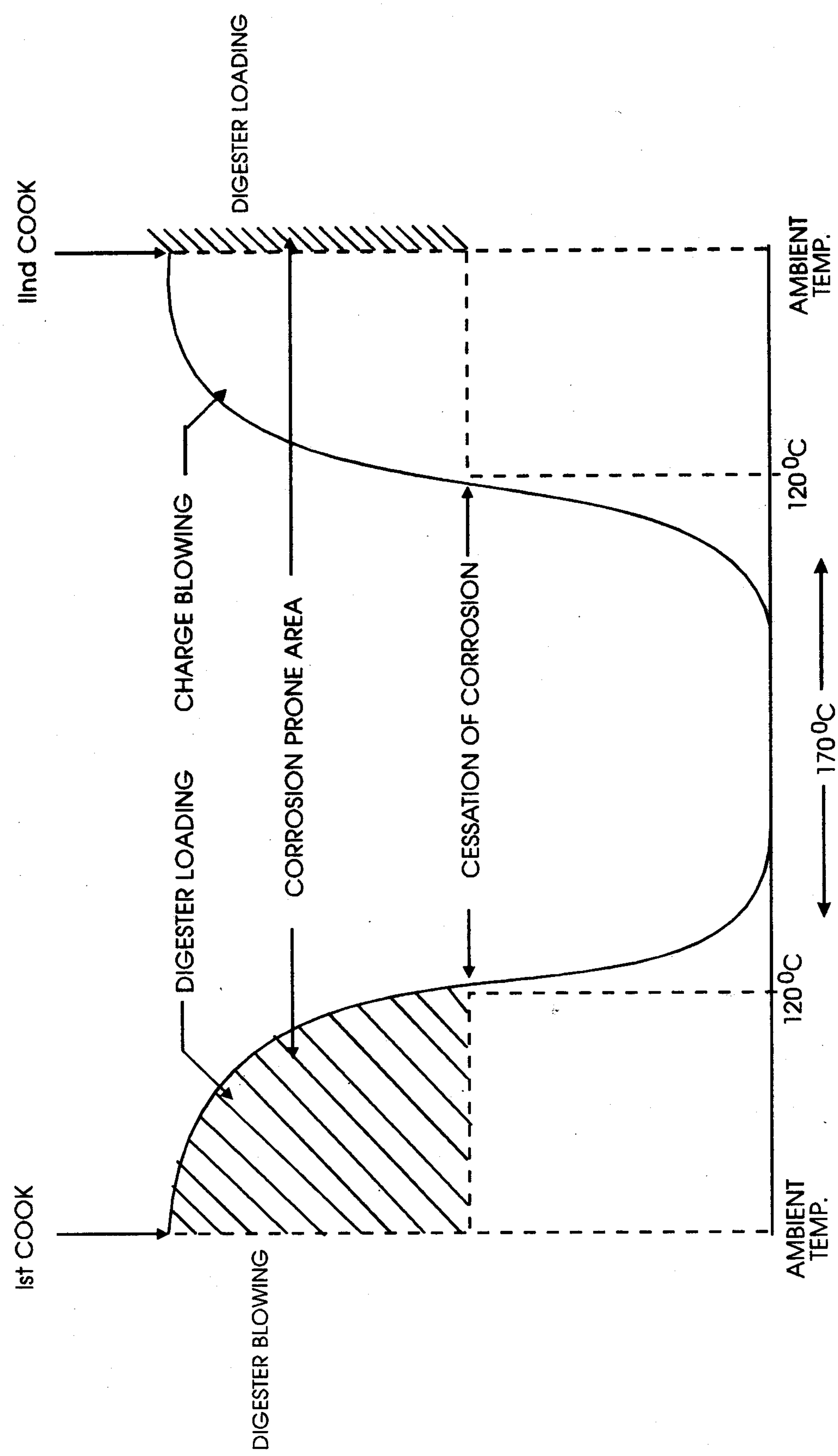

FIG.2. COOKING CYCLES IN A BATCH SULPHATE DIGESTER SHOWING CORROSION PRONE AREA AND CESSATION OF CORROSION.

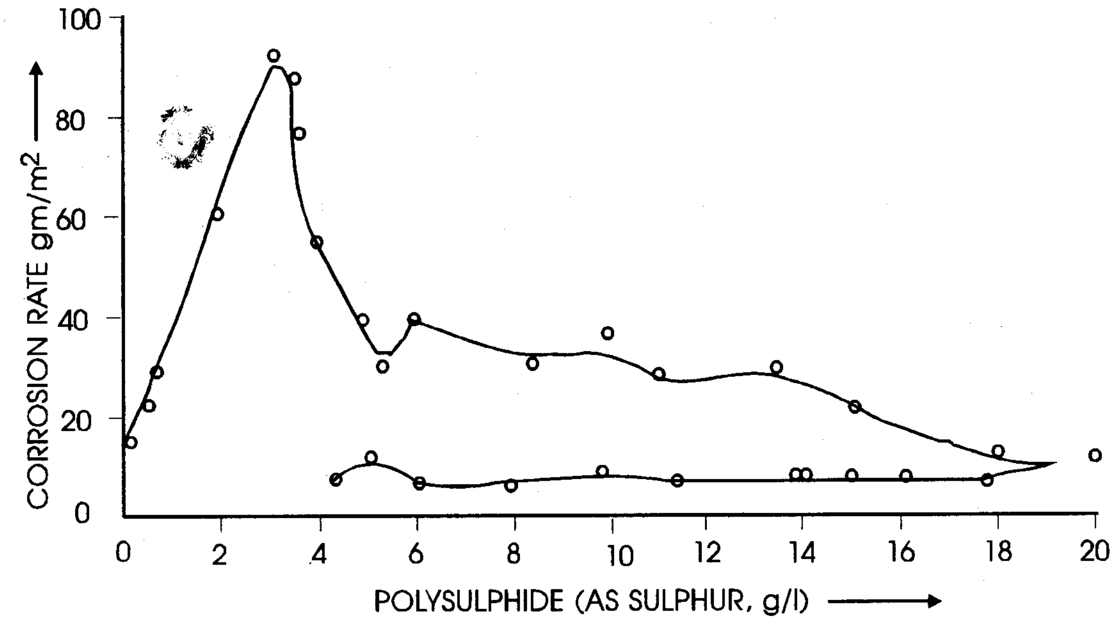

Fig.3. Plots of Corrosion Rate (gm/m²) of MILD Steel Vs Polysulphides, g/l in White Liquor of Average Strength.

Na_2S, g/l	= 14.87
$Na_2S_2O_3$, g/l	= 1.14
Na_2SO_3, g/l	= 0.71
SiO_2, g/l	= 0.15

Figure-1V indicates that the corrosion at polysulphide concentration 2.0-2.5 gpl is more severe but at higher polysulphide concentration, the corrosion is consistently weak.

Table-3 indicates the comparison between Kraft and polysulphide process in terms of pulp yield and strength. The pulp yield in polysulphide process is increased by 2.7% than that of Kraft process at same cooking condition and chemical treatment. The

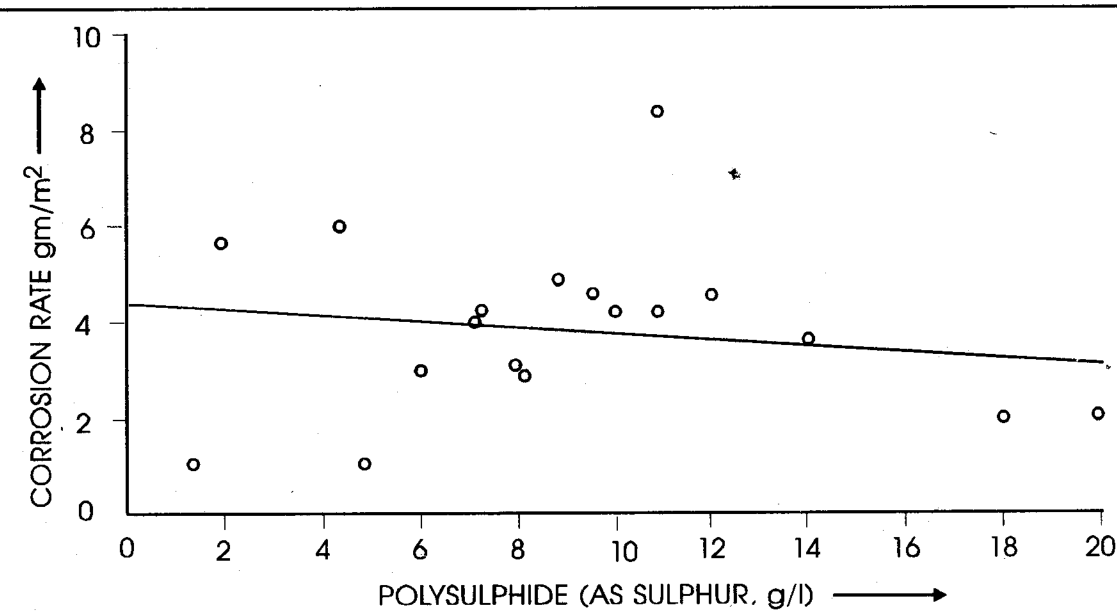

Fig.4. Plots of Corrosion Rate (gm/m²) of MILD Steel Vs Polysulphides, g/l in White Liquor of Medium Strength.

orange oxidised white liquor has the ability to preferentially oxidise end groups of hemicellulose rendering them more stable to alkaline attack and resulting in higher pulp yields. The increase in pulp yield is due to better hemicellulose retention which is also demonstrated by having lower tear factor (1.3% lower than that of Kraft pulp) and better beatability (40 °SR in 18 minutes). The hemicellulose retention increases the burst factor by 2.5% and breaking length by 10.01% in polysulphide pulp when compared to Kraft pulp. The bulk of handsheets prepared from polysulphide pulp was lower (1.65 cm^3/g for Kraft pulp and 1.45 cm^3/g for polysulphide pulp). This explains that the intermixed hemicellulose plays a dominant role for hydrogen bonding with hemicellulose. The viscosity of polysulphide pulp was 25.2 against 21.6 cps for Kraft pulp. The Copper number was lower 0.875 polysulphide pulp against 1.46 for Kraft pulp.

CONCLUSION

1. The rate of corrosion is higher at the start of each cooking and diminishes rapidly till it reaches to 120 °C.
2. The dead load of sodium thiosulphate in polysulphide liquor prepared by the addition of elemental sulphur is very high. It creats problem on recovery furnace.
3. The rate of corrosion was found maximum at lower polysulphide concentrations (1.5 to 2.5 g/l).
4. The corrosion can be reduced by increasing the polysulphide concentration around 19 g/l (expressed as sulphur).
5. The polysulphide pulp of Eucalyptus, Bamboo and Pine chips (80:15:5) shows an increase in pulp yield by 2.7%, burst factor by 2.5% and breaking length by 10.1% over Kraft pulp whereas it shows a decrease in tear factor by 1.3% bulk by 0.20 units and copper number by 0.587 units over Kraft pulp.

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