Studies on the Kinetic Characteristics of Sulphide Sulphur Oxidation in Suphate Black Liquor
Part I. Standardization of Analytical Procedure for the Estimation of Sulphide Sulphur in Sulphate Black Liquor

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SUMMARY

The standardization of the analytical procedure for the estimation of sulphide sulphur in the Black liquor, oxidized as well as in the synthetic Black liquor is discussed. The complex nature of the Black liquor with its multitudes of interfering organic sulphide sulphur make the analysis more difficult. The analysis of the Black liquor is fairly straightforward, and reproduceable till such time it is not oxidised. For an oxidised Black liquor, as the oxidation proceeds, and part of the sulphide sulphur compounds are stabilized the estimation becomes difficult and at one stage it is highly impossible through the conventional potentiometric methods.

The precipitation and again the filtration of the precipitated Black liquor has shown that there is an agglomeration of sodium sulphide with the precipitated organic compounds during Barium chloride precipitation. The loss of inorganic sulphides are substantial for the precipitated and filtered Black liquor and this should be taken as the criterion for the system designing of the Black liquor carbonation and regeneration systems. The Black liquor oxidation system is described. The oxidation of synthetic Black liquor is very difficult inspite of the higher air supply, thereby substantiating the catalytic effect of the phenolic compounds in oxidizing the sodium sulphide in Black liquor. The reversion trends in the stabilized sulphide sulphurs in the liquors are also discussed.

INTRODUCTION

Formation and atmospheric release of volatile sulphur compounds viz Hydrogen sulphide, Methyl mercaptans, Dimethyl sulphides, Dimethyl disulphides during pulping and Black liquor (BL) regeneration process are primarily responsible for the malodour in kraft mills [1-3]. The stabilization of these odourous volatile sulphur compounds can better be achieved by their conversion to stable non volatile sulphur forms through Black liquor oxidation (BLO) either with air or molecular oxygen in presence/absence of catalysit [4-10]. In addition to odour abatement the BLO technique offers

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considerable economic advantages in the form of (i) improved heat transfer in the evaporators, (ii) recovery of sulphur through fixation of malodourous volatile and nonconconsable gases (iii) time saving at the causticizers due to the increased sulphidity in green liquor (GL), (iv) reduced load in the recausticizers and clarifiers because of less lime handling plus improvement in pulp quality and yield. The oxidation can be carried out both with the thin as well as thick BL at elevated temperatures and atmospheric pressure. The efficiency of the oxidation system can be evaluated from the initial and final sulphide sulphur concentration in BL.

In BLO kinetic studies it becomes essential to develop a reliable method for the estimation of sulphide sulphur in BL. BL is a complicated mixture of organic and inorganic constituents, its analysis with reference to the sulphide sulphur remains a problem due to the presence of multitudes of interfering compounds. An attempt has been made in this work to highlight the difficulty associated with estimation of sulphide sulphur in BL, and of oxidized BL during analysis. The advantages of using a potentiometric method for the estimation of sulphur in BL with argentimetry titration, involves simple but a robust technique giving consistent results.

LITERATURE

The analysis of BL is to be viewed in two contexts. One the synthetic Black liquor (SBL) containing Na_2S in NaOH with the absence of other organic constituents. The SBL is prepared by the dissolution of Na_2S flakes in a caustic solution of approximate strength of 7 g/l. The properties of this liquor resembles the white liquor (WL). The other one a thin Black liquor (TBL) containing Na S in NaOH (NaOH being present as free alkali of approximate strength 7 g/l) in presence of all other interfering compounds of both organic and inorganic nature.

The sulphide suphur estimation in GL/WL/SBL is a simple and straight forward analytical problem. But in BL, the analysis becomes difficult because of the presence of low boiling organic compounds viz mercaptans and organic sulphides [11-14].

By critically reviewing the applicability of the evolutary method for the estimation of Na_2S in WL/GL/SBL and BL, Barlew and Pasco[15] concluded that the applicability of this technique to BL is open to questions due to the presence of low boiling volatile organic compounds. For BL the sulphide sulphur results obtained by H_2S method will be higher as compared to GL/Wl due to the total participation of organic sulphides

The oxidation techniques using specific oxidants[16] is again not suitable for BL because of the presence of organic sulphides and this technique is being criticized by many[17-19]. Added to the organic oxidants hypohalites are also suggested as oxidants[20,21].

Kesler[22] has critically reviewed the oxidation techniques for the estimation of Na_2S, Na_2SO_3, $Na_2S_2O_3$ and and Na_2SO_4 along with Na_2S and concluded that their applicability for the estimation of $Na S O_3$ and Na_2SO_3 is simple but more complex for a mixture like BL containing sulphides in addition to sulphite and thiosulphate.

An important observation made by Willard and Cake[23] is that quantitative oxidation of Na_2S by hypochlorite require a minimum hydroxyl ion concentration of 4N and hypobromite around 2.5N.

The IS 297—1970[24] which is similiar to the method sugguested by Kurtnacker and Wallack[25] rather measures the total sulphide of the system than total sodium sulphide. The adaptability of selective absorption methods[2b,27 28] is highly time consuming and cumbersome and also the reliability is doubtful.

The petroleum industry also has to cope with a similar analitical problem during the sweetening of petroleum. The problem of estimating the Na_2S during/after sweetening the petroleum is more complex than BL because of the presence of high homologous organic compounds of both aliphatic and aromatic nature.

Tamela et al[29] had suggested a potentiometric method for the estimation of Na_2S in petroleum. This involves a titration using 0.1 N $AgNO_3$. Saturated calomel electrode has been used as a standard along with Ag/Ag_2S indicator electrode Lykkass and Tuemmler[30] supplemented this procedure with the usability of glass electrode along with the Calomel electrode.

The electrode potential developed in a pure solution of Na_2S of proper pH is a function of the sulphide activity and follows the Nernst equation.

$$E = E_o + \frac{2.303\ RT}{nF} \log A_{S^{2-}} \qquad (i)$$

where

E_o = Standard electrode potential
R = Molar gas constant
T = Absolute temperature
n = Number of electrons transferred
A_{S2} = Activity of sulphide ion.

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So any change in the sulphide ion activity gets a response in the electrical potential. But the ionic activity of S^{2-} is equal to the sulphide ion concentration (C_s2-) multiplied by its activity coefficients (T). So the Nernst equation can be written as follows : —

$$E = E_, + \frac{2\ 303\ RT}{nF} \log \Upsilon \quad \frac{2.303\ RT}{nF} \log Cs^2_{-}$$

(ii)

In the BL, the problem of finding out the ionic activity of S^{2-} ion is aggricated because the ionic strength of S^{2-0} ion which is resulted not only by the inorganic sodium sulphide sulphur but also by the organic sulphide sulphur ions. As per the Debye-Hiickal equation the activity coefficients can be equated to ionic strength, provided the ionic strength of the system is not subjected to any drastic changes. So the maintenance of constant ionic strength is essential in lower molar solutions.

At a higher concentrations as in BL, the electrical response of the system will be affected by pH, the sulphide ions S^{2-} forms complexes with hydrogen ions, giving hydrosulphide ions (HS−) and hydrogen sulphides

$$S^{2-} + 2H^+ \underline{\quad} (HS^-) \underline{\quad} H_2S(g)$$
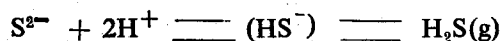
The amounts of complexed sulphide ions increase with an increase in the ionic activity. In acidic solutions sulphide will be present mostly as molecular hydrogen sulphide which easily evaporates from the solution (Figure 1). Since the dissociation
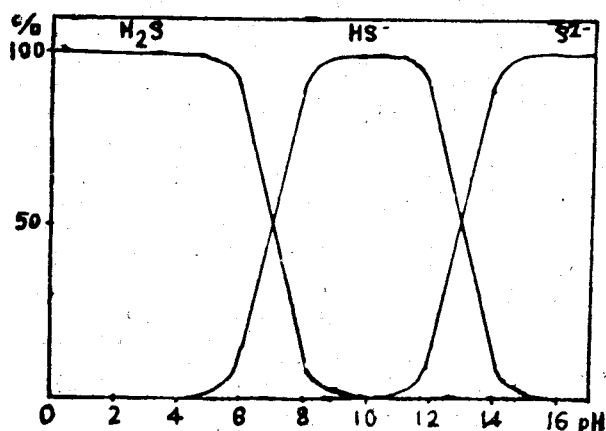

Fig. 1—Complexation of Sulphide ions with Hydrogen ions as a function of pH. The Diagram is Based on H2S Disassocition constants of PK_1 7.0 and $PK_2 = 13.0$ at 25°C.

$$2Na_2S + 2O_2 + H_2O \quad —Na_2S_2O_3 + 2NaOH$$

values of the organic sulphides are much lower as compared with inorganic sulphide sulphur, it is followed from the figure that by maintaining the pH of the stock solution at a very high alkaline level (Say above 13.0 pH), the ionic strength and hence the activity of the sulphide ion can be kept constant. At an alkaline pH level it may be safely assumed that the S− ion present in the system is contributed mostly from the inorganic sulphide sulphur. Different metallic/specific ion electrodes have been suggested for the potentiometric titrations of sodium sulphide[31]-[37]. The advantages/disadvantages of using various titrants mainly AgNO3, Hg (NO3), HgCl2, Cd (NO3) has been discussed elaborately in the literatures [31,32] , [37-39].

Raising the doubts on the versatility of AgNO3 as a titrant, on the pretext that the silver ions get reduced during the titration, Bilberg[38] suggested the use of Hg(NO3)2 as titrant. This titration can be done with the combination of either Ag/Ag2S or Pt/Pt Cl2 indicator electrodes along with either calomel or glass electrodes. Lingane[39] discussed the aspects of the analytical chemistry of Mercury (II) and professed that

(a) mercuric sulphide is soluble in strongly alkaline sulphide solutions, forming presumably a complex of the form HgS_2^{2-}

(b) mercury (II) compounds are highly reduceable. But it should be noted that BL is a highly alkaline solution having multitudes of reducing compounds and the suitability of Mercury (II) as a better titrant is doubtful.

Willard and Ferwick[23] proved that the potentiometric end point in the precipitation of sulphide by Ag NO3 in ammoniacal media is extremely sharp and chloride, thio-sulphate and polysulphides are interfering radica's.

Galo[10] concluded that the titration in a potentiometer having saturated, calomel reference electrode and Ag/Ag S indicator electrode, using 0.1 N AgNO3 give consistently good results for the estimation of Na2S. Another advantage pointed out by Temela and Ryland[29], is that DMDS is not precipitated by AgNO3 and as such potentiometric titration of Argentimetry can be used for oxidized BL too.

Weighing the pros and cons of various titrants, the potentiometric titration with 0.1 N AgNO3 using satd. calomel reference electrode and Ag/Ag S as indicator electrode appears to be the best for the estimation of sulfide sulfer in BL.

EXPERIMENTAL

POTENTIOMETER SYSTEM

APPARATUS

The apparatus used is a direct indicating colora Level potentiometer type 527. An Ag/Ag$_2$ S indicator electrode with saturated calomel reference is used in the analytical evaluation.

REAGENTS AND SOLUTIONS

Synthetic Black liquor (SBL) of various concentrations are prepared by the dissolution of tecnnical grade Na$_2$S (50% purity) in a caustic solution of approximate strength of 7 gpl. The Na$_2$S solution is filtered before mixing with the caustic solution.

Thin Black liquor (TBL) is collected from the chemical recovery plant of an integrated kraft mill.

The Black liquor is filled in a bottle containing nitrogen gas upto the brim to exclude the air column over BL and tightly sealed. Except one sample, BL is stored at a temperature of 5±1°C. One sample is stored at the temperature of 25±1°C. (room temp.).

The (SBL) is stored in the similar manner taking all the precautions to exclude air column over the liquor. $\frac{N}{10}$ AgNO$_3$, 5N NaOH and 1 : 99 NH$_4$OH are also prepared. 5N NaOH is standardized against 1NHCL. All the reagents are stored under controlled conditions and frequently checked for their strength.

PROCEDURE

Thin Black liquor/synthetic Black liquor is divided into 3 parts and labelled. One part labelled TBLU/SBLU) is used as such. From the second part, 25 cc. of the sample is pipetted and the organics are precipitated with 10% BaCl$_2$. The carbonate in case of synthetic BL is also precipitated in the same way. This thin Black liquor and synthetic Black liquor is used without filtration for the titration (TBLPU/SBLPU). The third part is precipitated with 10% BaCl$_2$ filtered and the aliquot is taken for the titration (TBLPF/SBLPF). Controls and duplicates had been run for all the samples.

In case of unprecipitated TBLU/SBLU liquors, 10, 25, and 50 ml of volumes are taken for titrations. To these analytical liquors, 200 ml of 5 N NaOH (40 gms of NaOH equivalent) and 50 cc of 1:99 NH$_4$OH are added. The volume is made upto 400 ml using deoxygenated distilled water so that the strength of NaOH and NH$_4$OH is adjusted to 2.5 N and 0.03 N respectively. The titrations are carried out immediately, by an initial rapid addition of N/10 AgNO$_3$ and a gradual and fine additions of the titrant at the approach of end points. During the course of titration the potential drop per volume addition of N/10 AgNO$_3$ is noted and the end point is taken as that point at which the differential potential value per unit volume of N/10 AgNO$_3$ is maximum. The results for the TBLU/SBLU, TBLPU/SBLPU and TBLPF/SBLPF are tabulated in Tables (1-8).

Analysis are also made to determine the depletion of Na$_2$S strength in TBL/SBL stored at 5±1°C and at 25±1°C, due to auto oxidation. The estimations are carried out at an interval of 24 Hrs for a period of 7 days. (Table No. 9).

TABLE—1 STRENGTH OF Na$_2$S IN THIN BLACK LIQUOR — UNPRECIPITATED (TBLU)

| S.No. | SAMPLE | STRENGTH OF Na$_2$S (in gpl) | | | Average (gpl) | Variation from control Max/min (gpl) | %variation from control Max/min | %varition of average from control |
		CONTROL	1st Repetition	2nd Repetition				
1.	TBLU$_1$	2.340	2.574	2.153	2.356	+0.187/-0.234	+8.0/-10.0	+0.78
2.	TBLU$_2$	2.652	2.730	2.470	2.614	+0.078/-0.192	+2.94/-7.44	—1.43
3.	TBLU$_3$	2.009	2.028	2.067	2.034	+0.058/-0.000	+2.90/-0.00	+1.24
4.	TBLU$_4$	2.067	2.262	2.223	2.184	+0.195/-0.000	+9.44/-0.00	+5.66
5.	TBLU$_5$	2.028	1.950	2.126	2.035	+0.098/-0.078	+4.90/-3.85	+0.35
6.	TBLU$_6$	2.145	2.067	2.223	2.145	+0.078/-0.078	+3.63/-3.63	———
7.	TBLU$_7$	2.730	2.886	2.730	2.782	+0.156/-0.000	+5.00/-0.00	+1.92

TABLE—2 STRENGTH OF Na₂S IN THIN BLACK LIQUOR PRECIPITATED WITH 10% BaCl₂ AND UNFILTERED (TBLPU)

| S.No. | SAMPLE | STRENGHT OF Na₂S (in gpl) | | | Ave-rage (gpl) | Variation from control Max/Min | %Variation from control Max/Min | %Variation of average from control |
		CONTROL	1st Repeti-tion	2nd Repeti-tion				
1.	TBLPU₁	2.028	2.067	2.028	2.041	+0.039/-0.000	+1.9/-	+0.64
2.	TBLPU₂	2.340	2.379	2.301	2.340	+0.039/-0.039	+1.71/-1.71	———
3.	TBLPU₃	1.716	1.638	1.638	1.664	+0.000/-0.078	+0.00/-0.00	+3.03
4.	TBLPU₄	1.677	1.638	——	1.657	+0.000/-0.039	+0.00/-4.55	—1.20
5.	TBLPU₅	1.755	1.677	1.833	1.755	+0.078/-0.078	+4.44/-4.44	———
6.	TBLPU₆	1.872	1.872	——	1.872	+0.000/-0.000	+0.00/-0.00	———
7.	TBLPU₇	2.184	2.262	2.223	2.223	+0.078/-0.078	+3.57/-3.57	+1.80

TABLE : 3 STRENGTH OF Na₂S IN THIN BLACK LIQUOR PRECIPITATED WITH 10% BaCl₂ ADN FILTERED (TBLPF)

| S. No. | SAMPLE | STRENGTH OF Na₂S (in gpl) | | | Ave-rage (gpl) | Variation from control Max/Min (gpl) | % Variation from control Max/Min | % Varia-tion of average from control |
		CON-TROL	1st Repeti-tion	2nd Repeti-tion				
1.	TBLPF₁	1.911	1.910	1.911	1.924	+0.039/-0.000	+2.04/0	+0.70
2.	TBLPF₂	2.184	2.223	2.184	2.197	+0.039/-0.000	+1.80/-	+0.60
3.	TBLPF₃	1.638	1.521	1.677	1.612	+0.039/-0.117	+2.38/+7.00	—1.59
4.	TBLPF₄	1.482	1.521	1.482	1.496	+0.039/0.000	+2.63/-	+0.90
5.	TBLPF₅	1.521	1.560	1.638	1.573	+0.117/-0.000	+7.00/-	+3.42
6.	TBLPF₆	1.677	1.710	1.677	1.690	+0.039/-0.000	+2.43/-	+0.80
7.	TBLPF₇	2.067	2.145	2.184	2.132	+0.117/-0.000	+5.66/-	+3.14

TABLE : 4 ANALYSIS OF SYNTHETIC BLACK LIQUOR-UNPRECIPITATED (SBLU)

| S. No. | SAMPLE | STRENGTH OF Na₂S (in gpl) | | | Ave-rage (gpl) | Variation from control Max/Min (gpl) | % Variation from control Max/Min | % Varia-tion of average from control |
		Con-trol	1st Repeti-tion	2nd Repeti-tion				
1.	SBLU₁A	1.209	1.190	1.190	1.196	+0.000/-0.019	+0.00/-(1.57)	—(1.0)
2.	SBLU₂B	1.190	1.190	1.190	1.190	—	—	—
3.	SBLU₂A	3.900	3.884	3.884	3.889	+0.000/-0.016	+0.00/-(0.41)	—
4.	SBLU₃A	4.524	4.415	4.407	4.472	+0.039/-0.117	+(0.090)/-(2.60)	—(1.1)
5.	SBLU₄A	3.775	3.788	3.822	3.795	+0.047/-0.000	+(1.30)/-(0.00)	+(0.5)
6.	SBLU₄B	3.788	3.788	—	3.788	—	—	—
7.	SBLU₅A	2.028	2.106	2.067	2.067	+0.78/-0.000	+3.85/-(0.00)	+(1.9)
8.	SBLU₅B	2.106	2.106	2.028	2.080	+0.000/-0.078	+0.00/-(3.70)	—(1.2)
9.	SBLU₆A	9.672	9.633	9.789	6.698	+0.117/-0.039	+1.21/-(0.40)	+(0.3)
10.	SBLU₇A	7.449	7.527	7.527	7.801	+0.088/-0.000	+(1.18)/-(0.000)	+(.70)

TABLE : 5 ANALYSIS OF SYNTHETIC BLACK LIQUOR PRECIPITATED
WITH 10% BaCl$_2$ AND UNFILTERED (SBLPU)

S. No.	Sample	STRENGTH OF Na$_2$S (in Gpl)			Average (gpl)	Variation from control Max/Min (gpl)	% Variation from control Max/Min	% Variation from average from control
		Control	1st Repetition	2nd Repetition				
1.	SBLPU$_1$	1.068	1.045	1.068	1.060	+0.000/-0.023	+0.00/-(2.15)	—(0.75)
2.	SBLPU$_2$	37.41	3.451	3.374	3.432	+0.000/-0.897	+0.00/-(2.80)	—(1.12)
3.	SBLPU$_3$	3.686	3.705	3.627	3.073	+0.019/-0.059	+(0.1)/-(1.60)	—(1.35)
4.	SBLPU$_4$	3.471	3.393	3.393	3.419	+0.000/-0.078	+(0.00)/-(2.25)	—(1.50)
5.	SBLPU$_6$	8.970	8.853	8.093	8.839	+0.000/-0.277	+(0.00)/-(3.09)	—(1.46)
6.	SBLPU$_7$	7.020	7.098	7.196	7.105	+0.176/-0.000	+(2.50)/-(0.00)	—(1.21)

TABLE : 6 ANALYSIS OF SYNTHETIC BLACK LIQUOR PRECIPITATED
WITH 10% BaCl$_2$ AND FILTERED (SBLPF)

S. No.	Sample	STRENGTH OF Na$_2$S (in gpl)			Average (gpl)	Variation from control Max/Min (gpl)	% Varition from control Max/Min	% Variation from average from control
		Control	1st Repetition	2nd Repetition				
1.	SBLPF$_1$	1.053	1.045	1.053	10.50	+0 000/-0.08	+(0.00)/-(0.76)	—
2.	SBLPF$_2$	3.354	3.393	3.315	3.354	+0.039/-0.039	+(1.16)/-(1.16)	—
3.	SBLPF$_3$	3.549	3.627	3.588	3.588	+0.078/-0.000	+(2.20)/-(0.00)	1.10
4.	SBLPF$_6$	8.775	8.931	8.685	8.827	+0.156/-0.090	+(1.80)/-(1.02)	+0.50
5.	SBLPF$_7$	6.942	6.903	6.825	6.890	+0.000/-0.117	+(0.00)/-(1.70)	+0.75

TABLE—7 VARIATION OF STRENGTH IN THIN BLACK LIQUOR PRECIPITATED
AND UNFILTERED (TBLPU) AND PRECIPITATED AND FILTERED (TBLPF)
FROM THIN BLACK LIQUOR UNPRECIPITATED (TBLU)

S.No.	SAMPLE	Strength of Na$_2$S in (TBLU) Avg. (gpl)	STRENGTH OF Na$_2$S in TBLPU				Strength of Na$_2$S in TBLPF	
			Avg(gpl)	Deviation from the TBLU (gpl)	%Variation	Avg(gpl)	Deviation from the TBLU(gpl)	%Varition.
1.	TBLUF$_1$	2.356	2.041	0.315	−13.3	1.924	0.432	−18.30
2.	TBLUF$_2$	2.614	2.340	0.274	−10.5	2.197	0.417	−16.00
3.	TBLUF$_3$	2.034	2.664	0.370	−10.2	1.612	0.422	−20.75
4.	TBLUF$_4$	2.184	1.657	0.527	−24.1	1.495	0.689	−31.55
5.	TBLUF$_5$	2.035	1.755	0.280	−13.8	1.573	0.462	−22.70
6.	TBLUF$_6$	2.145	1.872	0.273	−12.7	1.690	0.455	−21.22
7.	TBLUF$_7$	2.782	2.223	0.559	−20.1	2.132	0.650	−23.37

TABLE—8 VARIATION OF STRENGTH IN SYNTHETIC BLACK LIQUOR PRECIPITATED AND UNFILTERED (SBLPU) AND PRECIPITATED AND FILTERED (SBLPF) FROM SYNTHETIC BLACK LIQUOR UNPRECIPITATED (SBLU)

S.No.	SAMPLE	Srength of Na_2S in (Tblu) Avg.(gpl)	STRENGTH OF Na_2S in TBLPU				Strength of Na_2S in TBLPF	
			Avg(gpl)	Deviation from the TBLU(gpl	%Variation TBLU(gpl)	Avg(gpl)	Deviation from the TBLU (gpl)	%Vartion.
1.	A	1.196	1.060	0.136	−11.40	1.050	0.146	−13.04
2.	2A	3.889	3.432	0.457	−11.80	3.354	0.535	−13.04
3.	3A	4.472	3.673	0.799	−17.87	3.580	0.884	−19.77
4.	4A	3.795	3.419	0.376	−10.00	—	—	—
5.	5A	2.067	—	—	—	—	—	—
6.	6A	9.690	8.839	0.859	−8.86	8.827	0.871	−9.00
7.	7A	7.501	7.105	0.396	−5.28	6.890	0.611	−8.15

TABLE : 9 %DEPLETION OF Na_2S ON STORAGE IN THIN BLACK LIQUOR AND SYNTHETIC BLACK LIQUOR STORED AT $5\pm1°C$ & $25\pm1°C$

PERIOD	THIN BLACK LIQUOR STORED AT $5+1°C$		THIN BLACK LIQUOR STORED AT $25\pm1°C$		SYNTHETIC BLACK LIQUOR STORED AT $25\pm1°C$	
	CONCENTRATION	% DEPLETION	CONCENTRATION	% DEPLETION	CONCENTRATION	% DEPLETION
Initial	2.340	0.00	2.574	0.00	4.524	0.00
After 1st day	2.340	0.00	2.496	3.05	4.524	0.00
„ 2nd day	2.340	0.00	2.418	6.06	4.524	0.00
„ 3rd day	2.322	0.80	2.301	10.66	4.504	0.43
„ 4th day	2.302	1.60	2.204	14.40	4.496	0.62
„ 5th day	2.263	3.26	2.087	18.90	4.476	1.06
„ 6th day	—	—	—	—	—	—
„ 7th day	2.224	5.00	1.853	28.00	4.437	1.92

BLACK LIQUOR OXIDATION (BLD)

At one stage in kraft pulping process, the spent BL may be oxidized to stabilize sulphur compounds, to reduce sulphur losses and odour emissions.
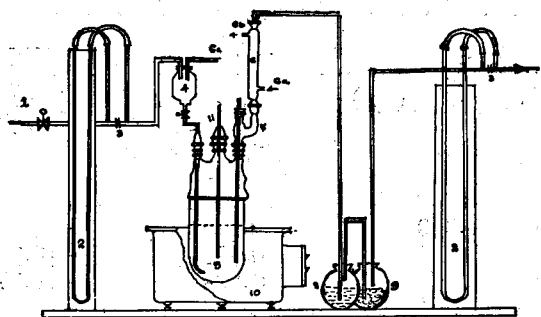
Though the standardization of the analytical procedure for the estimation of sulphide in BL is an integral part of this work, the main work is to evaluate the kinetic characteristics of sulphide sulphur oxidation in sulphate black liquor and also the activation energy for the Thin/Thick Black liquor to optimize the design feature for BLO reactors for sulphur based bamboo Black liquor.

Based on the works of Murray[5], Sakhuja and Basu[6] Karsat and Basu[41] the experimental Setup for batch BLO is designed, fabricated and standardized (Fig. 2). A "Norgran" flow regulator U/V issued forth precise regulation of inlet air to the system and the flow is measured using an 1 Cm ϕ orifice meter and U-tube differential manometer.

For every batch of experiment 1.5 litres of TBL/SBL is used. The TBL is analysed for the total dry solids (TDS) content, and Na_2S. The sulphur losses by carry over with air during oxidation is prevented by fitting a water cooled condenser and also passing the vapours through a bottle containing Benzene. The air is stripped off by passing the vapours further through an aspirator bottle containing $CaCl_2$. The outgoing air flow is again measured by a separate orifice meter and 'U' tube differential manometer. The theoretical amount of air to be supplied is calculated from the concentration of Na_2S in BL, taking a value that 1 gm of Na_2S requires 1.56 gms of air to

LEGEND :

1. Norgran Flowregulator
2,2. 'U' Tube Differential Manometer
3,3. Orifice Meter
4. Mixing Bulb
5. Batch Reactor
6. Water Condenser
6a, 6b. Water inlet/outlet to condenser.
6c. Saturated steam
7 Liquor sample
8. Benzene
9. Calcium chloride
10. Heating Mantle
11. Thermometer

complete the stochiometric equation (see fig 1). The theoritical to actual air supply ratio is kept at 10. Samples are drawn at 10 minutes intervals and analysed for the Na_2S content, using the potentiometric method outlined above. The oxidation is usually carried out for a period of 1 hr. The results of the oxidation of BL (oxidized for 30 minutes) along with the % oxidations has been given in the Table (11, 12).

Oxidation of SBL is carried out in a similiar conditions except for the ratio of theoretical to actual air supply which was kept at 50.

SUMMARY AND DISCUSSION

The Barlew and Pascoe method gives consistently good results and can be comparable with, the most sophisticated procedures like the selection methods[43] (Table 1-8). From the tables it is evident that in the synthetic Black liquor (SBLU), the strength of Na_2S, determined by the method outlined above, the % variation of average strength of Na_2S, from the control is only about ±3.0. In case of TBLU the % variation of average values from the control is remarkably low in the range of ±2.0 whereas in case of individual readings, the percentage variation from the control is ± 8.

From the figure 3 and table (13), the synthetic black liquor (SBL), which is similar in composition of W.L. witout having any interfering organic compounds, is giving a very steep potential drop. One of the factors that is responsible for this is the insolubility of the precipitated sulphide compounds even in a strong alkaline solution like this.

In case of Black liquor (unoxidized), it has been observed that, it also gives, a well defined steep potential drop (fig. 4) unlike the one as depicted by Swartz and Light [31]. The second influx points in the figure indicates that of chlorides and cyanides. This findings confirm, two things. One is that, $AgNO_3$ even in presence of high alkaline medium can give consistant results, thereby ruling out the fears expressed by Bilberg[3s] as unwarranted. Secondly the interference of organosulphur compounds in BL can be prevented by keeping the pH of the BL at a very high alkaline level (13.5 pH) and not allowing the pH to fall below 11.5, the pH at which the K_H —and K_{s},—is in equilibrium (fig. 1). This could be achieved by keeping the normality of the NaOH (2.5 N) than recommended (1 N) and also strongly buffering the BL with NH_4OH.

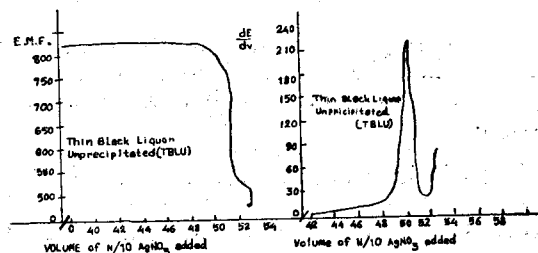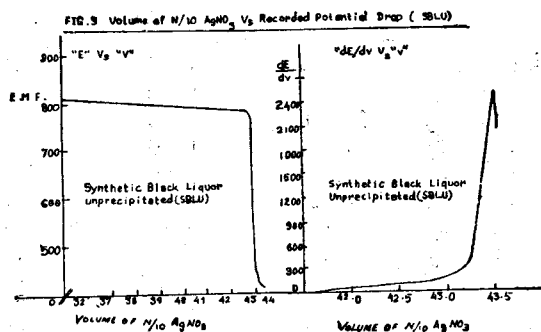FIG.3 Volume of N/10 $AgNO_3$ Vs Recorded Potential Drop (SBLU)

FIG.4 Volume of N/10 $AgNO_3$ Vs Recorded Potential Drop (TBLU)

It can be said that by making the solution highly ammoniacal as in our case (the strength of NH_4OH is around 0 03 N) the organo sulphur compounds can be made soluble in ammonia salts and their interference can thus be avoided.

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TABLE : 10 RATE OF OXIDATION OF BLACK LIQUOR

	O 'MIN' OXIDATION		30 MIN OXIDATION		60 MIN OXIDATION	
	Volume of N 10 AgNO$_3$ Added	Recorded potential drop	Volume of N/10 AgNO$_3$ Added	Recorded Potential drop	Volume of N/10 AgNO$_3$ added	Recorded Potential drop.
	(Vcc)	(E=mVs)	Vcc	(Ex=—mVs)	Vcc	(Ex=—mVs)
Initial reading of The burette	= 8.0	— 801.5	32.0	—790.8	=8.0	—750.5
	12.0	—79.35	33.0	—784.0	8.1	—748.5
	15.0	—779.5	34.0	—775.5	8.2	—743.5
	16 0	—767.0	34.3	—770.0	8.3	—743.5
	16.5	—752.0	34.4	—758.5	8.4	—742.5
	16.7	—730.0	34.5	—746.0	8.5	—740.5
	16.8	—680.0	34.6	—726.5	8.6	—737.5
	16.9*	—570.0	34.7*	—610.5	8.7	—732.5
	17.0	—490.0	34.8	—530.5	8.8	—730.5
	17.2	—360.0	34.9	—460.0	8.9	—HEAVY DRIFTING OF POTENTIAL READING

*End Point

TABLE—11 THE OXIDATION OF THIN BLACK LIQUOR; THEORETICAL: ACTUAL AIR SUPPLY = 1:10

S.No.	Temp.°C	Reaction time (min)	Initial conc. (gpl)	Final Conc. (gpl)	%BLO
1.	75±1°	30	6.942	2.106	69.8 Approx 70.0 (say)

TABLE—12 RATE OF OXIDATION OF Na$_2$S DURING BLO

S.No.	Temp.°C	Reaction time (min)	Initial conc. (gpl)	Final Conc. (gpl)	%BLO
1.	75 + 1°	0	6.942	6.942	0
2.		10	6.942	5.538	20
3.		20	6.942	3.822	55
4.		30	6.942	2.106	70

|	
Initial Conc. of Na$_2$S in thin BL	6.942 gpl
Strength of Na$_2$S after 30 min. oxidation	2.106 gpl
Strength of Na$_2$S after 60 min. oxidation (approx)	0.833 gpl (also refer Table no. 10)

The initial potential reading recorded for the TBLU is always little more than that recorded for the SBLU. This clearly indicates that in the Barlew and Pascoe Procedure, the inorganic sulphide sulphur in the system is measured and the contribution by the organic sulphide sulphur compounds is small, and insignificant.

The barium chloride precipitation of thin Black liquor and synthetic Black Liquor results in a considerable loss of sulphide sulphur by its occulsion to the precipitated collidal lignin complex. In case of synthetic Black Liquor (SBLPU), % reduction is ± 10% (Table 8) and Thin his Black Liquor it is ± 20% (Table 4).

If the precipitate is filtered out and the aliquot is used for the estimation, then the loss of sulphide sulphur by occulsion in SBLPF/TBLPF is increased to ± 13% and ± 25% respectively. This aspect of occulsion is more important for the system designing of a system engaged in the Black liquor regeneration by carbonation technique.

The figure and the results of the oxidized BL is given in fig. 5 and Table 10. They indicate that the initial potential recorded by the oxidized Black liquor is significantly lower (around 50 mVs lesser) and the titration becomes highly difficult because of the drifting potential, may be due to the increased polysulphides, $Na_2S_2O_3$ and may be of the oxidation reactions of organic sulphide sulphur.

FIG. 5 Volume of N/10 AgNO₃ added vs Recorded Potential Drop (OBL)
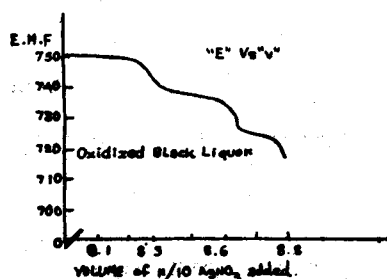
Although a much lower potential is to be expected for the oxidized BL because of the conversion of Na_2S to $Na_2S_2O_3$[37] during the oxidation nevertheless an increased potential is observed which confirm the findings of Lonz and Magnell and Fischer of NCASI[42].

In case of oxidized Black liquor, the stabilized organic sulphide sulphur compounds are complex in nature. From the Table 10, it is very much clear that though the estimation of the depletion of Na_2S is simple upto an oxidation period of 30 minutes, the drifting potential and other difficulties

are pronounced after this period. It is evident from this, that upto 30 minutes of oxidation it was only the Na_2S that is oxidized and after this the organic sulphide sulphur may also take part in the reaction. This reaction of organic sulphide sulphur may continue irrespective of the pH and the Na_2S content of the oxidized BL. Therefore, in addition to the measurements of inorganic sulphide sulphurs, it is also essential to measure the organic sulphide sulphur concentration of BL after 30 minutes during the period of oxidation.

Making a proper sulphur balance it has been found that 10 to 15 percent (depending upon mode of BLO equipments) of the sulphide sulphur could not be accounted for by the formation of $Na_2S_2O_3$ and Na_2SO_4. It seems likely that at least a part of the unaccounted sulphide sulphur may be present in the oxidized BL, as polysulphides, which could not be estimated during the analysis. From the sulphur balance it is also confirmed that the oxidation of sodium sulphide might be extended to the sulphate form providing excessive amount of interfacial surface area and air supply.

The oxidation of synthetic Black liquor is very difficult. It has been observed during the experimental investigations, that even by supplying air at 50 times more than the theoretical requirement and carrying the oxidation for 1 Hr, at 75 ±1°C, the percent depletion of Na_2S (and hence % Oxidation) is only 5%. It clearly indicates that though NaOH can help in oxidation, it is rather the catalytic action of phenolic compounds present in the BL, that is responsible for enhancing the oxidation rate. (This is also evident from the TBLU/SBLU/TBLPU/SBLPU and TBLPF/SBLPF results).

The BL stored at 5 ±1°C for 7 days has shown a negligible loss of Na_2S during storage (Table 9) whereas the one stored at a temperature of 25±1°C has shown a considerable reduction (around 28%) of Na_2S content during the same time interval. Since the BL container was air tight in both the cases, it is very much clear that the auto oxidation of sulphide sulphurs to thiosulphates by phenolic compounds is very much pronounced even at room temperature. In case of synthetic Black liquor the reduction of Na_2S strength is negligible, under similar conditions of storage, which confirms the absence of catalytic auto-oxidation of sulphide sulphur in SBL.

The studies also indicate that in the thin black liquor, the reversion of stabilized sulphur compounds back to their normal volotile state, during storage, is negligible if oxidized BL is kept at elevated temperature or at the oxidation tempe-

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TABLE 13 VOLUME OF N/10 Ag NO₃ ADDED Vs RECORDED POTENTIAL DROP FOR SBLU AND TBLU

SYNTHETIC BLACK LIQUOR (SBLU)			REMARKS	THIN BLACK LIQUOR (TBLU)			
SAMPLE Volume of N/10 AgNo₃ added	Recorded Potential Drop	dE/dv		SAMPLE Volume of N/10 AgNO₃ added	Recorded Potential Drop	dE/dv	REMARKS
SBLU₁B (v) CC	'E' mVs			TBLU₃ (v) CC	"E" mVs (−)		
INITIAL 4.5	800.0	0.0	Strength	INITIAL 17.5	814.0	0.2	Strength
VOLUME 5.0	800.0	1.0	of Na₂S	VOLUME 20.5	813.0	0.5	of B.L.
IN 5.5	7 9.5	2 0	in gpl	25.5	810.5	0.9	in gpl
BURETTE 6 0	798.5	2 0 =1.20-		BURETTE 30.5	806.0	1.3	=2.57 gpl
=4.580 6.5	797.5	2 0 gpl	=17.5cc 35.5	8r0.5	1.5		
7.0	796.5	4.0		41.5	792.5	2.5	
7.5	795.5	4.0		45.5	782.5	5.0	
8.0	792.5	4.0		46.0	780.5	5.0	
8.5	790.5	—		46.5	778.5	6.5	
9.0	789.5	6.0		47.5	772.0	9.0	
9.5	786.5	6.5		48.5	767.5	13.0	
10.0	783.5	7.0		49.0	761.0	19.0	
10.5	780.0	8.0		49.5	751.5	37.5	
11.0	776.0	37.5		49.7	744.5	60.0	
12.0	738.5	2385		49.9	732.0	67.5	
12.1	550.5	4220		50.1	718.5	100.0	
12.2	128.5	600		50.3	698.5	255.0	
12.3	68.5	500		50.4	673.0	725.0	
12.4	18.5			50.5	600.5	22.5	
				51.5	577.5	52.5	
				52.5	525.5		

rature, pronounced reaction reversion takes place when oxidized Black liquor is kept at room temperature. The quantitative estimation of Na₂S in these case are done after terminating the oxida tion after 30 minutes and storing them as outlined. Based on preliminary experimental investigations carried out in this work, it is recommended to do BLO in two stages.

For the achievement of most economical benefit through BLO installations, first stage BLO should be carried out upto the level of 60% in this BL, and, after concentration the BL in the multi-effect-evaporators, the BLO may be completed in thick BL stage, for optimal level of sulphide sulpur stabilization.

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