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RADIOLYTIC TRANSFORMATION OF SULFIDES IN SULFATE BLACK LIQUORS

ΈY

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ABSTRACT

The potentially volatile, malodorous sulfides $(H_2S, CH_3SH, CH_3SCH_3 and CH_3SSCH_3)$ in sulfate black liquros were transformed to stable compounds by exposure to gamma photon radiolysis. The product complex following radiolysis of sulfides in aqueous solution is partly resolved as: polysulfide (from H_S), sulfate (from H_S, CH_{SH} and CH₃SSCH₃), an intermediate, CH₃SSCH₃ (from CH₃SH), and a high molecular weight, amorphous substance (especially from CH₃SCH₃).

Variables studied with aqueous solutions and commercial black liquors have included sulfide concentration, solution pH, temperature, oxygen saturation and effects of soluble lignin, all of which adjusted to some extent the sulfide degradation kinetics. Lowering solution pH and increasing initial sulfide concentration, temperature and/or oxygen pressure increased apparent degradation yields (G), while lignin (thiolignin) acted as a radical scavenger in the process.

In gamma radiolysis of strong and weak black liquors (pH 12.85 -13.40) at Gammacell temperature (34° C), and atmospheric oxygen pressure, the apparent degradation yields of sulfide are proportional to the respective initial concentrations. Apparent degradation yields were 0.001-0.003 for CH₃SCH₃ at 0.20 x 10⁻³ -1.10 x 10⁻³g/l and 0.002-0.085 for CH₃SSCH₃ at 0.44 x 10⁻³g/l-39.71 x 10⁻³g/l concentration. Similarly, in carbonated black liquors (pH 8.20-9.15), the apparent degradation yields of sulfides significantly correlated with their initial concentration. The apparent sulfide degradation yields are 0.015 to 3.427 for H S at 0.89 x 10^{-3} -265.20 x $10^{-3}g/1$, 0.006-0.230 for CH₃SH at 0.48 x 10^{-3} -28.70 x $10^{-3}g/1$, 0.003 - 0.020 for CH₃SCH₃ at 0.60 x 10^{-3} -5.22 x $10^{-3}g/1$ and 0.004-0.035 for CH₃SSCH₃ at 1.03 x 10^{-3} -9.11 x $10^{-3}g/1$ concentration.

The presence of oxygen(1 atmosphere pressure) at higher concentration of $H_2S(247.75 \times 10^{-3}g/1)$ and $CH_3SH(967.50 \times 10^{-3}g/1)$ in carbonate black liquor (pH 7.50) showed high apparent degradation yields of 17 and 28 for H_2S and CH SH, respectively. This is considered to be due to a chain reaction occurring during degradation of sulfides.

Polysulfide may be generated by radiolysis of acidified sodium sulfide and sulfate green liquor. The apparent yields of polysulfide excess sulfur were 3 and 5 for acidification with carbon dioxide (120 psi) and hydrogen sulfide (270 psi), respectively.

As part of these studies, new techniques have been developed for recovery and analysis of sulfides at low concentrations in aqueous solution.

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1.0 INTRODUCTION

In North America, the pulp and paper industry occupies a prominent position (ninth) among natural product processing industries such as oil, mining and food processing industries. Canada alone produced 16.4% of the world's total supply of pulp, furnishing nearly 16 million short tons in 1969. Of this amount, 9.3 million tons was chemical pulp of which approximately 73% was produced by the sulfate (kraft) process (64).

Projections made for chemical pulp production anticipate that, of sulfate pulp will increase by two and one-half times, and that of the neutral sulfite semichemical (NSSC) process will approximately double the 1968 figures by 1985 in the United States. Sulfite pulp production will likely decrease slightly, whereas soda and dissolving pulp production is expected to remain constant (89). Therefore, the sulfate and NSSC processes are expected to dominate chemical pulping in the future, as they do at present.

The main reasons for such potential dominance of the pulping industry by the sulfate process are the comparative simplicity, rapidity of cooking, applicability to all wood variations and wood species, favorable pulp and paper properties and, most important of all, the availability of an efficient and economic recovery process. These intrinsic advantages have seemed to outweigh the drawbacks, which are the requirement of the high initial invest-

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ment and pollution problems of several types, usually of a complex nature. Opportunities for pollutant formation and escape occur at many points throughout the process.

Budgeting for pollution control has become a recognized factor in pulp mill operation today. Expenditures for pollution control by pulp mills have reached phenomenal figures during the past decade. Fortunately, the pulping process has been modified and improved through the years in such a manner that stringent recovery of process losses usually defray part of the capital costs for additional equipment. Besides, as a public service, governments have often recognized the need for various forms of assistance to increase pollution abatement. Such subsidies have increased the funds available, not only to public agencies concerned with pollution control, but have also provided direct research grants and tax relief to the industry.

The causes of air and water pollution relate mainly to dissolved organic wood residues (carbohydrates, lignin and extractives) and subsequent formation of methyl mercaptan, dimethyl sulfide, dimethyl disulfide and hydrogen sulfide in the digester, as well as during the chemical recovery process. Chemical recovery involves black liquor concentration, combustion and reconstitution of the cooking chemicals. During the digester relief, digester blow, and recovery operations, sulfur-bearing gases may be lost to the atmosphere in varying amounts. Other

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minor sources of pollutants are particulate matter from the recovery furnace.

The possible formation of water pollutants in sulfate pulping relates to digester relief, blow, and evaporator condensates, as well as to weak wash waters discharged from bleach plants. These water contaminants constitute sources of biological oxygen demand (BOD), chemical oxygen demand (COD) and may contribute to toxicity of the effluents. It is also recognized that most of the problem causing contaminants relate to the noncellulosic components released during the course of pulping. Among important pollutants, the sulfide and mercaptide ions have been identified as highly toxic constituents (214).

Recently, various efforts have been made to solve pollution problems associated with sulfate pulp mills. As is often the case, a process designed to resolve one problem may create yet another. Some solutions proposed for abatement of air pollution often create water pollution and <u>vice versa</u>. Retention and stabilization of sulfur-containing volatile compounds is difficult. Methods practiced or proposed for black liquor digester relief and blow gas treatments are oxidation (42, 92, 136), chlorination (60, 75, 201, 205), combustion (39, 50, 51) and absorption and desorption (1, 171); but none of these has been shown to be completely successful. Failure of such provisions often relate to the extreme human sensitivity to obnoxious sulfides, possibly

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evolutionary in nature as an index or warning precaution to food spoilage. Threshold concentration values of sulfide detection by humans lies below or at the detection limits of modern analytical instruments and, while none of the sulfides (except for hydrogen sulfide) has been directly associated with human illnesses, they do constitute a considerable nuisance to the public.

Increased availability of high energy isotopes from reactor by-products provides the possibilities in the near future for industrial processing, and process control developments. Although applications of industrial radiation processing are, generally speaking, in preliminary stages, the limited results indicate levels of achievements unobtainable by conventional means.

The application of ionizing radiation to wood product industries is currently being investigated for wood coatings, wood plastic combinations, prevention of wood chip deterioration in outside storage prior to pulping (43, 71) and wood substance modification to benefit pulp properties and pulping processes (34, 43, 71, 81, 208).

Considerable information has been made available on the effects and utilization of ionizing radiation for purposes of food and drug processing and new packaging technology. Although limited studies are available on the destruction of microorganisms and oxidation of organic substances in industrial

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effluents and waste water streams (118), specific technology and descriptive literature with pulp mill effluent treatments are almost completely lacking.

Most works have been only exploratory in nature. Detailed information is available only for sanitary effluent treatments, researched mainly in the United States. Treatment of industrial effluents, using radiation, is also described for pesticides such as dieldrin and DDT (41, 74, 206), decolorization of aqueous dye solutions from textile mills (74) and for decolorization and solids precipitation from sulfate and neutral sulfite pulp mill effluents (113). These treatment schemes offer examples of significant reductions in BOD/COD, color, toxicity and improved solids sedimentation and are connected only through highly reactive species created by radiolysis of aqueous solutions.

The transformations of volatile malodorous sulfides in sulfate black liquor, and recovery of polysulfide from aqueous sulfide and green liquor as induced by gamma radiation, are little studied. The present study is concerned with application of gamma radiation to industrial and laboratory sulfate pulping liquors with the following objectives:

 To explore influences of gamma photon radiation on the chemical transformations of characteristic sulfides in black liquor and carbonated black liquor.

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- 2. To determine the effects of system variables, such as solution pH, lignin concentration, temperature and oxygen pressure, on transformations occurring with various sulfide model compounds.
- 3. To explore the possibility of recovering polysulfide from aqueous sodium sulfide solution and sulfate green liquor.
- 4. To estimate the degree of sulfide stabilization attainable by a radiolytic process.
- 5. To reevaluate and possibly improve the analytical methodology available for determination of inorganic and organic sulfides in alkaline solutions, as well as in sulfate black liquor.

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2.0 LITERATURE REVIEW

2.1 Process Chemistry of Potential Air and Water Pollutant Formation in Sulfate Pulping of Wood

Waste liquor treatment from pulp and paper mills constitutes a major problem of pollution abatement with this industry (59). The amount of waste water effluent from sulfate pulp mills, with attached bleach plant, varies between 30,000 to 130,000 US gal/ton of air-dried (AD) pulp. This waste water has a low BOD (biological oxygen demand) when compared to such industries as canneries, breweries, dairies and the like; but it is the tremendous volume of water that makes pulp mill waste effluent treatment so expensive. Substantial improvements have been made towards upgrading the effluent quality by developing operating procedures which minimize the fibre loss, and nonrecoverable chemical discharge. A considerable amount of research effort and capital expenditure relating to new and alternate methods of effluent control have been added in older mills and are being incorporated into newly designed mills (1, 39, 60, 92, 120, 130, 136, 171, 203).

Generally, both effluent toxicity and BOD effects of sublethal concentrations of mill effluents are of major importance, especially if discharges occur to inland waterways (174). Among the waste and air pollutants from sulfate mills, sulfides occupy a special place and command dual attention. In aqueous solution,

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they are known to be toxic to aquatic fauna (21, 214), particularly to fish, whereas in gaseous form released to the atmosphere, they have drawn loud public outcries because of their obnoxious nature.

Organosulfide emissions from sulfate pulping are associated with the digester relief, blow tank, pulp washer, oxidation tower, liquor concentrators, recovery furnace, smelt dissolving tank and the lime kiln. While the range of odor causing sulfide emissions may differ from mill to mill, the types of compounds identified as occurring in the above operations are generally the same.

2.1.1 Sulfide reactions in the digester

The substances mainly responsible for odor emissions from sulfate mills are hydrogen sulfide (H_2S) and various forms of organosulfides, originating primarily from reactions with lignin methoxyl groups. First escape of these compounds from the digester is permitted in the form of condensates and non-condensible gases during the digester relief and digester blow operations. Approximate quantities of these compounds are given in Table 2.1 (15, 90).

The hydrogen sulfide is formed through a hydrolytic equilibria of sulfide ions in the aqueous sulfate cooking liquor.

s	+	$H_2 0 \rightleftharpoons$	нs	+	OH/2-1/
нs	+	H ₂ 0 ₹	H ₂ S	+	он/2-2/

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Thus, it is obvious that the quantity of hydrogen sulfide emitted from an aqueous system depends on the pH and temperature of the solution, with lower emissions occurring usually at high pH(pH 12-13) (176).

High cooking temperatures (in excess of 180°C) have been shown to aid the nucleophilic cleavage of the lignin methoxyl group during sulfate cooking to form methyl mercaptan (76).

Lig-OCH₃ + CH₃S⁻ \longrightarrow CH₃SCH₃ + Lig-O⁻/2-4/ The order of nucleophile power of mercaptide and hydrosulfide ions has been shown by Goheen (76) and Turunen (207) to be far greater than that of the hydroxide ion (OH⁻), thus explaining the low methanol content of sulfate cooking liquor.

Reaction kinetics of organosulfide formations have been studied extensively (11, 55, 126, 128) and were found to depend on hydrosulfide ion concentration (128, 166), pH (11, 166), cooking temperature (11), and availability of lignin methoxyls (55, 126). McKean <u>et al.</u> (128) were able to show that demethylation during sulfate cooking followed first order reaction with respect to hydrosulfide ion concentration. Andersson (11) estimated that approximately 2.3 to 2.5% of the total sulfur charge (at 30% sulfidity) is converted to organic sulfides. Recent studies by Douglass and Price (55) show that the rate of mercaptan formation is very accurately proportional to the

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sulfidity at constant effective alkali and liquor to wood ratio levels. McKean <u>et al</u>. (128) suggested that sulfate cooks could be made at much lower sulfidity levels (25%) without seriously impairing delignification rates.

The formation of organosulfides depends on the availability of methoxyl groups. Wood methoxyl is known to vary with wood source. Some observations in this respect were made by Douglass and Price (55) and McKean <u>et at</u>. (126). At identical cooking conditions, porous-wood chips (<u>Betula papyrifera</u> Marsh. and <u>Acer</u> <u>rubrum</u> L.) formed larger quantities of organosulfides than those of coniferous woods (<u>Picea excelsa</u> Link and <u>Pinus taeda</u> L.). In sulfate cooking of porous-woods, approximately 10% more organosulfides are liberated than in comparable pulping of coniferous wood. The higher methoxyl content and some labile methoxyl group in porouswood lignin (syringyl), were thought to contribute to the basic differences observed (128). However, the increase in organosulfides was not proportional to the higher methoxyl content of these hardwoods.

The pH effect upon liberation of hydrogen sulfide and methyl mercaptan is correspondingly indicated in Eqs./2-2/ and /2-3/. Since the pH of the cooking liquor is directly proportional to the alkali charge, the release of hydrogen sulfide and methyl mercaptan is highly dependent on residual alkalinity of the black liquor. Based on vapor pressure <u>vs</u>. pH measurements of hydrogen sulfide

-10-

and methyl mercaptan at various temperatures, Shih <u>et al</u>. (176, 177) found that methyl mercaptan, being a weaker acid than hydrogen sulfide, was highly sensitive to pH changes above pH 10. The vapor pressure curves suggested the desirability of retaining a final pH of 13. In view of the high sulfide concentration, changes in the solution above pH 10can result also in significant vapor pressure changes of hydrogen sulfide. A drop of pH from 13 to 10 can increase vapor. pressure of hydrogen sulfide onehundred-fold, especially under highly efficient steam stripping conditions. Dimethyl sulfide concentration, on the other hand, is not directly affected by pH because its vapor pressure is unaffected by the alkalinity of the cooking liquor.

The dependence of the formation of organosulfides on temperature has been demonstrated by Andersson (11), Douglass and Price (55), DeHaas and Hansen (51) and McKean <u>et al</u>. (126). Based upon the activation energies calculated from Eq. /2-3/andEq. /2-4/ (11.3 and 7.6 Kcal/Mole, respectively) as compared to that of delignification (30.2 Kcal/Mole), it is suggested that a rapid cook at high temperature is likely to produce less odor than a slow cook at low temperature.

The secondary product, dimethyl disulfide (CH₃SSCH₃), originates probably during the later stages of cooking and/or upon digester relief and blow operations. Its formation has been traced to oxidation of methyl mercaptan by oxygen at ambient

-11-

temperature (55).

 $4 \text{CH}_{3} \text{SH} + 0_{2} \longrightarrow 2 \text{H}_{2} 0 + 2 \text{CH}_{3} \text{SSCH}_{3} \dots /2-5/$ $4 \text{CH}_{3} \text{S}^{-} + 0_{2} + 2 \text{H}_{2} 0 \longrightarrow 40 \text{H}^{-} + 2 \text{CH}_{3} \text{SSCH}_{3} \cdot /2-6/$

Digester relief and blow operations are recognized as the largest points of organosulfur emissions within sulfate pulp mills. This is so because these compounds are primarily formed in the digester; and first opportunity to escape from this confinement is by steam stripping with pressure release and blowing. From the foregoing overview it is evident that in the cooking process alone a delicate balance of the main cooking conditions (sulfidity, pH and temperature) must be maintained for effective odor control.

2.1.2 Sulfide formation in stock washers

Stock washers can be a ready source of sulfide emissions and formation of dimethyl disulfide from oxidation of methyl mercaptan as described in the foregoing section. During brown stock washing, the slurry pH closely approaches neutrality, high rate of air flow, turbulence and temperature increase the vapor pressure of volatile sulfides, especially that of hydrogen sulfide, methyl mercaptan, and dimethyl sulfide (Table 2.1) (15, 90).

2.1.3 Gaseous emissions from the black liquor oxidation tower

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The major benefit of black liquor oxidation is removal of hydrogen sulfide and methyl mercaptan from the effluent stream by converting the volatile reduced sulfur compounds to non-volatile or less volatile states. Thus, inorganic sulfide ions in the waste liquor are converted to thiosulfate and oxidation of methyl mercaptide ions to dimethyl disulfide is obtained with ease. As seen in Table 2.2 sulfur dioxide and hydrogen sulfide emissions from oxidation towers are neglible, dimethyl disulfide being the only major source of emission in this operation.

2.1.4 Multiple effect evaporator emissions

Multiple effect evaporators are designed as the first step in concentrating weak black liquor (12-15% solids) to 50-55% solids level. In effect, water evaporation occurs under vacuum and heat, whereby non-condensible sulfur gases are also vaporized or stripped during boiling. The vapors vented from the multiple effect evaporator are condensed by barometric or surface condensers.

Condensates from the barometric condenser of the multiple effect evaporator usually contain a limited quantity of hydrogen sulfide and methyl mercaptan. Discharge of the condensate causes potential water pollution (90). On the other hand, air pollution usually occurs from the surface condenser by which the noncondensible sulfides are separated from the condensate (90).

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Sulfur gases originating from multiple effect evaporators represent a major emission source of sulfate pulp mills. Black liquor oxidation preceding evaporation, however, significantly reduces hydrogen sulfide and methyl mercaptan emissions during evaporation (Table 2.2).

Sulfur loses occurring from multiple effect evaporators processing unoxidized black liquor can be described by the following reactions (121):

2.1.5 Emissions from direct contact evaporators

Most recovery furnaces are operated in series with direct-contact evaporators. The sensible heat in furnace flue gases is used to raise the black liquor concentration in the multiple effect evaporators to the firing concentration of 65-70% solids (90).

Gas emissions from the direct-contact evaporation are caused by stripping of dissolved gases from the black liquor by hot flue gases. Further, pH reductions are also believed to take place due to CO_2 and SO_2 content of gas streams originating in the furnace. This causes a considerable shift in hydrogen sulfide and methyl mercaptan equilibriums.

нŤ	+	HS [−] ₹	SH ₂ /2-9/
н	+	CH ₃ s [−] ₹	CH ₃ SH/2-10/

Some recent studies by Buxton (36) and Thoen <u>et al</u>. (198) indicate that the direct contact evaporator is the major source of hydrogen sulfide, methyl mercaptan and sulfur dioxide emissions from sulfate mills. However, gaseous sulfur emissions from oxidized black liquor are considerably reduced (139). Emission ranges from direct contact evaporation or unoxidized and oxidized black liquor are shown in Table 2.2 (90).

Practically odor free operation is claimed with the socalled air contact evaporator as described by Hochmuth (93). In this new design the flue gases are used only for preheating the furnace air supply which primarily pass through the black liquor in direct contact evaporator is used as an evaporation media for the black liquor. The process has no effective change in black liquor pH. Any sulfur gases picked up from the evaporator will be burned in the furnace, thus black liquor oxidation is not required.

2.1.6 Emissions from the recovery furnace

The purpose of the recovery furnace is to burn the concentrated black liquor, and to recover sodium and sulfur as sodium carbonate and sodium sulfide. Useful steam is also produced at this stage.

A recovery furnace is usually composed of three sections: the drying and pyrolysis zone, the reducing zone, and the oxidizing zone. Each section is designed for the purpose of supplying

-15-

the reactants required to achieve the end results (90, 93). The concentrated black liquor (65-70% solids) is introduced into the furnace drying zone where the remaining water is evaporated. The pyrolysis of black liquor produces large amounts of hydrogen sulfide and a large number of organic sulfur compounds (33, 56, 68). The pyrolysis reaction combines the oxidation and reduction stages because of introduction of primary air. In the pyrolysis zone the sulfur compounds are either oxidized to the appropriate oxidation state of the particular sodium salt or reduced to volatile sulfides (140). The oxidized sulfur salts will fall into the reducing zone where the oxidized state sulfur is further reduced to sodium sulfide.

The volatile sulfides formed in the pyrolysis zone are carried into the upper region of the oxidation zone where the sulfides are either oxidized to sulfur dioxide or are partially discharged to the atmosphere directly. If the furnace is properly operated, the volatile sulfides will be oxidized to sulfur dioxide in the oxidation zone. When the oxidation zone is improperly operated, complete sulfide oxidation will not occur and the sulfides may escape unchanged from the furnace (140). This results in considerable sulfur loses and air pollution in the form of sulfur dioxide and sulfides.

Variables affecting sulfur emissions from the recovery

-16-
furnace were extensively studied by Blosser <u>et al</u>. (30), Harding and Landry (82), Murray and Rayner (140) and Thoen <u>et al</u>. (198). A significant correlation was found between sulfur emissions and furnace operation variables, such as black liquor firing rate, ratio of secondary air to black liquor firing rate, per cent excess oxygen in furnace flue gases, black liquor spray droplet size, turbulence within recovery furnace and ratio of sodium to sulfur in the black liquor. Recovery furnaces are rarely operated at their optimum conditions (140). Ranges of emissions as estimated under non-optimum conditions are given in Table 2.2 (90). Under optimum conditions sulfur dioxide (0.04-0.08ppm)/was the only sulfur containing gas detected by Thoen <u>et.al</u>. (198).

Newer developments, described by Arhippainen and Jungerstam (16), Clement and Elliott (38), and Lankenau and Flores (112), are concerned either with elimination of the direct contact evaporator (16, 112) or use of newer furnace designs (38). The use of recovery boiler, in conjunction with economized surface to recover heat from flue gases, has been shown to provide acceptably low total reduced sulfur emissions and is claimed to provide for odor free sulfate cooking (29).

2.1.7 Smelt dissolving tank emissions

Hydrogen sulfide and organosulfide emissions from

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the smelt dissolving tank are minor (Table 2.2) (90) and usually command little concern.

Under normal operating temperatures, the smelt contains only hydrogen sulfide. Organosulfides detected in the off-gases are incidental and have been traced to drafting gases from the reducing zone of the furnace into the smelt tank and recycle water coming from evaporator condensates containing organosulfides.

2.1.8 Emissions from the lime kiln

Lime kiln emissions have been found (39, 215) to include minor amounts of reduced sulfur (0.01-0.83 lb/ADT of pulp)originating both from the lime mud (193) and the fuel used to fire the unit (90).

2.1.9 Summary

In the foregoing sections special emphasis was placed on the formation of various forms of bivalent sulfur compounds as potential air and water pollutants associated with sulfate pulping. While under the normal operating conditions large quantities of these sulfides appear in the gas phase, equally important concentrations are detected in aqueous streams originating as wash waters, condensates, and unavoidable spills throughout the whole pulping operation (21). Most of these sulfides are formed preferentially in aqueous solution. Their confinement and retention throughout recovery yields sulfur in the form of sodium sulfide useful for regenerating necessary cooking chemicals. Such treatments not only increase the overall economy of pulp production, but also help to reduce air and water pollution.

2.2 Physical and Chemical Treatment of Sulfides in Aid of Air and Water Pollution Abatement in Sulfate Pulping of Wood

In sulfate pulping about one cubic meter (264 gallons) of digester condensates are formed per air-dry ton of pulp (173). The organic components of the condensate, mainly alcohols, acetone, and terpentines greatly contribute to the BOD load of this effluent. Approximately 80 to 85% of the condensate toxicity is attributed to hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide (18).

The multiple effect evaporators contribute about 4-7 m³/ air-dry ton of pulp. Although these condensates represent low BOD loads, their sulfide content was found to contribute heavily to the discharged effluent toxicity from sulfate pulp mills (173).

Considerable efforts have been expended during the past decade to remove sulfides from condensates by various procedures. Most of these attempts have involved treatment with air and steam (97). On hot-air stripping, most of the sulfur compounds are oxidized and volatile substances escape. The efficiency of

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sulfide removal from condensates by hot-air stripping is over 90% (18, 173). Steam stripping provides higher efficiency for removal of alcohols and acetone than hot-air (80°C) stripping (18).

2.2.1 Some physical and chemical properties of sulfate pulp mill malodorous sulfides

Hydrogen sulfide and methyl mercaptan are gases, and dimethyl sulfide and dimethyl disulfide are volatile liquors at ambient temperature (25[°]C) and pressure.

Hydrogen sulfide and methyl mercaptan can dissociate in aqueous solutions according to the following equilibriums (126, 169, 176).

2.2.2 Oxidation of sulfides

hold in ambient air (114) are shown in Table 2.3.

The gas phase oxidation of the four sulfides, hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, by mixing with air, is explosive within the limiting concentrations shown in Table 2.3 (54). Harkness and Murray (84) have indicated that mixtures of oxygen and dimethyl sulfide explode when heated to 210° C.

Oxidation of hydrogen sulfide with oxygen in gas phase forms elemental sulfur (205).

 $2H_2s + 0_2 \longrightarrow 2H_20 + 2s \dots /2-14/$

Sulfide ions in black liquor are readily oxidized by air, as well as molecular oxygen (17, 73, 133, 135, 202). The practice of sulfate black liquor oxidation prior to evaporation is a well accepted process used to stabilize sulfides and reduce odor problems of sulfate pulp mills.

Black liquor oxidation was found to be accelerated by the presence of catalysts such as phenolic elements of thiolignin (115) and/or iron salts from crossion products (137). The mechanism of sulfide oxidation has been proposed by Murray (137, 138) and is believed to involve two stages, wherein sulfide ions are first oxidized to polysulfide.

 165^{-} + 70_2 + $14H_20 \longrightarrow 25_8^{--}$ + $280H^{-}.../2-15/$ Further, the polysulfide ions are oxidized to form elemental sulfur and thiosulfate at a lower temperature (below $61^{\circ}C$), or only to thiosulfate at higher temperature (over $71^{\circ}C$).

 $2S_{8}^{--} + 2H_{2}0 + 0_{2} \rightarrow 2S_{8} + 40H^{-} \dots /2-16/$ $2S_{8}^{--} + 90_{2} + 120H^{-} \rightarrow 8S_{2}0_{3}^{--} + 6H_{2}0 \dots /2-17/$ Elemental sulfur formed during low temperature black liquor

-21-

oxidation disproportionates in storage to reform some of the original sulfide ions (135, 137). This reduces the effectiveness of black liquor oxidation as a means of odor control, especially over long term liquor storage.

 $s_8'' + 120H' \rightarrow 4s'' + 2s_2o_3'' + 6H_20..../2-18/$

Gas phase oxidation of methyl mercaptan with oxygen between 210 and 260°C has been studied by Cullis and Roselaar (44). The products identified included sulfur dioxide, aldehyde, methanol, methane, carbon monoxide and dimethyl disulfide. The oxidation mechanism has been described as follows (44, 83):

$$\begin{array}{rcl} CH_3 SH & + & 0_2 \longrightarrow CH_3 S^{\bullet} & + & H0_2 \cdots \cdots \cdots /2 - 19/\\ CH_3 S^{\bullet} & + & 0_2 \longrightarrow CH^{\bullet} & + & S0_2 \cdots \cdots \cdots /2 - 20/ \end{array}$$

In aqueous phase, the methyl mercaptan can be oxidized to dimethyl disulfide at ambient temperature in the presence of air as described previously in Eqs. (2.5) and (2.6).

Dimethyl sulfide and dimethyl disulfide gases were found to be practically unreactive to oxygen at ambient temperature. However, Cromwell (42) claimed that oxidation of sulfides can be performed by treatment of the foul gases with ozone. The mechanism of organic sulfide ozonization was also discussed by Douglass (54). Further, aqueous solutions of dimethyl sulfide are readily oxidized to dimethyl sulfoxide in the presence of 30%hydrogen peroxide below 20° C (211).

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At high temperature, dimethyl sulfide can be reacted with oxygen. Harkness and Murray (84) have shown that the reaction is non-explosive at 195° C, exhibiting an initiation and a main stage. The major oxidation products from this reaction are sulfur dioxide, carbon monoxide, and sometimes formaldehyde. Similarly, Cullis and Roselaar (45), studying the gas phase oxidation of dimethyl sulfide at 200°C temperature, found that sulfur dioxide, aldehyde, methanol and carbon monoxide were present among the oxidation products.

Gas phase oxidation of dimethyl disulfide at 240° C also had been studied by Cullis and Roselaar (46). The oxidation products were sulfur dioxide, methanol, carbon monoxide and carbon dioxide.

The oxidation of dimethyl disulfide with molecular oxygen in alkaline aqueous solution in the 25 to 152° C range has been studied by Murray and Rayner (141). The mechanism is considered to be base-catalyzed disproportionation to form mercaptide and methyl sulfenic acid (CH SOH). The latter substance is readily oxidized further to methyl sulfonic acid (CH₃SO₃H). However, the possibility of methyl disulfide reduces the effectiveness of black liquor oxidation under these conditions (141).

Bilberg (26) studied the behavior and formation of thiosulfate from oxidized and nonoxidized polysulfide black liquors by heating with sulfite. He was able to show that non-oxidized liquors had little influence on the amount of thiosulfate formed,

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whereas the oxidized black liquor resulted in marked increase in the thiosulfate content.

In summary, proper operation of black liquor oxidation, combustion of resident sulfide gases collected from the oxidation tower, air and steam scrubbing of the digester, blow tank and evaporators condensates, are an efficient means of pulp mill odor control (92).

2.2.3 Chlorination

Malodorous sulfides have been found to react readily with chlorine, both in aqueous acidic and/or alkaline solutions. The most likely end products of the chlorination are elemental sulfur, methyl sulfonyl chloride (CH_3SO_2Cl), dimethyl sulfoxide(CH_3SOCH_3), and methyl sulfonic acid($CH_3SO_3CH_3$)(50,169,205).

The chlorination of hydrogen sulfide gas produces elemental sulfur. Sulfur dioxide and sulfur trioxide were formed when hydrogen sulfide was chlorinated in aqueous solution (50, 205).

The chlorination of methyl mercaptan goes through a series of complicated reactions. Douglass (54) indicated that excess chlorine in the presence of water formed methyl sulfonyl chloride, methyl sulfonic acid and other unstable intermediate compounds. In case of inadequate chlorine supply, the products would be composed of a mixture of methyl sulfonyl chloride, unreacted mercaptan, dimethyl disulfide and methyl methane thiosulfonate

-24-

(CH SO SCH). Appropriate reaction mechanisms for the formation 3 2 3 of these products have also been proposed (54).

Products from chlorination of dimethyl sulfide are determined by the reaction conditions, particularly by the presence or absence of water. Thus, anhydrous chlorination proceeds stepwise with replacement of all hydrogens on one carbon atom before any attack at the second carbon atom occurs (164). Chlorination of dimethyl sulfide in the presence of water is said to be a very complicated reaction. Bennett <u>et al</u>. (23) have shown that this produces dimethyl sulfoxide, methyl sulfonyl chloride, dimethyl sulfone (CH₃SO₂CH₃) and methyl sulfinic acid (CH₃SO₂H). Mechanisms for these reactions were also proposed by the above authors.

The chlorination of dimethyl disulfide in aqueous solution produces methane sulfonyl chloride and methyl sulfinic acid (50).

Oxidation of the combined relief and blow gases with chlorine has been practiced, and it also has proven to be an efficient and relatively inexpensive method of reducing sulfate pulp mill air pollution (60).

Direct chlorine oxidation of digester condensates and noncondensible gases has been practiced (75). The system includes a first stage of air oxidation in the presence of water, then treatment of the gases in a chlorination tower, and finally washing of the gases with water. The process is claimed to

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provide completely odor free operation (201, 205). Recovery furnace odor gases also can be similarly treated with a small quantity of chlorine and washed with water (201). Tomlinson and Ferguson (203) reported odor reductions by passing digester non-condensible gases through a scrubber in which the absorbant contained residual chlorine in spent bleach liquor.

2.2.4 Photolysis

A number of studies have been devoted to the irradiation and photolysis of sulfides in gas and/or liquid Malodorous sulfides have been irradiated recently for phases. the purpose of eliminating the foul smell from sulfate pulp mills (159, 184). Rayner and Murray (159) studied gas phase photolytic oxidation of methyl mercaptan, dimethyl sulfide and dimethyl disulfide as induced by long wave (3,600%) and short wave (2,537%)ultraviolet radiation. The experiment has shown that oxidation rates are accelerated by radiation at both wave lengths of radiation. The short wave ultraviolet radiation rapidly catalyzed the oxidation of methyl mercaptan and dimethyl sulfide. Straforelli et al. (184) studied gas phase gamma radiolysis of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide in presence of dry air and indicated that all suffides are finally oxidized and possibly precipitated on the container walls. Sulfur dioxide was observed as the common intermediate product for all sulfides. Maximum sulfur dioxide concentration was observed

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usually at 0.2 Mrad. Within the concentration ranges of 50-2000 ppm, complete desulfurization required approximately 0.8 to 1.5 Mrad.

2.2.4.1 Photolysis of hydrogen sulfide

There is strong evidence that H+ and HS- are primarily formed by photolysis (2050-2288Å) of pure hydrogen sulfide gas (153, 157).

 H_2S + $hv \longrightarrow H_0$ + $HS^0 \dots /2-21/$ The SH, and H^0 atoms may subsequently react to form hydrogen and elemental sulfur as shown in the following schemes (49, 58):

 $H \cdot + H_2 S \rightarrow H_2 + HS \cdot \dots /2 - 22/$ $2 HS \cdot \rightarrow H_2 S + S \cdot \dots /2 - 23/$ $2 HS \cdot \rightarrow H_2 + S_2 \dots /2 - 24/$

Stiles <u>et al</u>. (183), studying the photolysis (2,200 -2,800Å) of solid hydrogen sulfide at low temperature (77^oK), also confirmed that the primary photolytic step with H_2S is loss of a hydrogen atom, which was detected by electron spin resonance (E.S.R.). Further, the sulfur chain (S_n) can be detected by E.S.R. spectra when the photolysis products are warmed to $125^{\circ}K$.

The liquid or gas phase addition of HS to an olefinic double bond, as promoted by short wave ultraviolet radiation $(2,800\text{\AA})$, between -78° C and room temperature has been investigated by Vaughan and Rust(210). The thiol is thought to arise via the following chain propagation reactions:

2.2.4.2 Photolysis of methyl mercaptan

Electron spin resonance studies following ultraviolet radiolysis of solid aqueous solution and pure solid methyl mercaptan at 77° K indicated that the primary photochemical process results in proton loss from the mercaptan and formation of a thiyl radical (213).

 CH_3SH + $hv \longrightarrow CH_3S$ + $H_{\bullet} \dots /2-27/$ The reaction also has been confirmed by Inaba and Darwent (98) in studies concerned with the photolysis of gaseous methyl mercaptan.

Products of complete methyl mercaptan gas photolysis were analysed by Skerrett and Thompson (178), and were shown to consist of hydrogen (80%) and methane (18%); the condensible products were elemental sulfur and dimethyl disulfide. The quantum yield of methyl mercaptan disappearance was measured to be 1.7.

However, Inaba and Darwent (98) stated that methane (CH_{4}) and elemental sulfur do not appear as a result of original photolysis of methyl mercaptan but are due to a secondary processes. The following schemes are proposed by Inaba and Darwent (98) to be the most important events in the photolysis of methyl mercaptan.

 $\begin{array}{rcl} CH_{3}SH & + & hv \longrightarrow CH_{3}S^{\bullet} & + & H^{\bullet} & \dots & /2-28/\\ H^{\bullet} & + & CH_{3}SH \longrightarrow CH_{3}S^{\bullet} & + & H_{2} & \dots & /2-29/\\ 2CH_{3}S^{\bullet} & \longrightarrow & CH_{3}SSCH_{3} & \dots & /2-30/ \end{array}$

2.2.4.3 Photolysis of dimethyl sulfide

The primary mechanism of dimethyl sulfide photolysis was found to be exclusively C-S bond cleavage. Mercury photosensitized decomposition of pure dimethyl sulfide vapor was investigaed by Jones <u>et al</u>. (100), using mass spectrometric techniques. The products, ethane (41%), dimethyl disulfide (29%), methyl mercaptan (12%) and methane (3%), together with thioformaldehyde (not measured), were accounted for by simple combination-disproportionation reactions of the CH₃ and CH₃S^o fragments.

Similarly, Ogoro and Inaba (148) studied the effect of photolysis time, temperature, pressure and presence of argon or nitric oxide (NO) on the radiolytic degradation of dimethyl sulfide gas. The major products were methane, ethane, methyl mercaptan and dimethyl disulfide. Ethane and hydrogen sulfide were formed only at high temperature photolysis (above 250°C). The possible reactions have been proposed as follows:

CH3 SCH3	+	h v →	CH ₃ SCH ₃ */2-31/
сн _з sсн [*]	\rightarrow	Сн. З	+ CH ₃ S•
сн ₃ sch [*]	→ c ₂ H _L	+	H_2 (above 250°C)/2-33/

2.2.4.4 Photolysis of dimethyl disulfide

The direct photolysis of organic disulfides both in vapour and liquid phases has been investigated. The primary step of photolytic decomposition was shown to be formation of two thiyl radicals by homolytic S-S bond cleavage.

The photolysis of vapor phase dimethyl disulfide in the presence of ethylene (C₂H_{μ}) and acetylene (C₂H₂) was first investigated by Ueno and Takezaki (209). No pressure change was observed in the reaction with ethylene, while with acetylene an obvious pressure decrease was observed. Smissman and Sorenson (179) were able to demonstrate the E.S.R. spectra of a number of thiyl radicals (RS) produced by ultraviolet irradiation of several liquid phase disulfides, including that of dimethyl disulfide in chlorobenzene solution at 77⁰K. These results have been confirmed by Rao et al. (158) in a study of the effect of pressure (2-25 torr) and temperature (28-186°C) on the photolysis of dimethyl disulfide at 2,300 to 2,800Å, and at 2,288Å wave The following photolytic schemes have been shown to be lengths. possible:

-30-

CH_SSCH_3	+	$h\mathbf{v} \longrightarrow 2CH_3 S^*$	/2-34/
CH SSCH	+	$CH_3 s \rightarrow CH_3 SH + CH_2 SSCH_3$.	/2-35/
•CH_SSCH_3	+	$\begin{array}{c} \text{CH} \text{ SSCH} \longrightarrow \text{ polymer} \\ 3 & 3 \end{array}$	/2-36/

Jones <u>et al</u>. (100), in studies of mercury photosensitized decomposition of dimethyl disulfide vapour, found two primary decomposition mechanisms as S-S cleavage (80%) and C-S cleavage (20%). The major products involve dimethyl sulfide (27%), dimethyl trisulfide (26%), methyl mercaptan (22%), ethane (13%) and methane (2%). Thioformaldehyde (CH S), methyl hydrodisulfide (CH₃SSH) and carbon disulfide are also produced but were proposed by suitable self- and cross-combination and disproportionation reactions of the primary fragments CH₃, CH₃S, and CH₃SS.

2.3 Gamma Radiolysis of Water

Gamma rays are electromagnetic radiation of very short wave length $(10^{-8}-10^{-11}$ cm) and hence of great photon quantum energy. The relative position of gamma rays in the spectrum of electromagnetic radiation is shown in Fig. 2.1 (163).

In gamma radiation, only part of the radiation energy may be transferred at an interaction site and the process is not selective. There is sufficient energy available to break any bond, but in practice certain bonds are broken preferentially. The ionizing photon or particle and the displaced electron are often both capable of producing further ionization. Thus, one incident photon may affect many thousands of molecules.

The passage of gamma radiation (about 1 Mev) through water or dilute aqueous solutions gives initial electrons, positively charged water ions and excited water molecules which are produced by Compton scattering and by the photoelectric effect (9, 91, 147, 180).

$$H_2 0^+ \longrightarrow H^+ + H0^{\bullet} \dots /2-37/$$

or $H_2 0^+ + H_2 0 \longrightarrow H_3 0^+ + H0^{\bullet} \dots /2-38/$

The excited water molecules may exist for microseconds only and then decompose to H atoms and HO radicals or perhaps undergo ionization.

Within the spurs containing e_{aq}^{-} , H and HO₂, the various fragments may react to form H, H₂O, H₂O, OH⁻, H₃O⁺ and H₂O as shown in the following schemes.

H•	+	$H \cdot \longrightarrow H_2 \cdot \dots \cdot \dots \cdot /2 - 41/$
но•	+	$H0 \rightarrow H_2 0_2 \dots (2-42)$
eao	+	$H_30^+ \rightarrow H_30^+ (2-43)$
e ag	+	$e_{ad} \longrightarrow H_2 + 20H^- \dots /2 - 44/$
eaq	+	$HO \rightarrow OH$
н•	+	$H0 \rightarrow H_2 0_{\odot} \cdots /2-46/$

2.3.1 Molecular products

The molecular products, hydrogen (H_2) and hydrogen peroxide $(H_2 0_2)$, are formed in a spur, but both H_2 and $H_2 0_2$ are decomposed by a chain reaction. The hydrogen gas escapes readily, whereas the hydrogen in solution can further react with oxidizing radicals (H0).

aq $H_2 O_2 + e_{aq} \rightarrow HO + HO \dots /2-48/$ $H_2 O_2 + H \rightarrow HO + H_2 O_2 \dots /2.49/$ and on escape of hydrogen from the solution, oxygen is produced.

H202	+	$H0 \cdot \longrightarrow H_2^0$	+	$H0^{\circ}_{2}$
H0•2	+	$HO_{2} \rightarrow H_{2}O_{2}$	+	0 ₂ /2-51/
H0• 2	+	$H0\bullet \longrightarrow H_2 0$	+	0 ₂ ,/2-52/

The molecular hydrogen peroxide is usually retained in solution, and becomes available for reaction with solutes.

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2.3.2 Primary radical species

Both the hydrated electron (e_{aq}) and hydrogen atom (H) are powerful reducing agents, while the hydroxyl radical (H0) is a powerful oxidizing agent (123). The solution pH has a considerable effect on formation of primary radical species.

In neutral solution, the reducing radicals are hydrated electrons and hydrogen atoms. In acid solution, the hydrated electrons are readily converted to hydrogen atoms (104).

 e_{aq}^{-} + $H^{+} \rightleftharpoons H^{+} \rightleftharpoons H^{+} \circlearrowright H^{+}$

Hydrated electrons react with CO_2 at a high rate (k = 7.7 x 10⁹ M⁻¹ sec⁻¹) (77).

Saturated hydrocarbons, as well as alcohols, are unreactive toward e_{aq}^- . Hydrated electrons were shown to be the most efficient nucleophiles, whereby, they may react with carbon atoms

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adjacent to any double bond. The fair reactivity of e_{aq}^{-} with aldehydes and ketones is found to be due to the positively polarized carbon on carbonyls. In reaction with aromatic compounds, e_{aq}^{-} acts as a very reactive nucleophilic agent (10, aq

The hydrogen atom (H) is a reducing agent, but it is not as strong as the hydrated electron (147). Main reactions of the hydrogen atom with organic compounds are hydrogen abstraction and additions to double bonds or rings:

The principal oxidizing species found in the gamma radiolysis of water is the hydroxyl radical (H0.) (9, 147, 180). In the absence of solutes, H0. reacts with reducing radicals, as shown in Eqs. /2-45/ and /2-46/ and addition reaction shown in Eq. /2-42/. In the presence of solutes, the oxidizing agents undergo four types of reactions, such as charges transfer, hydrogen abstraction addition or displacement.

The presence of hydroperoxyl radicals (H0.2) in the gamma radiolysis of deaerated water has been demonstrated through the following scheme:

Hove the H $_2^0_2 \longrightarrow H_2^0$ the Hove $_2^{\circ} \dots (2-58)$

The hydroperoxyl radical is an acid with a pK value of 4.5 (47). It is formed in acid solution, whereas 0.2 is formed only in neutral solution (47, 91).

Ho. + Ho. $\xrightarrow{}$ H $\stackrel{0}{\underset{2}{\longrightarrow}}$ + $\stackrel{0}{\underset{2}{\longrightarrow}}$ H $\stackrel{0}{\underset{2}{\longrightarrow}}$ + $\stackrel{0}{\underset{2}{\longrightarrow}}$ H $\stackrel{0}{\underset{2}{\longrightarrow}}$ + $\stackrel{0}{\underset{2}{\longrightarrow}}$ H $\stackrel{0}{\underset{2}{\longrightarrow}$ H $\stackrel{0}{\underset{2}{\longrightarrow}}$ H $\stackrel{0}{\underset{2}{\longrightarrow}$ H $\stackrel{0}{\underset{2}{\longrightarrow}$

2.3.3 Radiolysis of oxygenated water

In gamma radiolysis of aerated aqueous solution secondary radicals, such as 0_2° , $H0_2^{\circ}$, $H0_3^{\circ}$ and 0_3° , are formed (47, 91). The 0_2° is formed by reacting molecular oxygen with the hydrated electron:

 OH reacts with HO. radical to form O. The ozonized ion radical is further formed by reaction of O. with oxygen.

OH_	+	$H0 \leftarrow H_2 0$	+	0/2-65/
07	+	$0_2 \rightarrow 0_3^{\bullet}$	• • • • • •	•••••/2-66/

From the foregoing, it becomes evident that pH has a significant effect on the yield of molecular and radical yield in aqueous solutions. Thus the radical products of H and HO, as well as the molecular products H_2 and $H_2 O_2$ are varied according to different pH of the media (87). The hydroperoxyl radical (HO₂) is formed in acid solution, but its dissociation reaction to O_2^- occurs in neutral solution (Eq. /2-59/) (47). The hydroxyl radical (HO) behaves like an acid at high alkalinity to form O^- (Eq. /2-65/) (47). In addition, both hydrogen atoms (H and hydrated electrons (e_{aq}^-) exist in neutral solution. In acid solution, e_{aq}^- is converted to H (Eq. /2-53/), whereas in solution above pH 13, H is readily reacted to form e_{aq}^- (Eq. /2-54/) (10).

The yields (G) of radicals and molecular products (e_{aq}^{-} , H, aq^{+}) HO, H₂, H₂O₂) in the gamma irradiation of water appear to be a function of solution pH (87). All yields tend to decrease with increase in pH, except G(HO) and G(H) which increase from neutral to acid and from neutral to alkaline media.

2.4 Radiolysis of Sulfides in Aqueous Solution

Sulfate black liquors usually contain low concentrations of organic malodorous sulfides and fairly high concentration of inorganic sulfide. Physico-chemical distinctions of gamma radiolysis of sulfides in black liquor have not been reported, although radiation chemistry of organic sulfides, contained in biological systems, have been studied quite widely. It is this area of interest that provides useful examples to the radiolysis of malodorous sulfides as contained in numerous industrial effluents, particularly that of kraft mill black liquor.

Very low concentrations of sulfides were found earlier to protect other materials against destruction by gamma radiation in aqueous solution (165, 220). The sulfur linkage is particularly reactive toward free radicals and is likely to be selectively damaged by radiation (187). Considerable information is available on radiation chemistry of simple organic sulfide solutions, as well as more complicated structures such as sulfhydryl-containing enzymes.

The high energy of X- and gamma-ray radiolyses of hydrogen sulfide in aqueous solution forms elemental sulfur (117, 122). Sulfate was also obtained as the higher oxidation product by

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Nanobashivili and Gvilava (145) and Nanobashivili <u>et al</u>. (144) on X- and gamma radiolysis of various metallic sulfide solutions (sodium, potassium, ammonium, etc.) and aqueous suspensions of sulfide minerals (pyrites, sphalerites and galenites). These results were confirmed by Markakis and Tappel (122). The possible intermediate products and reaction rates of hydrogen sulfide and radicals produced by pulse radiolysis of water were studied by Karmann <u>et al</u>. (103), who found also that polysulfide ions existed.

Radiolysis of mercaptans has also been considerably investigated. X- and gamma-ray radiation of butyl-, amyl- and hexylmercaptans, and thiophenols formed corresponding disulfides and sulfate ions (144, 145).

The gamma radiolysis of amino acid cysteine $(\text{HSCH}_2 \text{CHNH}_2 \text{COOH})$ has been extensively studied because of its association with biological protective agents (20, 48, 186, 219, 220). Swallow (186) investigated the gamma radiation of cysteine hydrochloride solution in aerated and deaerated aqueous solution. In air saturated solutions, irradiation of cysteine was shown to produce cystine <u>via</u> a chain reaction. These findings were further confirmed by Barron and Flood (20) in that the oxidation of thiols by gamma radiation may be considerably increased in oxygenated solutions.

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The formation of hydrogen sulfide from gamma radiolysis of cysteine aqueous solution has been investigated by Dale and Davies (48), as well as Whitcher <u>et al</u>. (219). Markakis and Tappel (122) quantitatively identified the products of gamma radiolysis of aqueous cysteine solutions in the presence and absence of oxygen. They found cystine, hydrogen sulfide, elemental sulfur and sulfate ion as the products of radiolysis.

The chemcial reactions accompanying radiolysis of dimethyl sulfide are reduction and oxidation by radicals through water radiolysis. Meissner <u>et al</u>. (129) have determined the absolute rate constants existing between reactions of hydroxyl radicals (H0) and hydrated electrons (e_{aq}) formed with respect to pulse radiolysis of dimethyl sulfide in aqueous solutions. The effects of solution pH and oxygen on formation of intermediate products, such as $CH_3SCH_2^{-}$, $CH_3SOCH_3^{-}$ and $(CH_3SCH_3)_2^{+}$, were discussed.

The radiolysis of disulfide in form of cystine has been considerably investigated. The disulfide bond was found to be particularly sensitive to ionizing radiation. Protein damage is readily averted by the radio-sensitivity of cystine which is contained in usual biological systems. The protection against radiation is generally afforded through the ready reaction of the disulfide with the radicals available in aqueous systems (165).

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Ionizing radiation of the organic disulfides cystine in acidic aqueous solutions produces the thiosulfuric acid (CySSO3H) through fission of the C-S bond, sulfinic acid (CySO2H) and cysteic acid (CySO₃H) through fission of the S-S bond (69, 78, 175). Markakis and Tappel (122) identified cysteine (CySH), hydrogen sulfide, elemental sulfur and sulfate ions from gamma radiolysis of acidified cystine aqueous solutions. A more detailed investigation of gamma radiolysis of cystine aqueous solutions has been performed by Purdie (156). Yields (G) were determined for the following products: $CySO_2H(0.3-1.7)$, $CySO_3H(0-1.2)$, $CySO_2SH(0.05-$ 0.1), $CySSO_3H(0.1-0.1)$, CySH(0-2.5) and CySSSCy(1.3-5.6). Mechanisms for the above radio-chemical reactions were also presented and discussed. Their relevance to the treatment and stabilization of black liquor sulfides through the particular radio-sensitivity of the C-S and S-S bonds is believed, thereby, to be demonstrated.

2.5 Reaction of Sulfides with Hydrocarbons Induced by Gamma Radiation in Black Liquor

Black liquor is a very complicated solution. In addition to sulfur compounds, it contains various organic components and component fragments such as sugars, lignin, extractives and their derivatives. During gamma radiolysis of black liquor, organic radicals can be formed either directly by photon attack or indirectly by hydrogen atom abstraction as initiated by H. and HO. made available through radiolysis of water.

Organic radicals are considered to be very reactive toward sulfide compounds. The reactions operate either through abstraction of one hydrogen atom from the sulfide compounds to form sulfide radicals, or by addition to the sulfide compounds by direct attack on the sulfide bond. The addition reaction, as the most favorable reaction, has been demonstrated by Pryor and Guard (154), and Pryor and Pickering (155), although the reaction mechanism is still not clear for this process in black liquor. Pryor and Pickering (155) have demonstrated, however, that the reaction may occur with polystyryl radicals and various disulfides (methyl, ethyl ... etc.) at the S-S bond and by a reaction that could be regarded as a direct displacement:

 $M \cdot + RSSR \longrightarrow M-SR + RS \cdot \dots /2-67/$ Pryor and Guard (154) demonstrated the reaction of phenyl radicals with disulfide in two schemes: either by attack on the disulfide bond (Eq. /2-67/ or by hydrogen abstraction (Eq. /2-68/).

 $M \cdot + RSSR \longrightarrow M-H + RSSR \dots (2-68)$

The attack of radicals on the disulfide bond usually occurs to a larger extent than hydrogen abstraction. Pryor and Guard (154) confirmed that the reaction rates of phenyl radicals with disulfide bonds in dimethyl- and diethyl disulfide were as high as 98% and 93%, respectively.

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Other possible reactions able to increase the molecular weight of sulfides are addition of thiyl radicals (HS• and CH₃S•) to large molecular weight hydrocarbons. Addition of the methane sulfenyl radical (CH₃S•) to derivatives of cyclohexene and butylmethyl sulfides have been illustrated by Readio and Skell (161) and Huyser and Kellogg (96). Addition of benzenethiol (C₆H₅S•) to allene has also been shown by Heiba (88). The sulfhydryl radicals (HS•) which are able to add to allene and conjugated olefine, have been demonstrated by Griesbaum <u>et al</u>. (80).

2.6 Gamma Radiolysis of Pulp Mill Effluents

Only one previous publication (113) treats radiolysis of aqueous pulp mill effluents. However, the work does not deal directly with ionizing radiation effects on chemical reactions, but investigated some practical aspects (residual color and COD)) of irradiated effluents. Thus Lenz <u>et al</u>. (113) investigated the effects of gamma radiation of aerated strong and weak effluents originating from effluent streams of sulfate linerboard and neutral sulfite semichemical (NSSC) mills. The extensive treatment (approximately 16-32 Mrad) significantly removed and even eliminated effluent color, and simultaneously reduced the level of chemical oxygen demand (COD) to 50 to 80% of the original. Further, the treatment brought the solution pH within the neutral range and promoted flocculation and precipitation of solids.

3.0 MATERIALS AND METHODS

3.1 Model Compounds

Recent chemical analyses of sulfate black liquors consistently show the presence in varying amounts of hydrogen sulfide (H₂S), methyl mercaptan (CH₃SH), dimethyl sulfide (CH₃SCH₃), and dimethyl disulfide (CH₃SSCH₃) (67). Hydrogen sulfide and methyl mercaptan are present as sodium salts in a dissolved state under alkaline conditions, but are easily freed from the solution upon neutralization and acidification. Dimethyl sulfide and dimethyl disulfide can be stripped quantitatively from their respective alkaline solutions both by degassing with nitrogen or by liquid/liquid extraction techniques.

Due to the complexity of black liquors, the calibration of analytical techniques, as well as most radiolysis experiments of the present study, were carried out on model systems including the above mentioned substances. Further reagents, such as sodium hydroxide (NaOH), silver nitrate (AgNO₃), 95% ethanol (C_2H_5OH), 40% hydrochloric acid (HCl), boric acid (H_3BO_3), carbon dioxide (CO_2) and oxygen gas were secured from local chemical supply houses. All chemicals were reagent grade and the water used for dilution/dissolution was distilled water. 3.2 Black Liquors

For practical extrapolation of results some commercial black liquors were analysed. Further, to observe the range of the variation in the four major sulfate black liquor sulfides (H2S, CH₃SH, CH SCH and CH SSCH₃), liquor samples were secured from four different mills of one company and one further sample was obtained from another company, as well as one from pilot cooking conducted by the Western Forest Products Laboratory (Vancouver), Pulping Section. In addition, two polysulfide black liquors were obtained from vapor and liquid phase cookings done by the Pulp and Paper Research Institute of Canada, Montreal, P.Q. The respective black liquors were shipped in polyethylene containers during the winter months (November, December), immediately recharged upon arrival into sealed glass containers and stored in a cold storage room at 5° C in the dark. The source and composition of respective black liquors can be found in Table 3.1.

3.3 Analysis of Aqueous Sulfide Solutions

On reviewing the pertinent literature on sulfide analysis two points became clear: (1) The analytical techniques hitherto proposed are far from quantitative, and (2) for complete analysis of sulfides in aqueous alkaline solutions at least two methods have to be used. Reasons for this were briefly mentioned in the introduction of model compounds. Thus, under these conditions

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two methods of analysis were used for characterising black liquor sulfides.

3.3.1 Potentiometric determination of sulfides in sulfate black liquor

The pulping industry is not the first to run into problems of sulfide analysis (182). Early papers originating with the petroleum industry deal with this problem as related to "sweetening" or desulfurization of gasoline. The alkaline extracts of raw gasoline are found to contain sodium sulfide, mercaptans and organic sulfides and are thus, except for liquid and other organic solutes, somewhat similar to sulfate pulping black liquors.

First efforts of potentiometric precipitation of heavy metal sulfides are reported by Dutoil and Weiss (57). The use of silver nitrate as titrant was first reported by Treadwell and Weiss (204) in 1919, and applied to pulping black liquor analysis by Borlew and Pascoe (31) in 1946. The silver nitrate method was substantially improved by Tamele and co-workers (190, 191, 192) for hydrogen sulfide in mixture with mercaptans and was further refined for the analysis of dissolved sulfides in pulping black liquors by Bilberg (26) and Collins (40).

The great popularity of the silver nitrate method is due to the large insolubility and easy flocculation of silver sulfide in

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ammoniacal alkaline solution and the accuracy by which potential changes accompanying formation of such precipitates can be followed. For classical titrations the analysis is carried out in sodium acetate buffered solutions using a potential calibrated sulfide coated silver electrode (190). To date, difficulties were reported in locating the proper end points in sulfide ion titrations by classical methods. Since the titration curve is asymmetrical, an unusually large and rapid drop in potential is shown without a readily detectable inflection point just prior to reaching the equivalence point. To further aggrevate the problem, satisfactory results are obtained only with 0.002 M or greater sulfide concentrations; large errors arise below this limiting concentration of silver sulfide (111).

To resolve some of these difficulties several modifications of the silver nitrate method have been proposed. The TAPPI Standard T625 ts-64 (13) gives the closest procedure to that proposed by Borlew and Pascoe (31). Coshen and Bauman (37) determined sulfide and mercaptan in black liquor by employing a vacuum tube circuit and a "magic eye" or tuning control tube for detecting the sharp potential inflection occuring at the equivalence points. Olsson and Samuelson (149) used anion exchange resin to separate the sulfide from the organic constituents (non-sulfur) of black liquor. The sulfides retained on the resin

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are sequentially eluted and quantitatively determined by potentiometric titration with mercuric chloride (HgC1₂) in the presence of sodium hydroxide. Swartz and Light (188) studied the sulfide ion-selective electrode as an analytical tool for the analysis of sulfide in black liquor, and claimed that silver reduction also occurred.

Bilberg (26), comparing the black liquor potentiometric titration of silver nitrate, mercuric chloride and cadmium sulfate (CdSO_h), found that the method based on mercuric chloride titration gave the least effect with components in black liquors other than the sulfide. Frant and Ross (70) recently proposed the use of an anti-oxidant solution for storing black liquor. Further, a known cadmium activity solution is added to the black liquor and the sulfide is determined quantitatively by measuring the decrease of cadmium activity in the solution with a cadmium activity electrode. Other methods, such as that by Bethge et al. (24) for the colorimetric determination of hydrogen sulfide and mercaptans in industrial effluents, have been proposed recently. Although precision and accuracy were found to be satisfactory for hydrogen sulfide, inaccuracies were reported in simultaneous determinations with methyl mercaptan due to the expected short life of mercaptan complexes formed in the presence of hydrogen sulfide and some interference of oxygen. Thus, the potentiometric

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titration with silver nitrate is accepted as the easiest and most accurate sulfide determination method if correct interpretation of the titration curve is made.

3.3.1.1 Experimental

3.3.1.1.1 Apparatus

The potentiometric titration apparatus used in these studies was manufactured by the Radiometer Cooperation, Copenhagen, Denmark, and consisted of a Model TTT-11 Automatic Titrator and Type ABU-1 Autoburette unit coupled with an X-Y recorder for automatically recording titrant volume and associated change in potential. The electrodes were Corning triple purpose glass electrode (No. 476024) (119) and Radiometer type silversilver electrode (P4011, KT). The silver sulfide electrode was prepared by electrolytically coating a layer of silver sulfide (AgS) on the silver electrode (31).

3.3.1.1.2 Theory of silver nitrate potentiometric titration

The solubility product or ion product constant of silver sulfide is extremely low $(K_{sp} = 1.6 \times 10^{-49}, 25^{\circ}C)$. The activity product (a_{sp}) of the silver ions (a_{Ag}^{+}) and the sulfide ions (a_{sp}^{--}) is constant at a particular temperature:

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The titration cell consists of a silver sulfide-silver electrode and a high pH glass reference electrode. The cell may be written as:

Ag/AgCl// 0.1N HCl// Sample Solution// Ag₂S/Ag...../3-2/

The difference of potential between the two electrodes when both are immersed in a solution containing sulfide ions (S^{-}) can be expressed as:

$$E = K + \frac{RT}{F} \ln a_{A_g} + \frac{RT}{F} \ln \left(\frac{a_{sp}}{a_{s}-1}\right)^{\frac{1}{2}}$$

Where:

 $E_1 = potential$ $K_1 = constant$ R = gas constant T = absolute temperatureF = faraday

It should be noted that the sulfide ion activity (a --) in S Eq. /3-3/, being a strong base, will contribute to the acid/base balance in accordance with the following schemes:

Eq. /3.3/ also indicates that the potential difference (E_1) , is dependent on the sulfide ion activity (a_{S}^{--}) . Tamele <u>et al</u>. (190), studying behaviour of the silver electrode in potentiometric titration of sulfide ions in cases of extreme dilution, indicated that if the solution contains hydrosulfide ion (HS⁻) concentrations below $10^{-5}N$, the high negative potential drops abruptly on further dilution and approaches a low constant value. Thus, the limiting concentration for normal sulfide ion response in potentiometric titration becomes $10^{-5}N$ or greater, if spurious behaviour is to be avoided.

In typical analysis, to a 150 ml beaker equipped with a magnetic stirrer, 20 ml of 20% sodium hydroxide, together with 5 ml of about 30% aqueous ammonium hydroxide solution, and a layer of paraffine oil was needed. Under continued stirring an aliquot of the sulfide sample containing at least 0.005 g of sodium sulfide (equivalent to about 2 ml of strong black liquor) was injected into the solution by using a 5 ml syringe. The sample was then titrated with 0.05 or 0.1 N silver nitrate solution. The volume of titrant and potential read-out were recorded automatically on the recorder in the X-Y mode. The end point for the mono-sulfide was read at the first inflection of the titration curve. The reactions for the titration are as follows:

 $s^{--} + 2Ag^{+} \longrightarrow Ag_{2}S$ (black ppt)...../3-6/ $CH_{3}S^{-} + Ag^{+} \longrightarrow CH_{3}SAg$ (yellow ppt)...../3-7/

The following calculations give sulfide and mercaptan in grams per liter (g/1):

$$Na_{2}S = 1.951 x \frac{m1 \text{ of } AgNO_{3}(0.05N)}{m1 \text{ of liquor sample}} \dots /3-8/m1 \text{ of liquor sample}$$

or $H_{2}S = 0.852 x \frac{m1 \text{ of } AgNO_{3}(0.05N)}{m1 \text{ of liquor sample}} \dots /3-9/m1 \text{ of liquor sample}$
$$CH_{3}SNa = 3.505 x \frac{m1 \text{ of } AgNO_{3}(0.05N)}{m1 \text{ of liquor sample}} \dots /3-10/m1 \text{ of liquor sample}$$

or $CH_{3}SH = 2.405 x \frac{m1 \text{ of } AgNO_{3}(0.05N)}{3} \dots /3-11/m1 \text{ of liquor sample}$

m1 of liquor sample

The potentiometric titration curves for four sulfate and two polysulfide black liquors are shown in Fig. 3.1. Obviously, two inflection points "a" and "b" can be identified as sulfide titration end points. According to usual reading of these curves, black liquor shows mercaptan content. By convention (67, 188), inflection point "b" is taken as endpoint for calculating the solution sulfide content. The difference of reading between inflection points "a" and "b" can affect the sulfide calculation as shown in Table 3.2. This indicates that gross errors are
introduced by the practice of reading inflection "b" for monosulfide calculations. This will be discussed further in a later section.

3.3.1.1.3 Interpretation of titration curves

The behavior of sulfide ions in black liquor is complicated. Trace quantities of elemental sulfur may exist in both white and black liquors. The elemental sulfur also may be formed by oxidation of black liquor monosulfides on contact with air. The secondary reaction with methyl mercaptan is considered as follows (102):

Their effect on sulfide determination by silver nitrate potentiometric titration is proposed as (102):

$$2CH_{3}SS^{-} + 2Ag^{+} \longrightarrow 2CH_{3}SSA_{g}$$

$$2CH_{3}SSAg \longrightarrow Ag_{2}S + CH_{3}SSCH_{3}$$

$$2CH_{3}SS^{-} + 2Ag^{+} \longrightarrow Ag_{2}S + CH_{3}SSCH_{3} \cdots (/3-14/3)$$

$$s_{n}^{--} + 2Ag^{+} \longrightarrow Ag_{2}S_{n}$$

$$Ag_{2}S_{n} \longrightarrow Ag_{2}S + S^{0}_{n-1}$$

$$s_{n}^{---} + 2Ag^{+} \longrightarrow Ag_{2}S + S^{0}_{n-1} \cdots (/3-15/3)$$

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Titration curves of Fig. 3.2 show sodium sulfide in alkaline solution, white liquor (WL 1-3), and black liquor (BL 1-2) samples with and without CH₃SNa addition as titrated with silver nitrate. Similarly, Table 3.3 shows the accuracy of sulfide determination with known quantities of hydrogen sulfide and methyl mercaptan in alkaline solution, with and without 1% thiolignin as additive. On the titration curve inflection point "a" is taken for calculation of sulfide, "a"-"b" for bound mercaptan, "b"-"c" for free mercaptan.

These results confirm that inflection point "a" is due to mono-sulfide, and inflection "b" originates from bound mercaptan. This also indicates that one mole of bound mercaptan is precipitated by one equal mole of silver nitrate in stoichimetric ratio as shown by calculations in Eq. /3-14/. The addition of 1% thiolignin did not seem to affect the titration results.

Fig. 3.2 clearly indicates that alkaline sulfide solution, as well as kraft liquor, give similar potentiometric traces to those obtained with black liquor. This also indicates that inflection "b" is caused by presence of the mercaptide ion. Titration curves of sulfide and mercaptan mixtures having no inflection at "b" were shown by Tamele <u>et al</u>. (192), as well as Cashen and Bauman (37). However, Felicetta <u>et al</u>. (67) reported that inflection "b" was indeed present for mixtrues of sulfide and

-54-

mercaptan. Their reasoning, and decision to calculate the sulfide content from inflection point "b", was unclear and can not be followed. For quantitative demonstration, a 10 g/l sodium sulfide solution was prepared by dissolving the appropriate amount of reagent grade sodium sulfide in 1 N NaOH solution with and without 1% thiolignin added. One ml of the sodium sulfide solution gave a titration curve typical for excess free mercaptan. The inflection points at "a" and "b" were read for calculation of sodium sulfide with results tabulated in Table 3.4. The data indicate that sodium sulfide calculated from inflection point "a" agrees well with the original quantity of sulfide added. However, great error was found if sodium sulfide was calculated from inflection "b".

Bilberg (26) proposed that the presence of aromatic polyhydroxy compounds (such as lignin or thiolignin) in black liquor reduces the silver ion which may contribute to errors with silver nitrate titration. From Table 3.4, it is obvious that there is little difference in titration responses of alkaline sulfide liquor samples with and without added thiolignin.

3.3.1.1.3.1 Effect of mercaptide ion concentrations on titration

The potentiometric titration of sulfide and mercaptide ion mixture is based on silver sulfide being precipitated

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first at a high negative potential followed by considerable change in potential after all of the sulfide ion has reacted. The precipitation of silver mercaptan commences at a lower potential and on completion of mercaptide ion precipitation, another sharp change in potential occurs. Again, elemental sulfur interferes with this procedure as it reacts with the mercaptide ion and its product, as shown in Eq. /3-12/, imparts to the electrode a potential close to that observed from the monosulfide ion.

In order to demonstrate the effect of the presence of mercaptide ion on outcome of the sulfide determination, a certain volume of commercial pulp mill white liquor (WL 1-3) and black liquor (BL 1-2) were pipetted into the titration cell. In a series of titrations (using the above mixture as stock solution) various quantities of sodium mercaptan solution were added and the solution was titrated immediately with 0.1 N silver nitrate. The titration curves reproduced in Fig. 3.3, show clearly the case of excess elemental sulfur and its effect on mercaptan, whereby all the mercaptide ions are converted to organo polysulfide (CH_SST). The excess elemental sulfur remains unreacted. By increasing the quantity of mercaptan solution to react with excess elemental sulfur, free mercaptan inflections were obtained on the titration curve. Thus it is reasoned that there are few if any methyl mercaptide ions in black liquor, since most of the

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mercaptide ions are converted to organopolysulfide in black liquor.

3.3.1.1.3.2 Titration of inorganic polysulfide solution

As shown in Eq. /3-15/, polysulfide-

sulfide is precipitated and elemental sulfur is released by titration of polysulfide solutions with silver nitrate. A polysulfide sample was prepared by dissolving 0.164 g of elemental sulfur in 20 ml of 10 g/l sodium sulfide alkaline solution under nitrogen atmosphere. The solution was shaken for three days on an automatic shaker at room temperature $(25^{\circ}C)$. A golden-yellow polysulfide solution was obtained. For titration 0.25 ml samples of the polysulfide solution were transferred with microsyringe to the titration cell and titrated with 0.1 N silver nitrate. For a further series of titrations, varying amounts of sodium mercaptan were added to 0.25 ml portions of polysulfide solution. As seen in Fig. 3.4, two inflection points are found again on these titration curves of inorganic polysulfide solutions. A similar pattern was reported earlier by Bilberg (26), and recently by Papp (151) and Murray et al., (142) for titration of a solution containing sulfide and polysulfide. Bilberg (26) and Papp (151) further showed that when the polysulfide solution was pretreated with sodium sulfite, the inflection "b" disappeared. The following chemical reaction is thought to be involved:

 s_{n}^{--} + $(n-1)s_{3}^{--}$ $(n-1)s_{2}o_{3}^{--}$ + $s^{--}.../3-16/$

-57-

By adding varying amounts of sodium mercaptan, inflection point "b" gradually became the constant value "b" (Fig. 3.4). This is taken as further proof that inflection point "b" of the black liquor titration curve is due to the presence of organic and inorganic polysulfides in the solution, rather than mono-sulfide alone.

3.3.1.1.3.3 Titration of oxidized sulfide liquors

Black liquor was oxidized in a 500 ml jar equipped with a rubber stopper and with inlet and outlet tubes. A 400 ml liquor sample containing about 10 g/l sodium sulfide in 1 N sodium hydroxide, with and without 1% thiolignin added, was purged with oxygen through a porous glass gas-dispersion tube immersed in the solution. The oxygen flow rate (44 ml/min) was controlled by means of a reducing valve and measured with a calibrated rotameter. Simultaneous to oxygen purging the solution was stirred by a magnetic stirrer. Foam was reduced by adding a few drops of octanol.

The change in sodium sulfide concentration was determined from time to time by withdrawing one ml samples of solution. These were mixed with 4 ml of 16.6 g/l sodium mercaptan solution, and the mixed solutions were then titrated with 0.1 N silver nitrate. Changes in sulfide and bound mercaptan concentrations due to the

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treatment are shown in Table 3.5. As expected, quantities of dissolved sulfide and bound mercaptan gradually decreased as oxidation progressed. The potentiometric titration of oxidized sodium sulfide with 1% thiolignin in alkaline solution before addition of sodium mercaptan shows that the sulfide end point was well defined (Fig. 3.5).

3.3.1.1.3.4 Titration of dimethyl sulfide and dimethyl disulfide in alkaline solution

Black liquor usually contains a small quantity of dimethyl sulfide and dimethyl disulfide. Swartz and Light (188) claimed that the end-point break in silver nitrate potentiometric titration of black liquor is caused by the presence of organosulfide compounds, such as methyl mercaptan and dimethyl sulfide, which may supply ions to the system. It is agreed that there is a considerable effect of mercaptide ions on the titration In order to test the interference caused by dimethyl procedure. sulfide, an experiment was done including the mixing of 1.0 ml of dimethyl sulfide with 100 ml 1 N sodium hydroxide solution. The solution was titrated with silver nitrate after having been stirred for 30 min at room temperature. This solution gave no sulfide ion potential. The same procedure was applied to dimethyl disulfide and, as expected, it gave organo-sulfide potential. For comparison, potentiometric titration curves of dimethyl sulfide, dimethyl

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disulfide, elemental sulfur-mercaptan and methyl mercaptan alkaline solutions are shown in Fig. 3.6. The potential of ionized disulfide (Curve II) and sulfur-mercaptan (Curve III) alkaline solutions are very close. Accordingly, the reaction of dimethyl disulfide in alkaline solution may be proposed as follows:

 $\begin{array}{rcl} CH & SSCH & + & OH^{-} & \longrightarrow & CH & SS^{-} & + & CH_{3}OH & \dots & /3-17/\\ 3.3.1.1.3.5 & Titration of mercaptan in the presence of \\ & elemental sulfur \end{array}$

Potentiometric titration of mercaptan in black liquor results in poorly defined titration curves (Fig. 3.1). As previously discussed, this may be explained as due to presence of elemental sulfur in solution, since this is capable of reacting further with mercaptide ions and forming organopolysulfides (Eq. /3-12/). In order to test this point, different amounts of elemental sulfur were dissolved in aliquot portions of 20 ml methyl mercaptan alkaline solution by shaking for three days under nitrogen atmosphere at room temperature. The silver nitrate potentiometric titration was conducted by sampling 4.0 ml of the prepared solution. Titration curves are reproduced in Fig. 3.7, while bound sulfur and bound mercaptan were calculated from Eq. /3-10/ and are tabulated in Table 3.6. The potentiometric titration of mercaptan in the presence of elemental sulfur was

-60-

dependent on the ratio of mercaptan to elemental sulfur. As shown in Table 3.6, as long as the amount of elemental sulfur was greater than the corresponding mercaptan concentration no free mercaptan inflection point was detected on the titration curves. The excess elemental sulfur remains unreacted or dissolved in the strong alkaline solution in the form of sulfide (Eq. /2-18/). This is also indicated by data of Table 3.6, as well as Fig. 3.7 (Curves II and III). Conversely, when mercaptan concentration is greater than elemental sulfur, organosulfide and free mercaptan are shown by the titration curves such as Fig. 3.7 (Curve II).

As a result of this it may be proposed to keep the ratio of elemental sulfur to mercaptan sulfur greater than one during sulfate cooking by adding small amounts of elemental sulfur. Thereby the methyl mercaptide ions should react with sulfur to form organopolysulfide before they react further to form dimethyl sulfide and dimethyl disulfide. Organopolysulfide is considered to be less volatile than methyl mercaptan. Part of the air pollution problem associated with sulfate pulp cooking might be abated by reducing methyl mercaptan, dimethyl sulfide and dimethyl disulfide .to the less volatile organopolysulfides.

In summary, sulfate black liquor potentiometric titration yields two inflection points: The first break ("a") is considered

-61-

to be mono-sulfide, the second inflection ("b") is thought to be due to the presence of organopolysulfides in unoxidized and organic/inorganic polysulfides in oxidized black liquors.

Most of the mercaptide ion in black liquor may be bound by traces of elemental sulfur present in black liquor to form organopolysulfide which also contributes to the potentiometric titration. Determination of methyl mercaptan by potentiometric titration in sulfate black liquor is most difficult, as mentioned above. Correct interpretation of the titration curve gives considerable promise for accurate determination of sulfide in oxidized black liquor.

It is proposed that partial abatement of air pollution originating with the sulfate pulping process might be obtained by adjusting the elemental sulfur to mercaptide sulfur ratio during the cooking stage. The mercaptide should be bound by elemental sulfur to form organopolysulfides which are less volatile than methyl mercaptan.

3.3.2 Gas: liquid chromatographic (GLC) determination of organic sulfides in black liquor

During the sulfate pulping process approximately 2.3 to 2.5% of the sulfur charge is converted to organosulfur compounds, mainly methyl mercaptan, dimethyl sulfide and dimethyl

-62-

disulfide. These, on escape from the black liquor, constitute the main sources of malodorous emissions (11).

Part of this spectrum of sulfide emissions, suitably identified and determined by potentiometric titration techniques, has been discussed at length in the foregoing section. Although mercaptide ions do respond to potentiometric titration their concentration limitations cause severe problems, especially below 0.002 M concentration. This is due to the limited response of the silver sulfide electrode below the above concentration. Thus, this technique becomes unsuited for analysis of mercaptans in commercial black liquors where the usual concentration does not exceed 0.002 M.

Colorimetric analysis of hydrogen sulfide and methyl mercaptan in sulfate effluents" has been reported, but the technique has been found to be extremely tedious for black liquor analysis (24). Other techniques, such as that of Bialkowsky and DeHaas (25) employing wet-chemistry and Felicetta <u>et al.</u>(67) who combine mass spectroscopy and titration methods, although capable of quantitative analysis, were found to be too involved and unsuited for routine black liquor analysis.

In recent years a large number of papers have been published on gas liquid chromatography of sulfides (2, 3, 33, 52, 55, 86, 95, 125, 127, 134, 160, 184, 199, 200, 205, 218). Many of the papers

-63-

deal descriptively with chromatographic conditions (2, 3, 86, 127, 134, 169, 205), while others concentrate on improvements in sampling techniques (55, 66, 95, 160, 221).

The direct analysis of sulfides in dilute aqueous solution (such as kraft black liquor) presents numerous problems in gas chromatography. Considerable interference is experienced from the water peak, which usually requires specially selected sample preconditioning attachments at the chromatograph sampling port.

Only limited attempts have been made on direct determination of malodorous sulfur compounds in aqueous effluents. The techniques developed to liberate the volatile solutes from aqueous solution, followed by gas chromatography without water interference, include distillation either at elevated temperature (62) and/or reduced pressure (146). Stripping with a stream of inert gas was developed by Swinnerton <u>et al</u>. (185) and considerably improved upon by Rayner <u>et al</u>. (160). Rayner <u>et al</u>. (160) determined methyl mercaptan, dimethyl sulfide and dimethyl disulfide by first collecting the samples in a stripping cell to eliminate the considerable dispersion of samples in continuous gas streams.

Douglass and Price (55) described a novel stripping technique which takes advantage of changing solubility characteristics of sulfides with solution pH. They followed sulfide formation kinetics

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by acidifying a known quantity of pulping liquor with excess Using chromatography, the vapor above the aqueous sulfuric acid. solutions was sampled and analyzed and the results converted to quantitative figures with the aid of conversion (liberation) factors. While reproducibility of the technique was quite acceptable, it does not account for more than one-third to onefourth of the mercaptan originally present in the sample. In a similar study McKean et al. (127) described dimethyl sulfide analysis by a slightly different technique. A calibration curve is prepared for the compound by heating the aqueous solution of known dimethyl sulfide concentration to a constant temperature and .subsequently sampling the vapour phase with a microsyringe through a septum. Gas chromatograph analysis followed. This technique requires a calibration curve for each (heating) temperature.

Recently, Matteson <u>et al</u>. (125) reported that malodorous sulfur compounds can be extracted with carbon tetrachloride from steam distillates of kraft black liquor. Thereby, they repeatedly extracted the oily distillate with carbon tetrachloride and subjected the extract to gas liquid partition chromatography (GLC). Further improvements of this technique were reported by Andersson and Bergström (12), who acidified the black liquor-carbon tetrachloride mixture to a pH of 9.3 with saturated boric acid solution. The organic layer was sampled and the sulfide content

- 65-

determined by GLC. It was claimed that both dimethyl sulfide and dimethyl disulfide are rapidly and almost completely extracted (98%) into the carbon tetrachloride layer by this technique but only part of the methyl mercaptan could be recovered. Thus, a conversion factor has been developed for methyl mercaptan.

On the hardware side, important improvements have been made available with columns and packings (3, 33, 160) and especially detectors. Among known detectors, Thermal Conductivity Detector (TCD) was often employed, since it responds universally to all types of compounds. Low sensitivity of TCD, however, has been a great handicap to accurate analyses. Especially poor response was obtained for low concentrations of organosulfides such as found in black liquors. Large advances were made with the Flame Ionization Detector (FTD) which has shown high sensitivity (1000 times lower detection limits than with TCD) for hydrocarbons and alkyl sulfides, but weak responses to hydrogen sulfide and sulfur dioxide (2,33, 160). It gives no response to carbon disulfide and water. It is known that in the presence of sulfur, halogens in the organic structure cause significant reduction in sensitivity, whereby the detector becomes of limited value in work with sulfides.

Possibly the largest recent improvements in sulfur detection were made with introduction of the Flame Photometric Detector (FPD) in 1966. The FPD is the first inexpensive detector, operated on

-66-

principles of spectroscopy, for sulfur and phosphorous containing compounds to be coupled with gas chromatography. The use of this detector was first reported by Stevens <u>et al</u>. (181) as an automated gas chromatographic analysis system for sub-ppm levels of sulfur compounds in ambient air. The analytical system developed for gas analysis required the use of 36-feet of 0.085 in (ID) Teflon column on 30/60 mesh Teflon coated with polyphenyl ether and 0.5 g of orthophosphoric acid. Further improvements and results on this system are described by Mulik <u>et al</u>. (134).

The detector is comprized essentially of a burner jet, reflective (collimating) mirror and narrow pass filter (394 nm for S, and 526 nm for P). The photomultiplier tube responds to the chemoluminescent characteristic light emitted by S at 394 nm wave length when sulfur is burned in a hydrogen-rich flame. The light monitored by the photomultiplier tube is fed to an electrometer and recorder.

The FPD is a mass flow rate dependent detector and as such the detector will yield a peak area independent of the volume of carrier gas eluted with the sample. It requires a particular calibration curve for every compound, as it has no linear portion at all (straight lines are obtained on log-log plots with slopes between 1.5 to 2.0 which has been found to be constant over a 500 fold range). While its specificity to hydrocarbons is good, the

- 67-

detector sensitivity for S is 10,000 fold the sensitivity for hydrocarbons (86). The filters are not completely selective as to S and P, with the sulfur filter phosphorus also detected at 100 fold lower sensitivity. The good ppb detection for S is obtained only under careful tuning of the instrument as described by Stevens <u>et al</u>. (181)

3.3.2.1 Experimental

3.3.2.1.1 Chemicals

Dimethyl sulfide (bp. $37-38^{\circ}$ C) and dimethyl disulfide (bp. $109-111^{\circ}$ C) were obtained from Eastman Organic Chemicals; hydrogen sulfide (bp. -61.8° C) and methyl mercaptan (bp. 7.6° C) from Matheson of Canada Ltd.; boric acid and carbon tetrachloride were reagent grade. The sulfate black liquor (2-1) was obtained from Canadian Forest Products Ltd., Port Mellon, B.C. and the white liquor (3-1) containing 38 g/1 effective alkali and 14.4 g/1 sodium sulfide was obtained from Department of Environment, Western Forest Products Laboratory, Vancouver, B.C.

3.3.2.1.2 Gas liquid chromatography (GLC)

A MicroTek MT-150 gas chromatograph,

equipped with a Melpar flame photometric detector (FPD) and flame ionization detector (FID), dual channel electrometer and dual pen recorder was used for these studies. The column was prepared by using a coiled glass column 7 feet long and $\frac{1}{4}$ in (OD) packed with didecylphthalate on 60/80 mesh Chromosorb P (25:75 by weight).

The chromatograph operating parameters were as follows: Carrier gas: Nitrogen, 45 ml/min 40 psi inlet pressure Oven temperature: 4 min at 25°C for H₂S and CH₃SH Program: Oven temperature rise from 25°C to

 $125^{\circ}C @ 22^{\circ}C/min \text{ for } CH_{3}SCH_{3} \text{ and}$ $CH_{3}SSCH_{3}$ Detector temperature: 150°C
Detector gas flow: H_{2} : 150 ml/min
Air: 30 ml/min O_{2} : 15 ml/min

The calibration curves for H_2S and CH_3SH were prepared directly by taking measured volumes of the gases with gas tight micro syringes at known pressure and temperature. The samples were taken through flexible rubber hoses connected to a manometer on one end and to lecture bottles of the gas on the other. The gas samples so taken were injected through rubber septums into an inverted volumetric flask containing 100 ml CCl_4 . Similarly, liquid sulfide samples (dimethyl sulfide and dimethyl disulfide) were withdrawn with appropriate microsyringes and mixed with CCl_4 in the above manner. Thus dilution series were prepared for all four sulfides and injected directly into the gas chromatograph. Under the above described conditions typical chromatograms were obtained which could be further evaluated as to characteristic retention times and detector response with changing concentrations.

Retention times of sulfide peaks eluting under the particular chromatographic conditions are described as follows:

Hydrogen sulfide (H S) 2	1 min 50 sec
Methyl mercaptan (CH_SH) 3	5 min 25 sec
Dimethyl sulfide (CH ₃ SCH ₃)	8 min 30 sec
Dimethyl disulfide (CH_SSCH_)	18 min 25 sec

Calibration curves constructed from the information obtained in the above described manner are presented in Fig. 3.8. As anticipated the concentration <u>vs</u>. detector response relationships were all straight lines when plotted on log-log scale (within the described concentration range).

Calibration curves for determining dimethyl sulfide and dimethyl disulfide in black liquor (above pH 12) were also prepared. One hundred ml of the black liquor (2-1) was thoroughly extracted with 8 x 50 ml carbon tetrachloride and then further stripped with nitrogen gas at room temperature for 12 hours. The treated black liquor was tested for no residual organic sulfides by extraction of 5 ml samples with 5 x 5 ml carbon tetrachloride which was combined

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and examined by GLC analysis. The organic sulfides free icewater-cooled black liquor was transferred into a 25 ml volumetric flask equipped with a rubber septum. Appropriate amounts of dimethyl sulfide and dimethyl disulfide were then injected into the black liquor samples. The solution was thoroughly shaken and stored in the cold $(5^{\circ}C)$ overnight. Further 5 ml of the organosulfide solution was syringed into a 20 ml separation funnel and thoroughly extracted with 5 x 5 ml carbon tetrachloride. The calibration curves of black liquor organosulfide concentrations <u>vs</u> detector response (represented by peak height) are shown in Fig. 3.9.

3.3.2.1.3 Sample procurement for gas liquid chromatography (GLC)

As stressed earlier, no convenient single technique is available for simultaneously and quantitatively determining all black liquor sulfides. Following a critical examination of the available techniques, liquid/liquid extraction with carbon tetrachloride, as originally proposed by Matteson <u>et al</u>. (125) and later modified by Andersson and Bergström (12), was chosen as most suited for sample procurement and analysis by gas liquid chromatography.

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3.3.2.1.3.1 Carbon tetrachloride liquid/liquid extraction

Before applying the 1/1 technique, extraction efficiencies on both enriched white and black liquors were determined. While white liquor needed no preparation for this determination, 100 ml portions of the black liquor were preextracted five times with 100 ml portions of $CCl_{l_{\downarrow}}$ followed by stripping with nitrogen gas for 24 hours in order to remove sulfides present.

Extraction efficiencies were tested on two replicate 5 ml liquor samples to which varying amounts of dimethyl sulfide $(0.845 \times 10^{-3} \text{ to } 0.212 \times 10^{-3} \text{g})$ and dimethyl disulfide (1.057 x 10^{-3} to 0.264 x 10^{-3} g) were added. The solutions were prepared in 20 ml separatory funnels equipped with silicone-neoprene rubber septums. The heterogeneous liquor-sulfide mixture was shaken by hand for 2 min and allowed to stand for at least 15 min. Following standing, the mixture was successively extracted five times with 10 ml CC1 by shaking each time for 1 min and allowing sufficient h_{μ} time (usually 15 min) for clear separation of the two layers. The combined organic layer (bottom) was drained into a 25 ml volumetric flask and immediately made up to mark with fresh CCl_{μ} . The sulfide content of the supernatant liquid was determined by gas liquid chromatography. Recovered quantities and efficiencies are

indicated in Table 3.7 and Fig. 3.10.

For determining dimethyl sulfide and dimethyl disulfide in experimental black liquor samples, the same procedure was followed except that 10 ml of cooled black liquor (-5° C) was extracted with 5 x 5 ml CCl, in 20 ml capacity separatory funnels.

Carbon tetrachloride extraction seems to be selective to sulfur compounds in black liquor. As shown in Table 3.7, the extraction efficiency of dimethyl sulfide and dimethyl disulfide is similar for both white and black liquors. This indicates little, if any, interference by dissolved lignin and carbohydrates or other organic and inorganic solutes usually found in commercial black liquors. The extraction efficiencies for dimethyl sulfide and dimethly disulfide, however, were significantly different being in the order 90 to 94% and 78 to 81% respectively. It also appears that change in concentration over the four fold range of 0.212 x 10^{-3} to 0.845 x 10^{-3} g in 5 ml sample had no detectable effect on extmaction efficiency of dimethyl sulfide by carbon tetrachloride. Similar observation was made on dimethyl disulfide as shown in Table 3.7.

In order to test effect of solution pH on extraction efficiency of dimethyl sulfide and dimethyl disulfide, the buffered solutions were prepared between pH 1.5 to 13.5 by mixing certain portions of 0.1 M potassium hydrogen phosphate with 0.1

-73-

M HCl or 0.1 M NaOH as described in the Handbook of Chemistry and Physics (94).

Aqueous solutions of 100 μ l dimethyl sulfide and dimethyl disulfide in 100 ml distilled water were cooled to 5°C overnight. To 5 ml buffered solution 1.0 ml of the aqueous solution was added in a 20 ml test tube equipped with a rubber septum. The solution was well mixed with the syringe, shaken several times and cooled to 5°C. The solution thus prepared was extracted five times with 10 ml aliquots of CCl₄. Sulfide concentrations were further $\frac{1}{4}$ determined by gas liquid chromatography.

The efficiency of CCl₄ liquid/liquid extraction of dimethyl sulfide and dimethyl disulfide was considerably affected by pH of the solution as shown in Fig 3.11. There was relatively little change in efficiency between pH 1.5 to 7.0 where nearly 100% of dimethyl sulfide and 95% of dimethyl disulfide was recovered. A rather sharp drop was observed by increasing the pH from 7.0 to 10.0 where the efficiencies dropped 10% for dimethyl sulfide and 15% for dimethyl disulfide. There was relatively little change between pH 10.0 to 13.5.

3.3.2.1.3.2 Acidification of black liquor with boric acid

The analysis of carbon tetrachloride extracts by gas liquid partition chromatography was designed to

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provide both qualitative and quantitative information on black liquor sulfides. Identification of a given sulfide compound involved evaluation of comparative and relative retention time data as provided by standard reference compounds. Further substantiation of all peaks obtained from black liquor extracts was made by enhancement of the initial peak through addition of known quantities of known compound to the black liquor before the extraction step.

The rather disturbing inaccuracy of the methyl mercaptan determination in black liquor by the previously described potentiometric titration technique prompted further search for a more accurate method. As indicated by the experiments of Douglass and Price (55) and Andersson and Bergström (12), both dissolved hydrogen sulfide and methyl mercaptan can be stripped from aqueous solutions acidification of the black liquor. This can be followed by CC1_liquid/liquid extraction.

For this experiment, extraction was done after adjusting liquor pH to approximately 6.5 with boric acid (H_3BO_3) . This also coincides with maximum extraction efficiency as determined for dimethyl sulfide and dimethyl disulfide (Fig. 3.11).

Boric acid is a tribasic acid. Dissolved in water the various hydrogen atoms undergo dissociation to different extents. The three dissociation constants at $20^{\circ}C(K_1, K_2 \text{ and } K_3)$ can be calculated from the following equations (94):

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Since the boric acid is a weak electrolyte, the law of mass action may be followed for the respective dissociation (94):

 $HBO_3^- \rightleftharpoons H^+ + BO_3^{---}$

 $(H^+) \times (H_2BO_3^-)/(H_3BO_3) = K_1 \dots (3-21)$ $(H^{+}) \times (HBO_{3}^{--})/(H_{2}BO_{3}^{--}) = K_{2} \dots (3-22)$ $(H^+) \times (BO_3^{---})/(HBO_3^{--}) = K_3 \dots (3-23)$

The magnitude of the dissociation constants indicates the extent of ionization at given concentrations.

The relationship between black liquor (BL 1-4) pH and boric acid addition is shown in Fig. 3.12. Above pH 6.8 the black liquor pH is a function of boric acid concentration while below pH 6.8 only small change in pH is observed with increased amounts of boric acid. This allows fairly good control of black liquor pH when pH 6.5 is chosen as target acidity for treated samples.

Changes in gas chromatograms due to black liquor acidification are illustrated in Fig. 3.13. The appearance of H_{2} S and CH₃SH is quite obvious while position of the earlier peaks remained unchanged following acidification. The boric acid acidification of black liquor was carried out in a vessel, hermetically closed with the aid of a rubber septum. The predetermined amount of

solid boric acid (1.1 g) was weighed into the vessel together with 20 ml of CCl₄. The black liquor (5 ml) was added with a syringe through the rubber septum. Contents of the vessel were shaken vigorously until all the boric acid dissolved. The vessel and contents were then frozen overnight in an inverted position and the organic layer sampled and analyzed by gas liquid chromatography next day.

During the course of GLC analysis of the various black liquors the expected compounds, hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide were identified in accordance with earlier findings of Felicetta <u>et al</u>. (67) and others. No further compounds were detected with the exception of "X" (Fig. 3.13) although Thomas (200) reported propyl mercaptan, ethyl disulfide and propyl disulfide in digester blow and relief gases entering the lime kiln. Similar results were indicated by Thoen and Nicholson (199) following infrared analysis of relief gases. In addition the possible existence of methyl hydrogen disulfide (CH₃SSH) in black liquor pyrolysates has been proposed by Brink <u>et al</u>. (32).

In this study an unidentified compound "X" (Fig. 3.13) was found as a constant and rather large component of the liquid/ liquid extraction of black liquor. The compound was present in CCl_{h} extracts of both normal and acidified black liquors of all

-77-

sources (including polysulfide black liquor). In some samples the concentration of the unkown was quite high. Limited further experiments indicated that the unknown contains no ionizable hydrogen and is a volatile sulfur compound with a boiling point slighter higher than that of dimethyl sulfide.

3.4 Chemistry and Analysis of Polysulfide

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3.4.1 Significance of polysulfide as an extention to sulfate pulping
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Polysulfide pulping is one of the few methods by which stabilization of wood carbohydrates occurs during alkaline pulping. This results in yield increases and some improved physical properties of pulps produced thereby.

By impregnation of wood chips with polysulfide liquor the carbonyl end groups of polysaccharides are oxidized to carboxyl groups, thus stabilizing the carbohydrates against alkaline degradation (8, 196, 132). The ability of a polysulfide solution to stabilize polysaccharides increases with the concentration of elemental sulfur and with the ratio of polysulfide excess sulfur to sulfide sulfur in alkaline solution (109, 197). The yield increases of polysulfide pulping are caused to a large extent by retention of glucomannan in coniferous woods (109, 167) and xylan in porous woods (110, 167). The modification of lignin by formation of carbonyl groups is believed to increase the rate of

-78-

delignification (131, 143, 167).

Pulp yield increases are found to depend mainly on the amount of elemental sulfur added, degree of impregnation, pulping conditions, and wood species being pulped (108). Maximum pulp yield increases are usually in the range of 2-5%, based on oven-dry wood (53, 108, 167, 212). The pulp yield increases of porous wood are moderate and only about one-half of those obtained with coniferous woods. It may be that xylan in porous woods is not as effectively stabilized by polysulfide cooking as glucomannan in coniferous woods (167).

As for pulp properties, Sanyer and Laundrie (167) reported that the strength properties of loblolly pine (<u>Pinus taeda</u> L.) polysulfide pulps were comparable with those of sulfate pulp, except for the slightly lower tear strength. Requirements for bleaching chemicals were about the same as those expected for sulfate pulps of the same Kappa number. Dillen and Noreus (53) indicated that Scots pine (<u>Pinus sylvestris</u> L.) polysulfide process pulps have of higher viscosity for cooks carried to low Kappa numbers than similar pulps originating from conventional sulfate cooks.

3.4.2 Composition and nomenclature of aqueous polysulfide solutions

The anions in an aqueous polysulfide solution are considered to be HS⁻, S⁻, OH⁻ and a variety of polysulfide ions

-79-

generally designated as $S_{0}S_{-}$. A whole series of polysulfide ions from SS_{-} to $S_{0}S_{-}$ has been isolated in crystalline form as sodium or potassium salts (197). Electrolytic procedures were also developed by which reduction of sulfur can provide. mixtures of still higher homologs of $S_{8}S_{-}$ and either $S_{6}S_{-}$ or $S_{7}S_{-}(65)$. According to the nomenclature of Teder (197), each polysulfide ion can conveniently be considered to consist of one atom of sulfide sulfur /S(-II)/ and n atoms of polysulfide excess sulfur /S(0)/.

 $S(-II) = (SH^{-}) + (S^{-}) + \sum (S_n S^{-}) \dots /3 - 24/$ $S(0) = \sum n(S_n S^{-}) \dots /3 - 25/$

Total amounts of sulfide and excess sulfur can be determined analytically. The average number of excess sulfur atoms per polysulfide ion (\overline{n}) is expressed as:

$$\bar{n} = \sum n(s_n s^{-}) / \sum (s_n s^{-}) \dots / 3-26 /$$

The average number (\bar{n}) is a theoretical concept which cannot be obtained from conventional chemcial analysis of polysulfide solutions. In practice, X, the ratio of polysulfide excess sulfur S(0) to sulfide sulfur S(-II) is used to characterize polysulfide solutions.

$$x_{s} = s(0)/s(-II)$$

= $\sum n(s_{n}s^{-})/((Hs^{-}) + (s^{-}) + \sum (s_{n}s^{-})/(..../3-27)$

Small values of n are observed with solutions of high alkalinity

and low X_s , while large \overline{n} values occur with solutions of high X_s and low alkalinity. By practical considerations in technical polysulfide solution \overline{n} is always considerably larger than X_s (197).

Aqueous polysulfide solutions have deep color ranging from yellow to red with increasing S_n in the chain. When polysulfide solutions are acidified slowly to below pH 9, the polysulfide decomposes into HS⁻ and elemental sulfur. Thermal decomposition over 90[°] of polysulfide in alkaline aqueous solution is strong due to decomposition into sulfide and thiosulfate (195).

3.4.3 Preparation of aqueous polysulfide solutions

Polysulfide solutions can be prepared by dissolving elemental sulfur in pure sulfide solution. Direct solution of elemental sulfur into sulfate white liquor, which is highly alkaline, causes extensive thiosulfate formation (189, 195). By partial oxidation of white liquor with air in the presence of black liquor, polysulfide can be formed. Besides the polysulfides, large amounts of thiosulfate, and small amounts of sulfite and sulfate are produced simultaneously (27). Barker (19) claimed that sulfide in white liquor can be selectively oxidized to polysulfide with manganese oxide.

Other ways of producing polysulfides have been proposed, such as electrolysis of sodium sulfide or expelling hydrogen sulfide from green liquor by carbon dioxide and recovery of

-81-

elemental sulfur by Claus' process (212). Partial reduction of sulfate and cathode reduction of sulfur dioxide to form polysulfide have been reported (7, 35). Hydrogen sulfide can be decomposed to elemental sulfur by irradiation with ultraviolet, alpha-particles or by passing the gas through an electric arc (35). The recovered elemental sulfur may be dissolved in sulfide solution for the preparation of polysulfide.

As a new approach, gamma radiolytic generation of polysulfide in carbon dioxide and hydrogen sulfide acidified sulfide solution was attempted in these studies.

3.4.4 Polysulfide determination

The analysis of polysulfide in aqueous solutions became important with the discovery of advantages provided by the presence of polysulfide in sulfate pulping liquors (197). The determination of polysulfide sulfur (S(0)) presents numerous problems (28, 197). The classical methods of analysis were reviewed and summarized by Blasius et al. (28) in 1968.

3.4.4.1 Gravimetric analysis

The technique is based on converting polysulfides into hydrogen sulfide and elemental sulfur. The latter is determined gravimetrically. The reaction schemes can be expressed as: Na S $\xrightarrow{H^+}$ HS $\xrightarrow{quartz \ catalyst}$ H₂S + (n-1)S .../3-28/ 90°C

3.4.4.2 Volumetric analysis

Total sulfur in polysulfide can be determined by iodometric titration in acid solution:

 $H_2 S_n + I_2 \longrightarrow 2HI + nS \dots /3-29/$

In alkaline solution, the sulfur is quantitatively oxidized to sulfate. Thus the polysulfide sulfur can be calculated from the difference of total sulfur and sulfide sulfur.

Polysulfide sulfur can be reduced quantitatively to sulfide with sodium amalgam:

 Na_2SS_n + 2n $NaHg_m$ \longrightarrow (n+1) Na_2S + 2nHg_m ../3-30/ Thus the polysulfide sulfur can be calculated from the difference of iodine consumption of mono-sulfide sulfur and the total reduced sulfide sulfur.

The reaction of polysulfide sulfur with sulfite to form thiosulfate is also known:

 Na_2SS_n + $n Na_2SO_3 \longrightarrow Na_2S$ + $n Na_2S_2O_3 \dots/3-31/$ The thiosulfate can be determined iodometrically when the sulfide and the excess sulfite are precipitated by $2n^{++}$ and Sr^{++} , respectively.

Similarly, the polysulfide sulfur will react quantitatively with cynide to form thiocynate and the thiocyanate can be analysed by iodometric titration.

 $Na_2SS_n + n CN \longrightarrow Na_2S + n SCN \dots /3-32/$

The above described methods are usually too difficult to perform for direct analysis of polysulfide cooking liquors, as they become involved and time consuming, due to interference from the impurities found in such liquors. Recently, several methods have been developed which allow quantitative determination of polysulfide sulfur in white or black liquors.

Johnsen (99) developed an acidimetric method for the determination of polysulfide sulfur in sulfate white and black liquors by using hydrochloric acid titration. Similarly, Ahlgren (5) modified the Scandinavian standard procedure (Scan-N 2:63) (170) for the analysis of polysulfide sulfur, hydroxide, sulfide and carbonate in polysulfide cooking liquor. This new technique uses hydrochloric acid as titrant. Olsson and Samuelson (149) developed a quantitative method for determination of sulfide, thiosulfate and polysulfide in black liquors by subjecting the liquor sample to anion exchange chromatography for the separation of inorganic sulfur compounds from organic impurities in the sample effluent. Further separation of thiosulfate and most of the sulfides is made by elution from the anion exchange resin with NaNO₃. Polysulfide and the remaining sulfides are subsequently eluted with a mixture of Na₂SO₃ and NaNO₃ solution. During elution, the polysulfide sulfur is transferred into thiosulfate. Both eluates contain sulfide and thiosulfate which can be determined potentiometrically. Rice and Zimmermann (162) determined sodium sulfide, thiosulfate, sulfite or polysulfide in white liquor by combination of argentometric, acidic iodine and alkaline iodine (hypoiodite) titration. The TAPPI method (T624 ts - 66) (14) analyses polysulfide sulfur by reacting the excess sulfur with sulfite to form thiosulfate which can be titrated quantitatively by acidic iodine.

In this study, the polysulfide sulfur was determined by redox titration, described by Ahlgren and LeMon (6), and spectrophotometry (195). For the redox titration, the apparatus consisted of a Radiometer pH meter, equipped with Platium (Sargent S-30440) and Calomel electrodes. The equipment was completed by adding an automatic titrator and X-Y recorder. The polysulfide sample (sodium tetrasulfide) was obtained from Hooker Chemical Corporation, New York. The sample (0.9 ml) for analysis was transferred into a vessel containing 50 ml of saturated sodium chloride solution and conditioned in a water bath at $90^{\circ} \pm 1^{\circ}$ C. The titration cell can be expressed as:

Pt//NaCl(sat.) sample // KCl, HgCl₂/HgCl₂(S)/ Hg/3-33/ solution // KCl, HgCl₂/HgCl₂(S)/ Hg/3-33/

Then, the solution was titrated slowly with 0.5 M sodium sulfite

-85-

(ca, 2 m1/min). The potential change due to addition of the titrant was recorded automatically. The end point was determined by reading the volume of sulfite solution consumed at the inflection point of the titration curve as shown in Fig 3.14. The end point is also indicated by disappearance of yellow color in the sample solution. The polysulfide excess sulfur is calculated according to the following formula (6):

 $S_n S^-$ + n SO_3^- + $H_2 O \rightleftharpoons n S_2 O_3^-$ + HS⁻ + OH⁻.../3-34/ Results of five determinations gave an average of 313.1 ± 3.0 g/l excess sulfur for the samples prepared. Comparing results of the above redox titration of polysulfide sulfur with different methods such as iodometric, acidimetric, ion exchange following potentiometric titration and copper column method, the value obtained is in good agreement with those reported above (6).

Excess sulfur in polysulfide was determined spectroscopically according to the procedure described by Teder (195). The calibration curve of polysulfide sulfur was prepared by mixing varying amounts of commercial polysulfide with 3 M NaCl and 10^{-2} M NaOH aqueous solutions. The prepared polysulfide sulfur concentrations ranged from 79.1 x 10^{-4} to 474.5 x 10^{-4} g/1. Absorption curves were obtained for the solution on a Unicam Sp. 800 spectrophotometer with 1 cm sample and reference cell (containing a blank solution of 3 M NaCl and 10^{-2} M NaOH aqueous solutions). The average of

two absorbance replications at 285 nm wave length was plotted against excess sulfur concentration and is shown in Fig. 3.15. This wave length (285 nm) was selected for reasons of least interference on absorptivity of varying hydroxyl ion concentrations and the ratio of the polysulfide sulfur to that of sulfide sulfur concentration (195). It was pointed out by Teder (195) that generally good agreement is obtained between the spectrophotometric procedure and acidimetric or redox titration of polysulfide solutions without the lignin present. The accuracy of the spectrophotometric method is not affected by the presence of other bases, such as carbonate ions in the sample, whereas the acidimetric method will be disturbed by the presence of high base content. Polysulfide samples with high lignin concentrations were found to be less suitable for analysis by the spectrophotometric method (195). However, the spectrophotometric method proved to have great advantages as it is less complicated and time consuming than other methods such as iodometric, acidimetric, ion exchanges followed by potentiometric titration and redox titration.

The sulfide sulfur / S(-II)/ is determined by pretreatment of the polysulfide solution with excess sulfite solution at $50^{\circ}C$ until disappearance of the yellow color. The monosulfide sulfur can be analysed by silver nitrate potentiometric titration as described previously.

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3.4.5 Determination of sulfate in polysulfide solution

The sulfate in the polysulfide solution, obtained as oxidative component from the gamma radiolysis of acidified sulfide solutions, can be accurately determined by turbidimetry (63). The method is based on conversion of sulfate ions to barium sulfate (BaSO₄) under conditions which lead to a colloidal suspension. The method is valid for concentrations as low as parts per million (ppm) (63).

The calibration curves for sulfate determination was constructed by pipetting 2, 5, 10, 25, and 50 ml of a standard potassium sulfate solution (0.0905 g/1) to 50 ml volumetric flasks. The measured solutions were diluted to the mark with distilled water. The sulfate solution was then poured into a 100 ml beaker containing 10 ml of salt-acid-glycerol (500 ml 20% NaCl : 10 ml conc. HC1 : 500 ml glycerol) conditioning solution and 0.3 g of barium chloride (BaC12.2H20) were added. The mixed solution was stirred for one min, let stand 4 min and transmittance was measured at 460 nm wavelength with a Spectronic-20 spectrophotometer. A blank solution for zero adjustment was also prepared with the same procedure except without adding potassium sulfate solution. The calibration curve of transmittance (%) vs. H_2SO_4 concentration is shown in Fig. 3.16.

In typical analysis of the sulfate in polysulfide solution

-88-
is determined by placing 5-10 samples of polysulfide solution into a 100 ml beaker containing 10 ml of 10% hydrochloric acid solution. The solution is boiled for 10 min to expel carbon dioxide and hydrogen sulfide gases, filtered and diluted to 50 ml with distilled water. The barium sulfate colloid suspension was further prepared according to the procedure described above for the calibration curve preparation.

3.5 Black Liquor Characterization

The various industrial and experimental sulfate black liquors (Table 4.1) were analysed as to pH, density, total solids and lignin concentration prior to storage. These data were thought to indicate origin and history of cooking, of which only limited information was available.

3.5.1 Determination of pH

A Radiometer pH meter, equipped with a Corning high pH glass electrode (No. 476024) was used. Calibration of the meter was effected with a pH 12.72 buffer solution (Fisher Sci.). All pH determinations were done at room temperature (25°C) within one week of receipt of the samples.

3.5.2 Density

The density of black liquors was determined at

-89-

25[°]C with the aid of a calibrated pycrometer (50 ml). Density values were determined relative to distilled water (at 25[°]C). The average densities were calculated from three replications for black liquor.

3.5.3 Total solids

Total black liquor solids were determined by TAPPI Standard T625 ts-64 (13). According to this method 10 ml of black liquor is weighed into a tared weighing bottle to the nearest 0.0001 g. The sample is dried overnight in an oven at $105^{\circ} \pm 3^{\circ}$ C (24 hr.). The samples are then cooled and the residue reweighed at room temperature. Average solid content was calculated from four independent replications of each black liquor.

This technique received severe criticism recently and has been discussed at length by Parker <u>et al</u>. (152). The problem associated with the TAPPI standard (13) are ascribed to incomplete evaporation of water and air oxidation during drying both of which result in higher yields. Several temporary remedies to these problems were suggested by Parker <u>et al</u>. (152), however, the method remained substantially the same.

3.5.4 Lignin determination

The accurate and rapid determination of dissolved lignin in pulping waste liquors is of a considerable interest.

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For this purpose various techniques have been suggested, but ultraviolet spectroscopy has gained most popularity for both fundamental and applied lignin analysis (101, 105, 106, 107). Most studies on lignin ultraviolet spectroscopy are limited to the 280 nm absorption. Unfortunately, absorption at this wavelength is also strongly influenced by dissolved carbohydrates and their degradation products (106, 107). Little information is available on the disturbed wavelength region between 205 to 280 nm (101, 105, 106, 107).

While sulfite spent liquors show characteristic absorbancies at 205 and 280 nm, sulfate black liquors have an absorption maxima only at 205 nm. The absorption at 280 to 290 nm is much less defined and is usually related to carbohydrate degradation products. Evidence of such effects was given by Kleinert and Joyce (106). The distinct maximum at 205 nm was shown to originate from the aromatic nucleous of lignin (105), which was found to give good linear response with change in concentration (101).

Black liquor lignin concentrations were determined by comparing absorbancies of ethanol diluted black liquors with a calibration curve prepared with purified thiolignin.

The thiolignin was prepared by acidification of a spruce sulfate pulping liquor (3-1) with 10% hydrochloric acid to pH 3-4. The precipitated thiolignin was collected by centrifuging

-91-

(6,620 G) and repeatedly washed with distilled water until no further brown color was detectable in the wash water. The centrifuged thiolignin wasair-dried and purified by filtration from ethanol solutions followed by evaporation to dryness. The procedure of purification in ethanol solution was repeated twice and the residue washed with dry ether followed by vacuum drying.

The calibration curve in Fig. 3.17 was prepared by dissolving various amounts of the dried thiolignin in 95% ethanol and plotting the concentrations against absorbancy obtained at 213 nm.

Black liquor samples were diluted to 2500 and 5000 parts with 95% ethanol. The absorbancies were measured with a Unicam Sp 800 spectrophotometer using a 1 cm quartz cell and 95% ethanol as reference. Similar absorption curves were obtained for all sulfate and polysulfide black liquors. All liquors examined exhibited the distinct absorption maximum at 213 nm and a flat shoulder at 285 nm. Slight shifts in absorption maxima were observed with lignin concentration in black liquors; shifts occurring towards the shorter wavelength (210 nm) with decreasing concentrations.

3.6 Acidification of Sulfate Black Liquor with Carbon Dioxide

Preliminary experiments showed that sodium sulfide and sodium mercaptan are quite inert to gamma irradiation in aqeous alkaline solution at high pH levels (pH 12-13.5). However, below

-92-

pH 9, both hydrogen sulfide and mercaptan are readily decomposed by gamma-radiation.

Further, practical reason for acidification of such liquors is due to the fact that sodium sulfide concentration is but little changed (20-30%) during sulfate cooking (73, 168). A high sulfidity cooking liquor gives high sulfur to sodium oxide ratio (S/Na_20) in the combustion furnace, whereby large amounts of hydrogen sulfide and sulfur dioxide are emitted to the atmosphere. At the same time this also produces a smelt with undesirably high melting point (72, 79). This problem is generally remedied by acidification of the black liquor to aid recovery of an appreciable proportion of the sulfide charge as hydrogen sulfide.

The acidification can be conducted by carbonation of black liquor using pulp mill stack gases (CO_2) (166); and the evolved hydrogen sulfide can be absorbed in green liquor (168). During acidification, lignin phenolic groups are liberated, resulting in lignin precipitation (166). It is further assumed that the residual hydrogen sulfide and organic sulfides can be easily stabilized by exposure to gamma radiation. In acidified black liquor, odor of the precipitated lignin was found to be eliminated by gamma radiation.

Acidification of black liquor was originally patented by

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Gray <u>et al</u>. (79). According to their method the black liquor is pressure carbonated and the treatment is followed by stripping with vacuum. The procedure was reported to aid recovery of 55-62%of the total sulfur from black liquor.

The carbon dioxide acidification apparatus used in the present experiments consisted of a 500 ml glass vessel for containing 400 ml black liquor and a magnetic stirrer. Carbon dioxide gas was admitted through a dispersion tube and degree of acidification was monitored with a pH meter. The CO flow rate was controlled by a rotometer reducing valve which had set at 54 ml/min. The five 100 ml capacity gas traps each contained 25 ml carbon tetrachloride and 25 ml of 20% NaOH. During black liquor acidification, changes in pH were recorded automatically. The relationship of pH change and the volume of CO bubbled through 400 ml samples of various black liquors at 25°C is shown in Fig. 3.18. Carbonation is considered to be completed when black liquor pH reached about 7.4.

The sulfide content of acidified black liquor (H_2S , CH_3SH , CH_3SCH_3 and CH_3SSCH_3) was determined by syringing 5 ml of ice-watercooled liquor into a 25 ml volumetric flask through a rubber septum. The flask contained 20 ml carbon tetrachloride and 1.0 g boric acid. The solution was then shaken vigorously several times during inverted storage in a $-5^{\circ}C$ freezer for 7 to 8 hours.

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Sulfides collected in the carbon tetrachloride layer were analyzed quantitatively by GLC and the results read from the calibration curve presented in Fig. 3.8.

The boric acid contained in the carbon tetrachloride further acidifies the carbonated black liquor to about pH 6.5. Concentrations of hydrogen sulfide and methyl mercaptan in the carbonated black liquor are too low to be determined accurately by silver nitrate potentiometric titration. However, the above procedure has been found convenient and accurate for sulfides determination. The efficiency of hydrogen sulfide and methyl mercaptan carbon tetrachloride liquid/liquid extraction was not determined. However. the results appear to be reasonably quantitative by considering that the solubility of hydrogen sulfide is 41.9 g/l in carbon tetrachloride and only 3.8 g/l in water at 20° C and 1 atmosphere pressure (116), while the methyl mercaptan is highly soluble in carbon tetrachloride (no data available) and only slightly soluble in water (94). Thus most of the hydrogen sulfide and methyl mercaptan should be easily transferred into the organic solvent phase.

The efficiencies of dimethyl sulfide and dimethyl disulfide extractions were tested by preparing 50 ml organosulfide (42.4 x 10^{-3} g/1 CH₃SCH₃ and 52.8 x 10^{-3} g/1 CH₃SSCH₃) enriched carbonated black liquor (1-1). The black liquor had been preextracted with

-95-

5 x 50 ml carbon tetrachloride prior to enrichment. Five ml of the prepared solution were syringed into a 25ml volummetric flask which contained 1.0 g boric acid suspended in 20 ml carbon tetrachloride. The solution was then shaken vigorously several times during inverted storage in a -5° C freezer for 7 to 8 hours. GLC analysis followed and the sulfides were determined according to the calibration curves presented in Fig.3.8. The results are compiled in Table 3.8. Average efficiencies of dimethyl sulfide and dimethyl disulfide were 92.9% and 86.9% respectively.

3.7 Gamma Radiation

3.7.1 Cobalt-60 gamma photon source

The gamma ray source used in these studies, was a Gammacell 220, manufactured by Atomic Energy of Canada Limited (AECL). The Gammacell was initially loaded with 8610 curies cobalt-60 as pellets in 6 pencils and 6,860 curies of cobalt-60 as slugs (total, 15470 curies). The radiation shield consists of a large steel-encased lead barrier with provision for housing the cobalt-60 source.

Cobalt-60 has a half life of 5.24 years. Dose rate measurements according to ferrous sulfate chemical dosimetry on March 26, 1968 gave 1.26 x 10^6 + 2.5% rad/hr radiation intensity being

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certified by AECL. The sample chamber dimensions of this irradiator are 8.13-in in height and 6-in diameter. The irradiator controls consist of drawer movement control switch (for raising or lowering the sample drawer manual control, a digital timer (calibrated in hours, minutes and seconds) and mode selector switch for selection of time range. The Gammacell ambient temperature is 34° C.

3.7.2 Gamma ray dosimetry

The linear energy absorption coefficient varies considerably for different absorber materials. Absorption of gamma rays is a function of absorber mass. Thus the gamma ray intensity within the steel vessel used for treatments of the present study must be affected by the wall thickness of the steel vessel. In order to determine the dose available to samples processed in the vessel, ferrous sulfate dosimetry was conducted. Methods described by Weiss (216), Spinks and Woods (180) as well as 0'Donnell and Sangster (147) were followed.

The technique calls for triply distilled water for dilution and preparation of dosimetry solutions. This was prepared by using distilled water which was further distilled from 2% reagent grade potassium permanganate (KMnO₄) and potassium dichromate (KCr₂O₇) solutions, followed by exposure to gamma rays for 20

-97-

Mrad. The dosimetry solution contains 0.0014 M reagent grade ferrous sulfate (FeSO₄), 0.001 M sodium chloride and 0.4 M spectro grade sulfuric acid. A pre-irradiated 2 x 7.5 cm glass test tube containing 20 ml of the prepared dosimetry solution was saturated with oxygen by bubbling oxygen through the sample for 2 min. The tube thus prepared was placed in the steel vessel and irradiated for 241 sec on October 19, 1970. Simultaneously, an aliquot dosimetry sample was irradiated outside the vessel for the same period of time. The ferric ion (Fe⁺⁺⁺) concentration formed was determined by spectrophotometry on a Unicam Sp. 800 ultraviolet spectrophotometer at 305 nm wave length. The absorbed dose (D) was calculated as follows:

$$D = \frac{0.965 \times 10^9 (A)}{edpG_{(Fe^{+++})}} rad$$

Where: A = absorbance at 305 nm e = 2204 1/mol.cm, absorptivity of ferric ion at 25°C (180) d = 1 cm, sample thickness p = 1.024 g/ml, density of dosimetry solution at 25°C $G_{(Fe}^{+++}) = 15.5 \text{ mol}/100 \text{ ev}(180)$

As for absorbance measurement, an aliquot of the non-irradiated stock solution was used as blank and the absorbance determined at room temperature $(25^{\circ}C)$.

The absorbed dose (D) calculated from the three replications

of ferrous sulfate dosimetry outside the vessel were 106.18, 105.70 and 106.65% based on the value calculated from the AECL certified value. In contrast, the absorbed dose (D) inside the vessel was 94.48, 93.66 and 92.14% of the certified value. Thus the average difference between inside and outside the vessel is 12.75%. This indicates that the steel vessel reduced the absorbed gamma ray dose by 12.75%. All further dose calculations were based on these values by taking the above losses into account where applicable.

3.8 Sample Preparation and Analysis for Experimental Gamma Radiolysis of Aqueous Sulfide Model Compound Solutions and Sulfate Black Liquors

The four major sulfides $(Na_2S, CH_3SNa, CH_3SCH_3 and CH_3SSCH_3)$ which contribute to sulfate pulp mill odor problems, have been studied at ambient Gammacell temperature $(34^{\circ}C)$ and normal oxygen pressure. The radiolysis of dimethyl sulfide and dimethyl disulfide in aqueous solution and black liquor (2-1) were also studied extensively with response to a number of obviously important variables such as solution pH, lignin concentration, temperature and oxygen pressure. In these studies, the sulfides were irradiated at concentrations closely resembling the conditions under which the compounds occur in black liquor. The experiments were designed to follow major changes in concentration with increasing doses of absorbed radiation energy.

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The model experiments were conducted on sulfides, obtained from regular chemical suppliers as described in Section 3.1.

Further to the analyses, potentiometric titration always refers to the procedure described in Section 3.3.1, the gas liquid chromatography (GLC), the modified boric acid acidification and carbon tetrachloride extraction technique as described in Section 3.3.2, and turbidimetry as described in Section 3.4.5. Modifications of these procedures will be indicated where necessary in the following sections.

3.8.1 Gamma radiolysis of aqueous sulfide model compounds

The gamma radiolysis of sulfide model compounds involves aqueous solutions of sodium sulfide (Na₂S), methyl mercaptan (CH₃SH), dimethyl sulfide (CH₃SCH₃) and dimethyl disulfide (CH₃SSCH₃).

3.8.1.1 Sodium sulfide

Sodium sulfide solutions were prepared at two pH levels (pH 12.46 and 8.38). The pH 12.46 solution was made by dissolving 10g of reagent grade Na $5.9H_20$ in one liter of distilled water. The solution at pH 8.38 was prepared by dissolving 15g Na₂S.9H₂O in one liter of distilled water. Adjustment to pH 8.38 was achieved by acidification with 0.1N hydrochloric acid. A light yellow colour was observed after acidification, indicating

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that part of the sulfide had been oxidized to elemental sulfur.

Five ml samples of the sodium sulfide solution were transferred into 10 ml test tubes through rubber septums. The samples were irradiated with an absorbed dose of 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 Mrad at Gammacell ambient temperature.

Analysis for residual sodium sulfide was made by silver nitrate potentiometric titration (Section 3.3.1) while polysulfide sulfur was determined by UV spectrophotometry (Section 3.4.4).

3.8.1.2 Sodium methyl mercaptan

Sodium methyl mercaptan solutions of pH 13.54, 12.54 and 10.70 were prepared by bubbling methyl mercaptan gas into an ice-water-cooled 2N sodium hydroxide solution. The pH of the solution was adjusted by adding 0.1N hydrochloric acid. Five ml of the cooled sodium methyl mercaptan solution were then syringed through septum to ice-water-cooled and oxygen-flushed 10 ml test tubes. The aqueous mercaptan solutions were irradiated at ambient Gammacell temperature in the closed tubes to one of 0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9, 1.5, 2.0, 2.5 and 3.0 Mrad absorbed doses.

The sodium-methyl mercaptan was analyzed by silver nitrate potentiometric titration (Section 3.3.1). Formation of dimethyl disulfide was determined for the mercaptan solution of pH 13.54

by GLC analysis. The pH of the samples was also measured.

Sulfate formation also has been found as a radiolysis product of methyl mercaptan. Ten ml of the pH 10.70 methyl mercaptan solution were syringed into an oxygen flushed 50 ml test tube and irradiated up to 4 Mrad at Gammacell temperature. The irradiated solution was further acidified to about pH 3 by adding 0.1 N hydrochloric acid, boiled for 10 min to expel the residual methyl mercaptan and filtered through a filter paper to obtain a clear solution. Three ml of 3 M barium chloride were then added whereby precipitation of sulfate was observed.

3.8.1.3 Dimethyl sulfide and dimethyl disulfide

A comparative study was made by radiolysis of dimethyl sulfide and dimethyl disulfide in alkaline solution and in a commercial sulfate black liquor (2-1).

The dimethyl sulfide alkaline solution was prepared by syringing 55 μ l dimethyl sulfide through septum to an ice-watercooled and oxygen saturated volumetric flask containing 500 ml 0.25 N sodium hydroxide solution. The same procedure was also followed for preparation of the dimethyl disulfide alkaline solution. The organic sulfide black liquor solution was prepared by dissolving 80 μ l of dimethyl sulfide and dimethyl disulfide in 500 ml of cooled, oxygen saturated black liquor (2-1) contained in a volumetric flask. The solutions thus prepared were thoroughly

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mixed by shaking and then refrigerated at -5° C for three days. The initial pH values of the solutions were 13.12 and 13.14 for the alkaline and black liquor, respectively. From these stock solutions 10 ml portions were syringed through septum to icewater-cooled and oxygen flushed 50 ml test tubes. The samples were then irradiated to 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 Mrad at ambient Gammacell temperature. Residual sulfide concentrations after irradiation were determined by the GLC method.

In order to isolate larger quantities of the products from the gamma irradiated dimethyl sulfide alkaline solution, 5 ml dimethyl sulfide dissolved in 50 ml 0.25 N sodium hydroxide solution was stirred and irradiated for 5 Mrad in a 500 ml volumetric flask. Following irradiation the solution was placed in a 60° C water bath for 4 hours to distill off the residual dimethyl sulfide. The solution was then thoroughly extracted with chloroform. The organic layer was further washed with distilled water three times. On evaporation of the excess chloroform the residue was dried in vacuum at room temperature, which provided a white amorphous substance. The infrared spectrum of the substance was obtained by dissolving the sample in small amounts of ether and applying the paste to a potassium bromide window. The infrared spectrum was run on a Perkin Elmer Model 21 double beam spectrophotometer. A sample spectrum from the product is shown in Fig. 3.19. No sulfate precipitation was observed by adding 3M barium chloride to the acidified aqueous solution (pH 3).

A similar procedure was also followed for the radiolysis of dimethyl disulfide in alkaline solution. However, the chloroform extract could not be isolated; whereas precipitation of sulfate has been observed on addition of barium chloride to the acidified, irradiated solution.

Due to the fact that aqueous dimethyl sulfide and dimethyl disulfide solutions are relatively inert to gamma radiation, variables such as solution pH, dissolved lignin content, temperature and oxygen pressure were studied. These are considered as affecting the radiolysis degradation of dimethyl sulfide and dimethyl disulfide according to the following processes.

3.8.1.3.1 Effect of pH

Due to difficulties found with black liquor, pH was studied on buffered solutions of dimethyl sulfide and dimethyl disulfide in model systems. Solutions with varying pH were prepared by mixing desired proportions of 0.1 M hydrochloric acid (HC1), potassium dihydrogen phosphate (KH_2PO_4) and sodium hydroxide (NaOH) (94).

The dimethyl sulfide solution was prepared by dissolving about

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5 μ l dimethyl sulfide in 50-60 ml oxygen saturated buffer solutions. Similarly, dimethyl disulfide solution was prepared by mixing about 8 μ l dimethyl disulfide to 50-60 ml oxygen saturated buffer solution.

From the above stock solutions 5 ml portions of ice-watercooled organic sulfide solutions were then syringed through septum to 10 ml capacity oxygen flushed test tubes. The samples were irradiated to 3 Mrad at ambient Gammacell temperature. The initial and final (after 3 Mrad irradiation) organic sulfide concentrations were determined by GLC analysis following the usual 5 x 10 ml carbon tetrachloride extraction. No change was found in the pH of the buffer solution after 3 Mrad gamma-radiation.

3.8.1.3.2 Effect of dissolved lignin

Concentration of dissolved thiolignin could not be effectively controlled in black liquor without dilution or condensation. Thus, by necessity, the effect of dissolved thiolignin was best studied again on aqueous solutions of dimethyl sulfide and dimethyl disulfide.

Five hundred m1 aliquot samples of $165.0 \times 10^{-3} \text{g/l}$ dimethyl sulfide and $190.0 \times 10^{-3} \text{g/l}$ dimethyl disulfide solutions were prepared in 0.25 N sodium hydroxide. The sodium hydroxide solutions were saturated with molecular oxygen at ice-water

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temperature. The solutions thus obtained were mixed thoroughly and stored in a freezer (5° C) for three days. To 5 ml portions of these stock solutions various quantities of thiolignin (Section 3.7.4) were added to provide a concentration range of 10-120 g/l by weighing the appropriate amount of thiolignin into 10 ml test tubes. Then, 5 ml of ice-water-cooled organic sulfides, containing the alkaline solution, was syringed through a septum to the test tubes. The mixture was shaken thoroughly until the thiolignin was dissolved, and kept in the freezer (5° C) for two days. The samples were then irradiated to 1.5 and 3.0 Mrad.

The residual dimethyl sulfide and dimethyl disulfide concentrations were estimated by GLC following 5 x 10 ml carbon tetrachloride extraction. The pH of the 3 Mrad irradiated solutions was also measured.

3.8.1.3.3 High temperature and high pressure

A portion (30 ml) of cooled black liquor (1-3, 2-1) samples was introduced into a pre-cooled and oxygen flushed stainless steel pressure vessel $(3.5 \times 8.7 \text{ cm},$ wall thickness. 0.7 cm) through a rubber septum which could be inserted into the vessel outlet. This was designed for transfering samples in/out of the vessel by a syringe.

The high pressure and temperature apparatus used in the

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present studies is shown in Fig. 3.20. Gas connections were 316 stainless steel 1/8-in diameter tubing joined by Swedge-Lock connectors. Temperature control was achieved by a calibrated power regulator. Automatic temperature records were obtained with the aid of thermocouples (iron-constantan) and strip-chart recorder.

Irradiation of samples thus prepared was done in the Gammacell at a nominal dose rate of 1.26×10^6 rad/hr (March 26, 1968). A proper dose correction factor for the steel pressure vessel has been applied as determined by Fricke dosimetry (Section 3.7.2).

Irradiation temperatures of black liquor samples were controlled by a heating mantle and power regulator. The relation between setting and temperature is shown in Fig. 3.21.

Five hundred milliliters of the organosulfide enriched black liquor (1-3) and carbonated black liquor (2-1) samples contained . in a septumed volumetric flask were thoroughly shaken and stored in the freezer (5° C) for three days. From the stock solution, 30 ml of the cooled black liquor was syringed into an ice-water-cooled and oxygen flushed steel pressure vessel and placed under 50 psi oxygen pressure. The solution was stirred magnetically for a period of 10 min. The closed vessel was then irradiated to a total of 3 Mrad dose at heating mantle power regulator settings of 20, 25, 30, 40 and 45 (50 to 120° C).

The effect of oxygen pressure (between 25 to 100 psi) on the radiolytic degradation of dimethyl sulfide and dimethyl disulfide in black liquor (2-1) and carbonated black liquor (2-1) portions was also studied at ambient Gammacell temperature (34°C).

The control samples were prepared by the same procedure except without gamma irradiation.

After irradiation, the vessel was removed from the Gammacell chamber and cooled to -5° C overnight. The excess pressure was then released while the sample was frozen within the container. The sample was further stored in the vessel and allowed to thaw in ice-water. The solution was sampled with a 10 ml syringe for further analyses by GLC.

3.8.2 Gamma radiolysis of sulfate and polysulfide black liquors

Two 120 ml open glass beakers containing 80 ml black liquor (3-1) were irradiated at ambient Gammacell temperature (34° C) to 0, 0.06, 0.12, 0.24, 0.37, 0.49, 0.61, 0.92, 1.22, 1.52, 1.83, 2.13 and 2.44 Mrad. The solution was periodically sampled for analysis by potentiometric titration of monosulfide and polysulfide. Four ml of the black liquor sample were periodically withdrawn by a pipette for silver nitrate potentiometric titration.

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The consumption of 0.05 N silver nitrate at inflection "a" and "b" was taken to correspond to the monosulfide and polysulfide species, respectively.

In another series of experiments, the effects of gamma radiation on dimethyl sulfide, dimethyl disulfide and the unidentified sulfur compound (X) in the various sulfate and polysulfide black liquors were studied. Ten ml of the icewater-cooled black liquor were syringed into oxygen flushed and cooled $(0^{\circ}C)$ 50 ml test tubes which were equipped with rubber septums. The samples were then irradiated in the Gammacell for 0, 1.0, 2.0, 3.0, 4.0 and 5.0 Mrad, then chilled in ice water. In the meantime the control samples (0 Mrad) were conditioned in a $34 \pm 0.5^{\circ}C$ water bath. The organosulfides were determined by 5 x 5 ml carbon tetrachloride extraction followed by GLC analysis (Fig 3.9). The quantity of the unidentified sulfur compound (X) was estimated from dimethyl sulfide calibration curve (Fig 3.9).

3.8.3 Gamma radiolysis of carbonated sulfate and polysulfide black liquors

The various sulfate and polysulfide black liquors were carbonated by saturation with carbon dioxide. From these stock solutions 10 ml samples were syringed into oxygen flushed and ice-water-cooled 50 ml test tubes. Radiation doses of 0, 1.0,

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2.0, 3.0, 4.0 and 5.0 Mrad were used. Following irradiation, the samples were immediately chilled in ice-water. Similarly, the control samples (0 Mrad) were conditioned in a $34 \pm 0.5^{\circ}$ C water bath.

The sulfides were analysed by injecting 5 ml of the appropriate sample into a 25 ml septumed volumetric flask containing 20 ml carbon tetrachloride and appropriate quantity of boric acid (1.0 g) acidifies the carbonated sample to pH 6.5. The sulfides such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide and the unidentified sulfur compound (X) were determined directly by GLC by comparing the detector response plotted in the calibration curves (Fig. 3.8). The unidentified sulfur compound (X) was also estimated from the calibration curve of dimethyl sulfide (Fig. 3.8).

3.8.4 Effect of oxygen, air and nitrogen atmosphere on gamma radiolysis of sulfides in the carbonated black liquors

A 500 ml carbon-dioxide-acidified black liquor (1-1) was prepared in a septum sealed volumetric flask. The solution was further enriched with sulfides by bubbling hydrogen sulfide, methyl mercaptan, and adding 100 μ l dimethyl sulfide and 150 μ l dimethyl disulfide to the solution. The solution thus obtained was shaken vigorously and stored in a freezer (5°C) for

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three days.

Ice-water-cooled 50 ml test tubes were flushed with oxygen, air or nitrogen, as required for various experiments, and sealed with rubber septums. Ten ml of the acidified black liquor was syringed to each test tube. The samples were then homogenized and irradiated at Gammacell temperature to 0, 0.5, 1.0, 2.0 and 3.0 Mrad. The control samples (0 Mrad) were also prepared by the same procedure and conditioned in a water bath held at $34 \pm 0.5^{\circ}$ C. After the treatment, control and gamma irradiated samples were cooled in ice-water and stored in a -5° C freezer for four hours. Five ml portions of the cooled solution were syringed to 50 ml septumed volumetric flasks containing 45 ml carbon tetrachloride and an appropriate amount of boric acid (1.0 g) to reduce the solution pH from 7.5 to 6.5. The sulfides were then analyzed quantitatively by GLC.

3.9 Regeneration of Polysulfide from Sodium Sulfide and Green Liquor

During the course of these investigations it was discovered through chemical analysis that irradiated sodium sulfide solutions contained substantial amounts of polysulfide. This indicated that increased stability of aqueous sodium sulfide solutions is attained not only through an oxidation of sulfide toward higher valence states of sulfur (SO_{h}^{--}) , but also through formation of polysulfide. This phenomenon may provide a new opportunity for industrial manufacture or regeneration of polysulfide.

Experiments were conducted in a 50 ml stainless steel vessel (3.5 x 15 cm, wall thickness 0.7 cm). A proper dose correction factor has been determined for the vessel by ferrous sulfate dosimetry (Section 3.7.2). Forty ml of various concentrations of aqueous sodium sulfide and a pulp mill green liquor (1-2) were placed in the vessel and irradiated at Gammacell temperature up to 70 Mrad. The irradiation apparatus was similar to that depicted in Fig. 3.20. An air pressure driven magnetic stirrer was used for mixing of the sulfide solution and carbon dioxide or hydrogen sulfide gas.

After irradiation, the excess gas pressure was relieved and one gram of sodium hydroxide was added to stabilize the residual hydrogen sulfide.

The polysulfide excess sulfur was determined by ultraviolet spectrophotometry as described in Section 3.4.4. The formation of sulfate was measured as turbidity produced by treatment of the solution with barium chloride (Section 3.4.5).

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4.0 RESULTS

4.1 Gas Liquid Chromatography (GLC) Calibration Curves for Sulfides

The calibration curves for hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, generally found in acidified black liquor, are shown in Fig. 3.8, whereas the calibration curves presented in Fig. 3.9 were prepared for dimethyl sulfide and dimethyl disulfide as obtained by liquid/liquid extraction with carbon tetrachloride from unacidified black liquor (2-1).

4.2 Black Liquor Characteristics

A limited number of sulfate black liquor characteristics, such as pH, solids, density, lignin content and various sulfides have been determined. The results are given in Table 4.1.

4.3 Irradiation of Aqueous Sulfide Model Compounds

The degradation of sulfides induced by gamma radiation, was studied on sodium sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide as model compounds. The effects of such variables as solution pH, lignin concentration, temperature and oxygen pressure were investigated.

4.3.1 Sodium sulfate

The gamma radiolysis of aqueous sulfide solutions

of pH 12.46 and 8.38 were studied. Degradation of sodium sulfide is exponential with dose. Changes in sodium sulfide concentration and formation of polysulfide excess sulfur are shown in Table 4.2 and Fig. 4.1.

The yields of sulfide degradation $(G(-Na_2^S))$ and formation of polysulfide excess sulfur (G(S)) are determined with the aid of initial slopes of curves found in Fig. 4.1. The relationship between sulfide solution pH and $G(-Na_2^S)$ and G(S) are shown in Table 4.3.

The solution pH greatly affected the degradation yield of sulfides and yield of polysulfide excess sulfur. The sodium sulfide degradation yields ($G(-Na_2S)$) increase from 5.0 to 7.5, when solution pH is decreased from 12.46 to 8.38. Meanwhile, the yields of polysulfide excess sulfur (G(S)) increased from 0.1 to 1.1 when the solution pH was decreased from 12.46 to 8.38 (Table 4.3).

4.3.2 Sodium methyl mercaptan

Gamma radiolysis of methyl mercaptan in aqueous solutions of pH 13.54, 12.54 and 10.70 was studied. The mercaptan degradation as induced by gamma radiation, the observed pH changes and formation of dimethyl disulfide from mercaptan solution of pH 13.54 are shown in Table 4.4 and Fig. 4.2. The apparent methyl mercaptan degradation yields (G(-CH₃SNa)) were calculated from the initial slopes of curves in Fig. 4.2 and are given in Table 4.3.

The exponential plot of mercaptan degradation rate (slope) obviously increases as the initial solution pH is decreased from 13.54 to 12.54 and 10.70 (Fig. 4.2). Similarly, values of mercaptan degradation yields are greatly affected by solution pH; G(-CH SNa)) of 2.5, 11.3 and 15.4 correspond to solution pH 13.54, 12.54 and 10.70 (Table 4.3).

Two products, dimethyl disulfide (Fig. 4.2) and sulfate, were discovered in irradiated aqueous methyl mercaptan solutions. The actual quantity of sulfate was not determined.

4.3.3 Dimethyl sulfide and dimethyl disulfide

The results of gamma radiolysis of dimethyl sulfide and dimethyl disulfide in a selected black liquor (2-1, pH 13.14) and alkaline solution (pH 13.12), are presented in Fig. 4.3. Numerical values and respective pH changes are shown in Tables 4.5 and 4.6. The apparent degradation yields of dimethyl sulfide $(G(-CH_3 SCH_3))$ and dimethyl disulfide $(G(-CH_3 SSCH_3))$, calculated from the initial slopes of curves found in Fig. 4.3, are tabulated in Table 4.7.

The results indicate that radiolytic degradation of dimethyl sulfide and dimethyl disulfide in black liquor as well as in alkaline solution is exponential with dose. Degradation yields were significantly higher in aqueous alkaline solution than in black liquor. As shown in Table 4.7, the corresponding degradation yields of dimethyl sulfide and dimethyl disulfide were 0.73, 0.89 for aqueous alkaline solution, and only 0.50, 0.43 for black liquor, i.e., a definite protective effect in black liquor is observed.

The experiment also indicates that up to 4.5 Mrad dose the pH of black liquor is only slightly affected by the gamma radiation treatment (Table 4.6).

Sulfate has been found to be a product of gamma radiolysis of dimethyl disulfide aqueous solution but the concentration is too low to be determined quantitatively by the usual wet chemistry (barium salt gravimetric) method. On the other hand, sulfate could not be detected in irradiated dimethyl sulfide solutions, however, an unidentified amorphous carbonyl group containing substance was detected and analysed by infrared spectrum reproduced in Fig. 3.19.

The effect of solution pH, lignin concentration, temperature and oxygen pressure on the degradation yields of dimethyl sulfide and dimethyl disulfide were studied in some detail as indicated in the following series.

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4.3.3.1 Effect of solution pH

The relation of solution pH versus percentage decomposition of sulfides, degradation yields (G), and degradation yield to initial concentration (mole) ratio (G/Co) are shown in Table 4.8 as well as Figs. 4.4 and 4.5.

The results show a high correlation of solution pH on degradation of dimethyl sulfide and dimethyl disulfide as induced by gamma radiation. The per cent degraded dimethyl sulfide (91.2 to 44.0%) decreased linearly as solution pH was increased from acid (pH 0.5) to strong base (pH 13.5). Similarly, the degradation percentage of dimethyl disulfide (82.3 to 65.0%) decreased almost linearly as solution pH was increased from pH 1.5 to 10.1, then it slightly increased from 70.3 to 73.8% as the pH was further increased from pH 11.5 to 13.0.

The degradation yield of dimethyl sulfide $(G(-CH_{3}CH_{3}))$ decreased linearly from 0.43 to 0.17 as the solution pH was increased from strong acid (pH 0.5) to strong base (pH 13.5). While the degradation yields of dimethyl disulfide $(G(-CH_{3}SSCH_{3}))$ increased slightly from 0.47 to 0.50 when solution pH was increased from 1.5 to 5.5, the yield decreased from 0.48 to 0.36 when the solution pH was increased from 5.5 to 10.1. Again, the yield increased slightly from 0.36 to 0.39 as solution pH was increased from 10.1 to 13.5. Since initial concentrations of dimethyl sulfide and/or dimethyl disulfide were varied in the samples having various solution pH(Table 4.8), it would be more logical to compare the respective degradation rates by yields to initial sulfide concentrations (G/Co). As shown in Fig. 4.5, dimethyl sulfide G/Co also decreases linearly as the solution pH is changed from strong acid to strong base, whereas G/Co of dimethyl disulfide is decreased almost linearly from strong acid to pH 10.1 and G/Co then slightly increases from pH 10.1 to 13.5.

4.3.3.2 Effect of lignin concentration

The relationship of lignin concentration to percentage decomposition, and degradation yields (G) of dimethyl sulfide and dimethyl disulfide following irradiation between 1.5 to 3.0 Mrad are shown in Table 4.9 and Fig. 4.6. The results reveal that the presence of lignin (thiolignin) affects the radiation degradation of the organosulfides in diverse ways. The lignin in solution may gradually inhibit radiation degradation of the organosulfides as lignin concentration increases progressively up to about 50 g/1. On further increase of the lignin concentration from 50 to 120 g/1, the percentage of sulfide decomposition increases slightly for both 1.5 and 3.0 Mrad dose. Similarly, the average degradation yield (G) of dimethyl sulfide and dimethyl disulfide decreased obviously from 0.53 to 0.34, as lignin

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concentration was gradually increased from 0 to 50 g/1, thereafter on further increase of lignin concentration (50 to 120 g/1) the degradation yield increases only slightly.

4.3.3.3 Effect of temperature

Black liquor (1-3) and carbonated black liquor (2-1) enriched with dimethyl sulfide and dimethyl disulfide were irradiated for 3 Mrad under 50 psi initial oxygen pressure between 60 to 115°C.

The effect of solution temperature on decomposition rate of dimethyl sulfide and dimethyl disulfide, degradatiom yields (G), and relation of sulfide degradation, the change of black liquor pH of gamma irradiated and control (without irradiation) samples was compared in Tables 4.10 and 4.11 as well as Figs. 4.7 and 4.8.

The results indicate a significant effect of temperature on degradation rate of organosulfides, in both irradiated and control black liquors, as well as carbonated black liquor samples. However, the temperature did not confound the effect of radiation as the rate of organosulfide degradation of the irradiated liquors was considerably faster than that observed on the control samples.

The percentage of dimethyl sulfide and dimethyl disulfide decomposition in black liquor (1-3) under 50 psi initial oxygen pressure, following administration of 3 Mrad (305 min) radiation dose, shows that increasing the temperature from 60 to 115° C significantly increased the decomposition rate of dimethyl sulfide from 52.88 to 77.45% for the gamma radiation treatment and by the same relative amount of 34.79 to 56.25% for the control samples. Concurrently, dimethyl disulfide decomposition increased from 71.98 to 100% for the irradiated samples and only from 56.79 to 83.27% for the control samples. Similarly, dimethyl sulfide degradation yield (G(-CH₃SCH₃)) increases linearly from 0.44 to 0.64 as the temperature was increased from 60 to 115°C. The dimethyl disulfide degradation yield (G(-CH₃SSCH₃)) also increased linearly from 0.34 to 0.46 with increase in temperature from 60 to 83°C (Table 4.10).

Dimethyl sulfide and dimethyl disulfide in carbonated black liquor under 50 psi initial oxygen pressure, irradiated with a 3 Mrad (297 min) dose, also shows that an increase of temperature from 77 to 115° C greatly increases dimethyl sulfide decomposition percentage from 59.24 to 87.68% for the gamma radiation treatment and only 33.86 to 59.22% for control samples. With the same temperature changes, dimethyl disulfide decomposition percentage increased from 53.82 to 97.79% for the irradiated samples and only 36.17 to 78.86% for control samples. Similarly, the dimethyl sulfide degradation yield (G(-CH₃SCH₃)) increases linearly from 0.17 to 0.25 and dimethyl disulfide degradation yield $(G(-CH_3SSCH_3))$ increases from 0.18 to 0.34, when the maximum temperature was increased from 77 to $115^{\circ}C$ (Table 4.11).

Black liquor (3-1) pH is considerably decreased by irradiation at elevated temperature. On the irradiated samples (3 Mrad) pH decreased from 12.51 to only 11.42, when the maximum temperature was increased from 60 to 115°C and samples were kept under 50 psi initial oxygen pressure (Table 4.10). This indicates that gamma irradiation significantly lowers the black liquor pH when it is irradiated at higher temperature. On the other hand, the carbonated black liquor pH was little affected by gamma irradiation under the temperature range (Table 4.11).

4.3.3.4 Effect of oxygen pressure

Dimethyl sulfide and dimethyl disulfide in black liquor (2-1) and carbonated black liquor (2-1) were irradiated for 3 Mrad at Gammacell temperature $(34^{\circ}C)$ under various oxygen pressures (25-100 psi). The effect of oxygen pressure on decomposition percentage of dimethyl sulfide and dimethyl disulfide, degradation yields (G), and comparisons of sulfide degradation between irradiated and control samples, are tabulated in Tables 4.12 and 3.13 and presented graphically in Figs.4.9 and 4.10.

The results reveal that degradation of organosulfides in both

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black liquor and carbonated black liquor increases obviously as oxygen pressure is increased. In contrast, the degradation of organosulfides, as induced by gamma radiation, is usually considerably higher than that obtained with comparable control samples.

Decomposition percentage of dimethyl sulfide in black liquor (2-1), at ambient Gammacell temperature following 3 Mrad (297 min) dose, shows that variation of oxygen pressure from 25 to 100 psi increased the degradation linearly from 66.16 to 87.67% for gamma irradiated samples, and only from 29.33 to 57.41% for the comparable control black liquor. The rate of dimethyl disulfide decomposition increased from 46.72 to 77.87% for irradiated black liquor samples and only from 30.22 to 42.08% for the comparable control samples when the oxygen pressure was increased from 25 to 100 psi. Similarly, the apparent degradation yield (G(-CH₃SCH₃)) of dimethyl sulfide nearly doubled (0.16 to 0.31) and the apparent degradation yield of dimethyl disulfide also increased from 0.08 to 0.14, when the oxygen pressure was increased from 25 to 100 psi (Table 4.12).

The decomposition percentage of dimethyl sulfide and dimethyl disulfide in irradiated carbonated black liquor (2-1) was also investigated under 25 to 100 psi oxygen pressure. For irradiated dimethyl sulfide samples the decomposition percentage increased

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from 66.16 to 87.67% and only 29.33 to 57.41% for the comparable control samples. The decomposition percentage of dimethyl disulfide increased from 46.72 to 77.87% and 30.22 to 57.03% for gamma irradiated and comparable control samples, respectively, when the oxygen pressure was increased from 25 to 100 psi. Similarly, the calculated degradation yield of dimethyl sulfide $(G(-CH_3SCH_3))$ increased from 0.21 to 0.28 and 0.16 to 0.26 for dimethyl disulfide as the oxygen pressure was increased from 25 to 100 psi. These yields are definitely modest considering the substantially excess quantity of available oxygen.

4.4 Gamma Radiolysis of Sulfate and Polysulfide Black Liquor (pH 12.85-13.40)

Black liquor (3-1) was irradiated at Gammacell ambient temperature. Four ml samples were periodically withdrawn and analysed for monosulfide (S^{--}) and polysulfide $(S_{n}S^{--})$ by silver nitrate potentiometric titration. The consumption of 0.05N silver nitrate for monosulfide (-430 mv) decreased to almost zero and polysulfide (-250 mv) gradually increased to attain maximum when the black liquor was irradiated to about 1 Mrad. Further irradiation is expected to induce polysulfide degradation (Table 4.14 and Fig 4.11) due to possible competing reactions in the mixture.

The pH of the black liquor was found to be little affected by

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gamma radiation up to 2.44 Mrad (Table 4.14).

Gamma radiation induced degradation of dimethyl sulfide, dimethyl disulfide and the unidentified sulfur compound (X) in various black liquors is shown in Tables 4.15, 4.16 and 4.17 as well as in Figs. 4.12, 4.13 and 4.14, respectively. The degradation of dimethyl sulfide (Fig. 4.12) and dimethyl disulfide (Fig. 4.13) are also exponential with dose.

Apparent degradation yields of dimethyl sulfide $(G(-CH_3SCH_3))$ and dimethyl disulfide $(G(-CH_3SCH_3))$ of the various black liquors were calculated from the initial slopes of respective sulfide degradation curves as shown in Figs. 4.12 and 4.13. The results are also shown in Table 4.18. Due to the low concentration of dimethyl sulfide and dimethyl disulfide in process black liquors (Table 4.1), the sulfide degradation yields are considered to be greatly affected by their initial concentration. The plotting of dimethyl sulfide and dimethyl disulfide degradation yield (Tables 4.5, 4.6 and 4.18) <u>vs</u>. initial organosulfide(concentrations (Tables 4.1, 4.5 and 4.6) are shown graphically in Figs. 4.15 and 4.16 for dimethyl sulfide and dimethyl disulfide, respectively.

The results show that the degradation of dimethyl sulfide and dimethyl disulfide in black liquors was exponential with dose (\hat{E} igs. 4.12 and 4.13). The gamma radiation degradation yields of dimethyl sulfide (G(-CH_SCH_3)) and dimethyl disulfide (G(-CH_3SSCH_3))
in black liquor are very low and range from 0.001 to 0.003 for dimethyl sulfide and 0.002 to 0.085 for dimethyl disulfide (Table 4.18). As shown in Figs. 4.15 and 4.16, the apparent degradation yields correlate strongly with the initial concentration of organosulfides. Dimethyl sulfide degradation yields increased considerably from 0.002 to 0.56 when its initial concentration in black liquor (2-1) was increased from 0.56 x 10^{-3} to 171.8 x $10^{-3}g/1$ (Fig. 4.15). Similarly, dimethyl disulfide degradation yield (0.045 to 0.885) in black liquor (2-1) greatly increased as the concentration was boosted from 17.08 x 10^{-3} to 207.5 x $10^{-3}g/1$ (Fig. 4.15).

4.5 Gamma Radiolysis of Carbonate Sulfate and Polysulfide Black Liquors (pH 8.20-915)

The extent of radiolytic degradation of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide and of the unidentified sulfur compound (X) is shown in Tables 4.19, 4.20, 4.21, 4.22 and 4.23 as well as in Figs. 4.17, 4.18, 4.19, 4.20 and 4.21. The exponential degradation patterns of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide were further plotted in Figs. 4.17, 4.18, 4.19 and 4.20, respectively.

Apparent degradation yields given in Figs. 4.17, 4.18, 4.19 and 4.20 of hydrogen sulfide (G(-H₂S), methyl mercaptan (G(-CH₃SH)), dimethyl sulfide (G(-CH₃SCH₃)) and dimethyl disulfide (G(-CH₃SSCH₃)) in various carbonated black liquors, were calculated from the initial slopes of the respective sulfide degradation curves. The degradation yields of the sulfides are further shown in Table 4.24.

The results indicate that the degradation of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide in the carbonated black liquors was exponential with dose (Figs. 4.17, 4.18, 4.19 and 4.20).

The initial concentration of sulfides in the carbonated black liquor varied according to different sources. The sulfide degradation yields (Table 4.24) were also plotted against the initial concentration of sulfides in the respective liquors from Tables 4.19, 4.20, 4.21 and 4.22. The correlations of sulfide degradation yields and their initial concentration are shown in Figs. 4.22, 4.23, 4.24 and 4.25 for hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, respectively.

The sulfide degradation yield varies with sulfide species and highly correlates with its initial concentration existing in the carbonated black liquor. Hydrogen sulfide degradation yields $(G(-H_2S))$, as shown in Fig. 4.22, increased linearly from 0.015(1-2) to 3.427(4-1L) when the initial concentrations were increased from 0.89 x 10⁻³ to 265 x 10⁻³g/1. Methyl mercaptan degradation yields $(G(-CH_3SH))$ increased similarly from 0.006(4-2v) to 0.230(1-3) when

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the initial concentration was increased from 0.48 x 10^{-3} to 28.70 x $10^{-3}g/1$ (Fig. 4.23). The dimethyl sulfide degradation yield (G(-CH₃SCH₃)) showed a linear relationship with increasing yield from 0.003(1-4) to 0.020(1-2) when the initial concentration was increased from 0.60 x 10^{-3} to 5.22 x $10^{-3}g/1$ (Fig 4.26). Similarly, dimethyl disulfide degradation yield (G(-CH₃SSCH₃)) increased linearly from 0.004(1-2) to 0.035(2-1) as its initial concentration was increased from 1.03 x 10^{-3} to 9.11 x 10^{-3} g/1 (Fig. 4.25).

4.6 Effect of Nitrogen, Air and Oxygen Atmospheres on Gamma Radiolysis of Sulfides in Carbonated Black Liquor (pH 7.50)

The carbonated black liquor (1-1) enriched with hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide was irradiated in nitrogen, air or oxygen atmosphere. The comparative effects of nitrogen, air and oxygen atmospheres on gamma radiation degradation of the sulfides are shown in Table 4.25 as well as Figs. 4.26, 4.27 and 4.28. The exponential degradation patterns of hydrogen sulfide, dimethyl sulfide and methyl mercaptan are also plotted in Figs. 4.26, 4.27 and 4.28, respectively.

The apparent degradation yields of H_2S , CH_3SCH_3 and CH_3SH_3 in nitrogen, air and oxygen were calculated from the initial slope of respective sulfide degradation curves as found in Figs. 4.26, 4.27 and 4.28. The comparison of nitrogen, air and oxygen on degradation yield of hydrogen sulfide, methyl mercaptan and dimethyl sulfide is shown in Table 4.26. In this case, dimethyl disulfide is either degraded by gamma radiation or generated by radiolysis of methyl mercaptan. The degradation of methyl mercaptan and dimethyl sulfide in nitrogen, air and oxygen is graphically presented in Fig. 4.28.

There are indications that the degradation of hydrogen sulfide, dimethyl sulfide and methyl mercaptan is also exponential with dose in nitrogen, air and oxygen atmospheres. As shown in Table 4.26, the sulfide degradation yields in nitrogen, air and oxygen atmospheres are correspondingly 8.5, 9.7 and 16.7 for hydrogen sulfide, 10.2, 18.5 and 28.0 for methyl mercaptan, and 0.19, 0.43 and 0.74 for dimethyl sulfide. The degradation of dimethyl disulfide as shown in Fig. 4.28 is greatly affected by the presence of nitrogen, air and oxygen in carbonated black liquor; air and oxygen have the greatest effect on the degradation rate of dimethyl disulfide.

In the presence of oxygen in carbonated black liquor, the high degradation yields of hydrogen sulfide (16.7) and methyl mercaptan (28.0) indicate that the degradation reactions of the sulfides, induced by gamma radiation, created chain reactions.

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4.7 Regeneration of Polysulfide by Gamma Radiolysis of Sodium Sulfide Solution

A preliminary test shows that only insignificant amounts of polysulfide are formed by direct radiolysis of sodium sulfide solutions and green liquor (at pH above 12). However, if the solutions are acidified by carbon dioxide or hydrogen sulfide, the polysulfide yield greatly increases.

The formation of polysulfide excess sulfur and sulfate by gamma radiolysis of sodium sulfide solutions and green liquor (1-2)under 120 psi carbon dioxide or 270 psi hydrogen sulfide pressure is shown in Table 4.27. The apparent yields of polysulfide excess sulfur (G(S)) ranged from 1.47 to 2.96 for carbonated sodium sulfide solution; and 3.06 to 4.92 for hydrogen sulfide acidified aqueous sodium sulfide solutions and green liquor. The apparent yields of sulfate (G(H SO₂)) are relatively modest, from 0.16 to 0.40 for the carbonated sulfide solutions and only 0.03 to 0.08 for the hydrogen sulfide acidified sulfide solution. This shows that the yield of polysulfide excess sulfur is much higher than the yield of sulfate formation.

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5.0 DISCUSSION

5.1 Analysis of Total Sulfides in Sulfate Pulping Liquors

The mechanisms of formation and available analytical techniques of malodorous sulfides have been described at length by Sarkanen <u>et al</u>. (169), Douglass and Price (55), and McKean <u>et al</u>. (128). The main steps in these reactions leading to the various sulfides can be summarized as shown in Fig. 5.1.

In this work, an unidentified sulfur compound (X) present in substantial quantities in both natural black liquor and acidified black liquor was shown by carbon tetrachloride liquid/liquid extraction and GLC analysis. The presence of this unknown (X) has not been reported in the literature. It is believed that it is not an artifact of storage and analysis. This statement is based on the observation that if fresh black liquor was stripped with nitrogen gas, GLC analysis of the collected gas also showed the presence of the unknown (X) in the gas phase. The few tests indicated that the unknown compound (X) contains no ionizable hydrogen. Its retention time in GLC is very close to that of dimethyl sulfide (Fig. 3.12), thus it should be a volatile organic sulfur compound with a boiling point slightly higher than that of dimethyl sulfide. Exact identification of the unknown (X) was not accomplished.

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Organic polysulfides in black liquor may be largely formed by reaction of the mercaptide ion with elemental sulfur. A possible scheme may be proposed as (102):

 $CH_3S^7 + S \longrightarrow CH_3SS^7 \dots /5-1/$ This reaction is also indicated by experiments in which methyl mercaptan was added to black liquor and white liquor at room temperature. Analysis followed by silver nitrate potentiometric titration in which the inflection point "b" in the titration curves was resolved to be due to the presence of organic polysulfide (Fig. 3-2).

Another, possibly new reaction was also observed by stirring dimethyl disulfide in 1 N NaOH solution at room temperature, whereby alkaline hydrolysis of the sulfide leads to the disulfide ion:

 CH_3SSCH_3 + $OH^- \rightarrow CH_3SS^-$ + $CH_3OH \dots /5-2/$ This reaction has been demonstrated by potentiometric titration (Fig. 3.6) and was discussed at length in Section 3.3. However, in alkaline hydrolysis of dimethyl disulfide, the formation of methyl mercaptan can not be observed from Fig. 3.6. This seems to be in agreement with findings of Murray and Rayner (141) in that dimethyl disulfide is not hydrolyzed to mercaptan by treatment with 0.1 N NaOH at room temperature, but that mercaptide is formed only at $100^{\circ}C$ under nitrogen.

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Considerable difficulties were met during these investigations with respect to selection of suitable techniques which would provide means of assessment of total sulfides and adequate sensitivity needed for the description of intricate valence changes in sulfide energetics taking place in irradiated black liquors. To this end no single technique was available in the literature which could account for all the sulfides in black liquor.

For the purpose of this study, analysis of sulfides in unacidified black liquor was followed by silver nitrate potentiometric titration for hydrogen sulfide (inflection point "a") and organic polysulfide and inorganic polysulfide (inflection point "b") as discussed in Section 3.3.

A technique of corrected interpretation of the potentiometric titration curve was developed quite independently from other researchers whose findings appeared just recently in the literature (142, 151).

The results herein indicate that during the potentiometric titration of six sulfate and two polysulfide black liquors (Fig. 3.1) obviously two inflection points (a and b) appear as sulfide end points. According to the older convention, inflection point "b" is taken as end point for sulfide and no existence of mercaptan was assumed. The difference of readings between points "a" and "b"

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can be up to 112% but is, on the average, between 10 to 20% (Table 3.2). The validity of these observations was checked with aqueous alkaline model solutions (Section 3.3.1.4). The results clearly indicate that both the model solutions and white liquor give similar titration curves as black liquor. It is also indicated that the inflection point "b" is caused by the presence of the mercaptide ion in that one mole of found mercaptan is precipitated by an equal quantity of silver nitrate, as shown by the calculations in Eq. /3.14/.

Although discrepancy originating from using inflection "b" for calculating the sulfide content in aqueous solutions was reported by Felicetta et al. (67), recently published figures by Murray et al. (142) and Papp (151) support the above observations. Data obtained on model solutions and tabulated in Table 3.4 now clearly indicate the correctness of this procedure. It should be pointed out that most of the mercaptide ion in black liquor is converted to organopolysulfide (CH₂S5⁻) by reaction with elemental sulfur as shown in Eq. /3.12/. The addition of elemental sulfur to sodium sulfide solution formed polysulfide which also developed an inflection point "b" by silver nitrate potentiometric titration as discussed in Section 3.3.1.1.3.2. This further supports the observation that the inflection point "b" in the black liquor titration curve is due to the presence of organic and inorganic polysulfides in the solution rather than to the mono-sulfide ion.

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For the unionizable organosulfides such as dimethyl sulfide, dimethyl disulfide and the unidentified sulfur compound (X), the technique of carbon tetrachloride liquid/liquid extraction and GLC were adapted. Further, it was found that methyl mercaptan could also be determined by low temperature acidification of black liquor, with excess of boric acid suspended in carbon tetrachloride solution and followed by GLC analysis(Section 3.3.2). In carbonated black liquor samples the total sulfides (H_2S , CH_3SH , CH_3SCH , CH_3SCH_3 and X) were directly determined by the low temperature boric acid acidification and quantitative liquid/liquid extraction of the sulfides with carbon tetrachloride followed by GLC analysis (Section 3.6).

Liquid/liquid extraction with carbon tetrachloride of dimethyl sulfide, and dimethyl disulfide from unacidified black liquor, has been found to have quite acceptable efficiency and recovery rates (80-90%) depending on the type of organosulfide involved (Section 3.3.2.1.3.1). On carbonated black liquor, the extraction efficiency was further improved up to 3-7% by boric acid treatment (Table 3.11).

The concentration of methyl mercaptan in unacidified black liquor (Table 4.1), as well as that of hydrogen sulfide and methyl mercaptan in carbonated black liquor (Tables 4.19 and 4.20), were found to be too low to respond to silver nitrate potentiometric

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titration (Section 3.3.1). However, the carbon tetrachloride liquid/liquid extraction procedure was found convenient and accurate enough for interpretation of the sulfide energetics even at these low concentrations.

Although the efficiency of hydrogen sulfide and methyl mercaptan carbon tetrachloride liquid/liquid extraction was not determined due to technique difficulties, the method is considered to be reasonably quantitative when the high respective solubility of hydrogen sulfide and methyl mercaptan in carbon tetrachloride solution are considered. As discussed previously (Section 3.6), the solubility of hydrogen sulfide is 41.9 g/1 in carbon tetrachloride and only 3.8 g/1 in water at 20° C and 1 atmosphere; whereas the solubility of methyl mercaptan in carbon tetrachloride is very high (no data available), and it is only slightly soluble in water (12). Thereby, most of the sulfides should be easily transferred into the carbon tetrachloride phase on liquid/liquid extraction.

It was felt that methods suggested earlier for liberation (62, 146), stripping (55, 160, 185) and extraction (12, 125) were either too technical or largely inadequate for the purposes of this investigation. Although the method finally adopted could never duplicate the efficiencies (98%) of the Andersson and Bergström (12) technique, it was far superior to the method suggested by Douglass and Price (55) and McKean <u>et al.</u> (127) in both

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efficiency and reproducibility. The great sensitivity of the flame photometric detector (FPD) operated in conjunction with the MT-150 gas chromatograph contributed greatly to the success of this analytical techniques.

5.2 Gamma Radiolysis of Sulfides in Aqueous Solution and Sulfate Black Liquor

In order to study the degradation of sulfides in black liquor, sulfide model compounds such as sodium sulfide (Na_2S) , sodium methyl mercaptan (CH₃SNa), dimethyl sulfide (CH₃SCH₃) and dimethyl disulfide (CH₃SSCH₃) were irradiated in aqueous solution and black liquor at various pertinent experimental conditions.

Black liquors usually contain a high concentration of inorganic sulfide, organic components and minor amounts of organic sulfides (Table 4.1). The organic components are complicated in black liquor; they consist of various forms of carbohydrates (cellulose and hemicellulose residues), lignin, extractives and their derivatives. The radicals formed through gamma radiolysis of water, and the organic components of black liquor, may be particularly reactive toward the sulfide linkage.

5.2.1 Hydrogen Sulfide

Only a few investigations on sodium sulfide radiolytic degradation yields in aqueous solution have been reported in the past. In this study, the apparent degradation yield of sulfide (G(-Na₂S)) in aqueous solution is pH dependent. Values of G(-Na₂S) are found to range between 5.0 and 7.5 for sulfide solutions at pH 12.46 and 8.38, respectively (Table 4.3). Further investigations of apparent degradation yields of hydrogen sulfide (G(-H₂S)) in carbonated black liquors (Fig. 4.24) show that the degradation yields (0.015 to 3.427) correlate significantly with initial hydrogen sulfide concentrations (0.89 x 10^{-3} to 265.20 x 10^{-3} g/1). The comparison of hydrogen sulfide degradation yield of a carbonated black liquor (1-1) in presence of nitrogen, air and oxygen are corresponding 8.5, 9.7 and 16.7 (Table 4.26). The degradation of sulfide in aqueous solution and carbonate black liquor is exponential with dose (Figs. 4.1, 4.17 and 4.26).

The formation of polysulfide and sulfate by gamma radiolysis of sodium sulfide aqueous solution was found to prevail in this study (Table 4.2 and 4.27). This is in agreement with earlier reports by Loiseleur (117) who reported in 1942 that elemental sulfur was formed by X-ray radiolysis of hydrogen sulfide in aqueous solution. Further, Markakis and Tappel (122) reported that in gamma radiolysis of 6×10^{-3} M hydrogen sulfide aqueous solution with a dose of 10^{7} rad, 60% of the sulfur was recovered as elemental sulfur and 5% as sulfate.

Only limited information is available on the yield of

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polysulfide from gamma radiolysis of aqueous sulfide solution. Herein it was found that the yield of polysulfide excess sulfur (G(S)) was pH dependent (Table 4.4). The polysulfide excess sulfur generated from aqueous sodium sulfide solution acidified with $CO_2(120 \text{ psi})$ and $H_2S(270 \text{ psi})$, was determined as a function of irradiation dosage, initial sulfide concentration and preirradiation acidification treatment (Table 27). The response to the dose effect was found to increase linearly at constant initial sulfide concentration when aqueous sulfide solutions were acidified by CO_2 or H_2S (Table 4.27).

The hydrogen sulfide gas acidified sulfide solutions gave considerably higher yields of excess sulfur (G(S) = 3.06 to 4.92) than those expected in carbon dioxide acidified liquors (G(S) = 1.47 to 2.96). This may be due to increase of sulfide concentration by $H_2 \tilde{S}$ gas treatment.

Other experiments (Table 4.27) show the effect of gamma radiolytic generation of polysulfide from sulfate green liquor $(35 \text{ g/l Na}_2\text{S})$ acidified by hydrogen sulfide gas. The yield of polysulfide excess sulfur attained at 30.0 and 60.0 Mrad was 3.8 and 6.6 g/l(G(S) = 3.81, 3.34) respectively.

While the optimum conditions for generation of sulfide to polysulfide by gamma radiation has not been obtained in this study, the results indicate that conditions may be optimized to obtain maximum excess sulfur and minimum sulfate yields. Such limitations are prerequisite to maximum generation of polysulfide by gamma radiolysis from sulfide solution and sulfate green liquor.

The mechanism of formation of elemental sulfur and polysulfide by gamma radiolysis of sulfide aqueous solution may be proposed from the schemes of sulfide reaction with H•and H0•radicals as formed by the radiolysis of water.

но-	+	$H_2 S \longrightarrow HS^{\bullet}$	+	н ₂ 0	/5-3/
Н•	+	$H_2 $ $S \longrightarrow HS $ •	+	H ₂	/5-4/
		$^{2}HS \rightarrow H_{2}S$	+	· S	/5-5/
		$2 \text{HS} \rightarrow \text{H}_2 \text{S}_2$		• • • • • •	/5-6/

Karmann <u>et al</u>.(103), studying pulse radiolysis of hydrogen sulfide in aqueous solution, found that H_{\bullet} , HO_{\bullet} and e_{aq}^{-} reaction with $H_{2}S$ is very fast.

 $\begin{array}{rcl} \mathrm{K}(\mathrm{H}\cdot \ + \ \mathrm{H}_{2}\mathrm{S}) &=& 10^{9} \ \mathrm{M}^{-1}\mathrm{sec}^{-1} \ \dots \ /5-7/\\ \mathrm{k}(\mathrm{H}\mathrm{O}\cdot \ + \ \mathrm{H}_{2}\mathrm{S}) &=& 1.1 \ \mathrm{x}^{-1}\mathrm{O}^{-1}\mathrm{sec}^{-1} \ \dots \ /5-8/\\ \mathrm{k}(\mathrm{e}_{\mathrm{aq}}^{-} \ + \ \mathrm{H}_{2}\mathrm{S}) &=& 1.3 \ \mathrm{x}^{-1}\mathrm{O}^{-1}\mathrm{sec}^{-1} \ \dots \ /5-9/\\ \end{array}$ The reaction of $\mathrm{e}_{\mathrm{aq}}^{-} \ \mathrm{with} \ \mathrm{H}_{2}\mathrm{S}$ is shown as: $\begin{array}{r} \mathrm{e}_{\mathrm{aq}}^{-} \ + \ \mathrm{H}_{2}\mathrm{S} \longrightarrow \mathrm{SH}^{-} \ + \ \mathrm{H} \ \dots \ /5-10/\\ \ \longrightarrow \mathrm{S}^{-} \ + \ \mathrm{H}_{2} \ \dots \ /5-11/\\ \end{array}$

The rate constant of $k(H0 + H_2S)$ is independent of pH within

the pH range of 2 to 6. In alkaline solution H_2S is dissociated to HS⁻ which is able to react with HO·to form the intermediate (SHOH)⁻.

H0. + $SH^- \longrightarrow (SHOH)^- \dots /5-12/k(H0. + SH^-) = 5.4 \times 10^9 M^{-1} sec^{-1} \dots /5-13/Only S^- can be formed by gamma radiolysis of alkaline sulfide solution.$

$$(HSOH)^{-} + SH^{-} \rightarrow H_{2}O + HS_{2}^{-} \dots /5.14/$$
$$HS_{2}^{-} \rightarrow S^{-} + SH^{-} \dots /5-15/$$

Therefore, there is no overall change in radiolysis schemes of sulfide in alkaline solution. This affords an explanation for the low yield of excess sulfur from gamma radiolysis of high pH sulfide solutions.

In this study, the apparent yields of sulfate $(G(H_2SO_4))$ from gamma radiolysis of carbon dioxide acidified sodium sulfide solution range between 0.16 and 0.40; and even lower sulfate yields were obtained between 0.03 to 0.08 in hydrogen sulfide gas (270 psi) acidified aqueous sulfide solution (Table 4.27). This relatively higher yield of sulfate in carbon dioxide acidified sulfide solution as compared to that of hydrogen sulfide gas acidified sulfide solution is rather difficult to explain. However, it is worthy of note that the sulfate yield by gamma radiation is controllable to a minimum by hydrogen sulfide gas acidification of sulfide solutions.

The yields of sulfate in this investigation were substantially lower than that reported by Nanobashvili and Gvilava (145). They showed that gamma radiolysis of 0.005 - 0.5 M sodium sulfide solution gave sulfate yields (G(H₂SO₄)) up to 60. They also proposed that the chain reaction of sulfide oxidation to sulfate may be fundamentally maintained by the HO₂ radical through radiolysis of water (145).

5.2.2 Methyl mercaptan

Gamma radiolysis of methyl mercaptan in aqueous solution is scarcely reported; but ionizing radiation (X- and gamma rays) of cysteine aqueous solutions has been considerably investigated due to interests in radiostability of biological systems(9, 186).

The results of gamma radiolysis of methyl mercaptan in aqueous alkaline solutions (Table 4.4 and Fig. 4.2) show that the degradation of mercaptan is pH dependent. The mercaptan degradation yields (G(-CH SNa)) in the presence of air are 2.5, 11.3 and 315.4 for pH 13.54, 12.54 and 10.70, respectively. The products of radiolytic transformation were found to be dimethyl disulfide and sulfate. Further, investigations on the degradation yield of mercaptan (G(-CH SH)) in carbonated black liquor (Fig. 4.23) indicate that the degradation yields (0.006 to 0.230) are also significantly correlated with initial concentrations of methyl mercaptan (0.40 x 10^{-3} to 28.70 x 10^{-3} g/1).

Degradation of mercaptan was obviously affected by the presence of oxygen. Difference in mercaptan yields was observed with irradiated carbonated black liquor (1-1) in the presence of nitrogen, air and oxygen atmospheres. The corresponding $G(-CH_3SH)$ was 10.2, 18.5 and 28.0 (Table 4.26) at initial pH of 7.50.

Degradation of mercaptan in aqueous solution and carbonated black liquor was found to be exponential with dose (Figs4.2, 4.18 and 4.28).

These results are in agreement with the gamma radiolysis of cysteine in aqueous solution by Swallow (186). In air saturated solution, the yield of cystine (CySSCy) from gamma radiolysis of cysteine-hydrochloride solution (pH 1.9 - 3.3) may reach as high as 24. In deaerated solutions, the yield of cystine is reduced to 3.

Furthermore, Allen (9) also reported that cystine yields from radiolysis of cysteine solution were a function of oxygen, pH and initial concentration of cysteine. In oxygenated solutions, the cystine yields (G(CySSCy)) increased with increasing cysteine concentration; while in neutral solutions cystine yields as high as 60 were obtained under certain conditions, whereas the yields in acid and alkaline solutions were lower.

The extensive literature on the radiolysis of -SH functional group containing compounds has well established the fact that free radical attack at the -SH is the main initiating process(4, 61, 150, 156, 187).

The high yield in the oxidation cysteine to cystine in the presence of oxygen is reported to be the result of a chain reaction. Swallow (186) has postulated the following schemes:

RSH	+	$H0 \rightarrow RS \rightarrow H_2 0 \cdots (5-16)$
RS•	+	$RSH \rightarrow RSSR + H + H +$
H•	+	$0 H0_2 \cdots /5-18/$

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sulfo compounds were obtained from radiolysis of butyl-, amyl-, hexyl- and other mercaptans. The higher oxidation stage is observed by the increasing yield; of sulfate ions, and consequently decreasing pH of the aqueous solutions.

5.2.3 Dimethyl sulfide and dimethyl disulfide

As shown in Table 4.7, the degradation yields in alkaline model solutions were $G(-CH_3SCH_3)$ 0.730, $G(-CH_3SSCH_3)$ 0.885. Relatively speaking, these yields are considerably higher than those obtained in black liquor $G(-CH_3SCH_3)$ 0.503, $G(-CH_3SSCH_3)$ 0.427 at the similar pH values (pH 13.12 - 13.14) and irradiation levels. This indicates a scavenging and protective effect of black liquor organic components on the degradation of organosulfides.

The degradation of dimethyl sulfide and dimethyl disulfide model compounds in alkaline solution and black liquor is also exponential with dose (Fig. 4.3).

The effect of dimethyl sulfide and dimethyl disulfide degradations induced by gamma radiation is greatly affected by solution pH (Figs. 4.4 and 4.5), lignin concentration (Fig. 4.6), temperature (Figs. 4.7 and 4.8) and oxygen pressure (Figs, 4.9 and 4.10).

As shown in Table 4.8, as well as in Fig. 4.5, the dimethyl

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sulfide degradation yield to initial concentration (G/Co) decreased linearly when solution pH was decreased from strong acid (pH 0.5) to strong alkaline solution (pH 13.5). While G/Co of dimethyl disulfide was also decreased almost linearly from strong acid to pH 10.1, then it increased slightly from pH 10.1 to pH 13.5.

The products and mechanisms of gamma radiolysis of dimethyl sulfide have not been investigated. Meissner <u>et al</u>. (129) were able to measure the rate constants in the reaction of dimethyl sulfide with hydrated electrons (e_{aq}^{-}) and hydroxyl radical (H0·) by pulse radiation. The reaction rate constant of dimethyl sulfide and H0· (K(H0·+ CH SCH₃)) is 260 times higher than that of e_{aq}^{-} (K(e_{aq}^{-} + CH₃SCH₃)).

 $K(H0 + CH_3SCH_3) = 5.2 \times 10^9 M^{-1} sec^{-1} \dots /5-22/K(e_{aq}^{-1} + CH_3SCH_3) = 2.0 \times 10^7 M^{-1} sec^{-1} \dots /5-25/As$ discussed in Section 2.3, higher concentration of HO was found in acid solution, whereas higher concentration of e_{aq}^{-1} existed only in alkaline solution.

The slight increase of G/Co of dimethyl disulfide in strong alkaline solution (pH 10-13.5) is difficult to understand due to the unclear degradation mechanism. However, the higher yields of oxidizing species (H0., H0. and $H_2 0_2$) in radiolysis of aqueous acid solutions may increase degradation yields of dimethyl sulfide and dimethyl disulfide in low pH (acid) solutions.

As shown in Table 4.9, as well as in Fig. 4.6, the presence of lignin in alkaline solution shows a significant scavenging effect due to competition for reaction radicals (produced through water irradiation) between lignin and organosulfides. It seems likely that the great energy absorbing capacity of aromatic lignin protects organosulfides from degradation. Lignin concentrations in sulfate black liquor usually range from 18 to 48 g/1 (Table 4.1). According to Fig. 4.6, decomposition values of both dimethyl sulfide and dimethyl disulfide decrease consistently with up to 50 g/1 thiolignin concentration, with some inconsistencies being evident for dimethyl disulfide at higher irradiation dosages. Similar observations can be made for $G(-CH_3SCH_3)$ and $G(-CH_3SSCH_3)$ in that a clear scavenging trend is indicated only for the average G values at 50 g/1 lignin concentration.

The degradation of dimethyl sulfide and dimethyl disulfide by gamma radiation is also a function of temperature and oxygen pressure. At the initial oxygen pressure of 50 psi, the organosulfide degradation yields increased linearly as the temperature was increased from 60 to 115° C for the black liquor (Table 4.10, Fig. 4.7) and carbonated black liquor (Table 4.11, Fig. 4.8). On the other hand, at Gammacell ambient temperature (34° C), the organosulfide degradation yields also increased linearly as oxygen

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pressure was increased from 25 to 100 psi for black liquor (Table 4.12, Fig. 4.9) as well as carbonated black liquor (Table 4.13, Fig. 4.10).

As discussed in Section 2.3.3 on gamma radiolysis of water, oxygen is a very efficient scavenger for reducing species such as H and e_{aq} ; and various oxidation species (HO₂, O₃, O₂ and H₂O₂) are generated. Thereby, the degradation yields of dimethyl sulfide and dimethyl disulfide are greatly affected by the oxygen pressure. This has been confirmed by Purdie (156), Markakis and Tappel (122), and Forbes <u>et al</u>. (69), on radiolysis of cystine aqueous solutions. They were able to demonstrate that oxidation products were greatly increased in the aerated solutions.

In this study, due to low initial concentrations of dimethyl sulfide and dimethyl disulfide in black liquors, the apparent degradation yields were low. They do, however, correlate significantly with their respective initial concentrations in black liquors (Table 4.18, and Figs. 4.15 and 4.16) and carbonated black liquors (Table 4.24, and Figs. 4.24 and 4.25).

The effect of nitrogen, air and oxygen atmospheres on gamma radiolysis of dimethyl sulfide in carbonated black liquor (1-1) is shown in Table 4.25 as well as Fig. 4.27. Dimethyl sulfide degradation in nitrogen, air and oxygen is exponential with dose

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(Table 4.25 and Fig. 4.28).

The degradation yields $(G(-CH SCH_3))$ are 0.185, 0.426 and 0.741 for presence of nitrogen, air and oxygen, respectively. Gamma radiolysis of dimethyl disulfide, in conjunction with methyl mercaptan in the presence of nitrogen, air and oxygen in carbonated black liquor, shown in Fig. 4.28, suggests that the presence of oxygen and air promoted the formation of dimethyl disulfide in the radiolysis of methyl mercaptan and greatly elevated the degradation of dimethyl disulfide. These results conform with the earlier observations that the presence of oxygen is very beneficial to the increase of methyl mercaptan, dimethyl sulfide and dimethyl disulfide degradation rates.

The infrared spectrum reproduced in Fig. 3.19 reveals that a product of gamma irradiated dimethyl sulfide shows strong absorption at 1710cm⁻¹ which is assigned to the carbonyl group. The product is a nonvolatile, stable, amorphous substance. However, sulfate ions have not been detected from the gamma radiolysis of dimethyl sulfide aqueous solution, whereas they were present in irradiated solutions of dimethyl disulfide. This is further evidence that stabilization of organosulfides in black liquor can be obtained by gamma radiation.

The products and mechanisms of gamma radiolysis of dimethyl

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sulfide and dimethyl disulfide in aqueous solution have not been investigated, except by Meissner <u>et al</u>. (129), who showed some intermediate compounds from pulse radiolysis of dimethyl sulfide aqueous solutions. Radiation of cystine has been studied in considerable depth. The effects of solution pH and oxygen on radiation degradation of the organosulfide and their possible mechanisms, are thoroughly discussed in the following sections to help to explain the degradation of dimethyl sulfide and dimethyl disulfide in model solution and black liquors.

Change in the three absorption maxima of the intermediate compounds were observed following impingement of the pulse by Meissner <u>et al</u>. (129). Pulse radiolysis of dimethyl sulfide in alkaline solution produces absorption maximum at 3500Å. Further absorptions occur at 2900Å and 4700Å :

 $\begin{array}{rcl} \text{Ho} &+ & \text{CH}_{3} \text{SCH}_{3} \longrightarrow \text{CH}_{3} \text{SOHCH}_{3} & & & & /5-24/\\ \text{CH}_{3} \text{SOHCH}_{3} \longrightarrow \text{CH}_{3} \text{SOCH}_{3} (3500\text{Å}) &+ & \text{H}^{\dagger} & & /5-25/\\ \text{Ho} &+ & \text{CH}_{3} \text{SCH}_{3} \longrightarrow \text{CH}_{3} \text{SCH}_{2} (2900\text{\AA}) &+ & \text{H}_{2}0 & & //5-26/\\ \text{2Ho} &+ & 2\text{CH}_{3} \text{SCH}_{3} \longrightarrow (\text{CH}_{3} \text{SCH}_{3})_{2}^{\dagger} (4700\text{\AA}) &+ & 20\text{H}^{-} & & //5-27/\\ \end{array}$

The intensities at these absorption maxima (intermediate products) were shown to be dependent on solution pH and presence of oxygen. In oxygenated solutions, the absorption maximum at 2900Å disappeared, because the 0_2 was shown to react readily with

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 CH_3SCH_2 radicals. With increasing pH from 7 to 13, the absorption at 2900Å ($CH_3SCH_2^{\circ}$) increases slightly in contrast to the substantial change observable at 3500Å (CH_3SOCH_3), whereas the absorption at 4700Å((CH_3SCH_3)⁺) decreased rapidly when the solution pH was raised to 9.

The disulfide bond is particularly sensitive to ionizing radiation. The radicals formed through gamma radiolysis of water attacked the -S-S-group as the main initial process (4, 150, 156, 187). Due to the limited solubility, radiolysis of dimethyl disulfide has not been favored for theoretical studies. However, the radiolysis of cystine (CySSCy) aqueous solutions has been considerably investigated by many researchers. Markakis and Tappel (122) determined the products of gamma radiolysis (between 10^4 -8 x 10^7 rad) of cystine in 100 x 10⁻⁴ M hydrochloric acid solutions and found cysteine (CySH), hydrogen sulfide, elemental sulfur and sulfate. In these experiments the yields of cysteine (0-11 x 10^{-4} M) and hydrogen sulfide $(0-1.8 \times 10^{-4} M)$ were lower than the yields of elemental sulfur $(0-140 \times 10^{-4} M)$ and sulfate $(0-85 \times 10^{-4} M)$. For the stabilization of disulfides it is particularly important to note that the formation of sulfate was increased greatly in aerated cystine solutions (122).

The details of initial products resulting from gamma radi-

olysis (8 x 10⁴ rad) of cystine acidified aqueous solutions (3 x 10⁴M) were first analyzed by Grant <u>et al</u>. (78), using paper chromatography and electrophoresis. The sulfur products of the oxygenated or aerated solutions were cystine disulfoxide (CySO₂Cy) with yield (G) of less than 0.1, cysteic acid (CySO₃H) with yield of 0.3-1.5, cysteine sulfinic acid (CySO₂H) with yields of 0.1 or less, and cysteine (CySH) with yields of 0.1 to 0.9. Similar studies were also conducted by Forbes <u>et al</u>. (69). The yields of oxidized sulfur compounds were affected by factors such as radiation dose, solution pH and the presence of air. During the ionizing radiation (X- and γ -rays) treatment of cystine, the products were derived from both fission of the S-S bond (e.g. CySO₂H and CySO₃H) and fission at the S-C bond (e.g. CySO₃H).

Purdie (156) studied the gamma radiolysis (10⁴ rad) of 3 x 10^{-4} M cystine water solutions. The products, which have been determined, were cystine disulfoxide, cysteic acid, cysteine sulfinic acid, cysteine, cystine thiosulfonic acid (CyS0₂SH), cysteine thiosulfuric acid (CySS0₃H) and cystine trisulfide (CySSSCy). The principal oxidation products in aerated solutions were CyS0₂H(G = 0.9-1.7) and CyS0₃H(G = 0.7-1.2). In deaerated solutions, the yields of CyS0₂H(G = 0.3-1.2) were relatively lower, and CyS0₃H was present in only trace amounts. Similarly, only trace amounts of cysteine were detected in aerated solutions (G = 0=0.7). Substantially higher yields of cysteine were obtained in deaerated solutions (G = 0.4-2.5). Cystine trisulfide, on the other hand, was produced in significant amounts in both aerated (G = 0.4-0.6) and deaerated (G = 1.0) solutions. The yields of minor products of $CySSO_3H$ and $CySO_2SH$ correspond to 0.1 and 0.05 for both aerated and deaerated solutions.

Several schemes have been proposed for the radiolysis of cystine and the related disulfides in aqueous solution (69, 78, 156, 175). These reactions may provide an explanation of the oxidation of dimethyl disulfid aqueous solutions as induced by gamma radiation.

The disulfide bond is readily attacked by HO. to form sulfenic acid (RSOH).

 $\begin{array}{rcl} \text{RSOH} & + & 0 & & \hline & 2 & \hline & & \\ & 2 & \text{RSOH} & + & 0 & \hline & & \\ & 2 & \text{RSOH} & \longrightarrow & \text{RSO}_2 \text{H} & + & \text{RSH} & \dots & /5-29/\\ & & & \text{RSOH} & + & H_2 & 0 & \longrightarrow & \\ & & \text{RSOH} & + & H_2 & 0 & \longrightarrow & \\ & & & \text{RSO}_2 \text{H} & + & H_2 & \dots & /5-31/\\ & & & \text{The formation of sulfenic acid and thiosulfonic acid are also}\\ & & & \text{proposed via a displacement reaction (69):} \end{array}$

RSSR + $HO_2 \longrightarrow RSO_2 H$ + $RS \dots /5-32/$ RSSR + $HO_2 \longrightarrow RSSO_2 H$ + $R \dots /5-33/$

Purdie (156) proposed the following reactions of formation

disulfoxide (RSO₂SR), sulfenic acid (RSO₂H) and sulfonic acid (RSO₃H) in aerated solution:

RS•	+	$0_2 \rightarrow$	RS0:	• • • • • • • •		••••	••/5-34/
RSO•	+	RS·→	RSO ₂ SR .		• • • • • • • •	•••••	••/5-35/
2 RS0• 2		>	RS02S02R	••••	• • • • • • • •		••/5-36/
RSO ₂ SC	R 2	+ B	$I_2 0 \longrightarrow RS$	о ₂ н +	^{RSO} 3 ^Н	• • • • • • • •	••/5-37/

The trisulfide (RSSSR) is formed during the radiolysis of cystine both in aerated and deaerated solutions (156):

The formation of sulfate was observed from the gamma radiolysis of dimethyl disulfide in aqueous alkaline solution. Markakis and Tappel (122) also confirmed that sulfate was formed by the gamma radiolysis of cystine aqueous acidic solutions. Forbes <u>et al</u>. (69) indicated that thiosulfuric acid (RSSO₃H) is an intermediate for the formation of sulfate from the ionizing irradiation of disulfide in neutral or alkaline solution.

 $2 \operatorname{RSSO}_{3} H$ + $2 \operatorname{H}_{2} O \longrightarrow 2 \operatorname{RSH}$ + $2 \operatorname{H}_{2} \operatorname{SO}_{4} \cdots \cdots / 5 - 39 /$

These processes indicate the strong tendency of sulfide stabilization in aqueous solutions <u>via</u> various oxidation transformations. The mechanisms should be directly applicable to gamma radiolysis of sulfides in sulfate black liquors.

5.2.4 Unidentified sulfur compound (X)

The gamma radiation degradation of the unidentified sulfur containing compound (X) in unacidified (Table 4.17, Fig 4.14) and acidified (Table 4.23, Fig. 4.21) sulfate and polysulfide black liquors has followed a pattern similar to that observed with the radiation degradation of organosulfides, discussed in detail in the previous sections.

5.3 Kinetics of Gamma Radiolysis of Sulfides in Aqueous Solution and Black Liquor

The indirect action of radicals from water decomposition alone is not sufficient to explain the mechanism of the gamma radiolysis of sulfides in black liquor. The sulfate black liquor contains very high concentration and complicated inorganic and organic compounds, in the highly concentrated aqueous solution, and the hydration shells of the hydrated molecules or ions are overlapping. This affects a number of physico-chemical properties and profoundly changes the microscopic volumes of the solution at the moment of energy dissipation in the tracks or spurs of ionizing particles (22).

Radicals produced from the radiolysis of water and hydrocarbons in black liquor are able to react with the sulfides in numerous ways. As radiation proceeds, the reacted sulfide molecules will

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likely remain in the solution, still capable of further reaction with other radicals with a frequency equal to the unreacted sulfide molecules. A complete description of the chemical reactions by gamma radiolysis of black liquor is impossible. However, tentative schemes are illustrated in Fig. 5.2.

The fundamental radiolytic reactions of sulfides in black liquor are proposed as follows:

н ₂ 0		cwI → H•	-	+ 1	но•.	* * * *		 	0000	•••/5	5-40/
RH(o	orga	l anic)~	°I	R• +	H	1		 		•••/5	5-41/
S	+	H• _1	\rightarrow	Produ	ıct			 		•••/	5-42/
S	+	но• — ^к 2	\rightarrow	Produ	uct		9 9 9 9 9	 		•••/	5-43/
S	+		[}] →	Produ	uct			 		•••/5	5-44/
(s		<u>5</u>)	+]	k	$\stackrel{!}{\rightarrow}$	Prod	uct	 		•••/	5-45/
(s _o	-	S)	+]	HO•		Prod	uct	 		•••/	5-46/
(s _o	-	S)	+]	R•	, 3→	Prod	uct	 		•••/	5-47/
RH	+	H•	1	<u>4</u> >	Pro	duct	e	 		•••/	5-48/
RH	+	HO	<u> </u>	<u>5</u>	Pro	duct		 		•••/5	5-49/
RH	+	R•	1	⁶	Pro	duct		 		•••/5	5-50/

- Where, I = dose rate, absorbed energy intensity, in 100 ev/g k_w , k_o , k_{1-6} and k_{1-3}' = specific rate constant, in M⁻¹ min⁻¹
 - S_= initial sulfide concentration, in molecules
 S = sulfide remaining in solution after irradiation time
 t, in molecules
 - $S_0 S = concentration of the transformed sulfide, in molecules$
- Let, $G_w = primary$ yield of gamma radiolysis of water, in molecules /100 ev

$$\frac{d(H^{\bullet})}{dt} = G_{w}I + G_{o}I - k_{1}(S)(H) - k_{1}'(S_{o}-S)(H^{\bullet}) - k_{4}(RH)(H^{\bullet}) \dots (5-51)$$

$$\frac{d(H0\cdot)}{dt} = G_{W}I - k_{2}(S)(H0\cdot) - k_{2}(S_{0}-S)(H0\cdot) - k_{5}(RH)(H0\cdot) \dots / 5 - 52/$$

$$\frac{d(R\cdot)}{dt} = G_0 I - k_3(S)(R) - k_3(S_0-S)(R\cdot) - k_6(RH)(R\cdot) \dots (5-53)$$

The reactions are rapid, and the system can reach a steady state in a small fraction of a second. If Eqs. /5-51/, /5-52/ and /5-53/ are taken as zero, the system of equations can be solved for the various radicals as shown below.

$$(H \cdot) = \frac{G_{W}I + G_{0}I}{k_{1}(s) + k_{1}^{*}(s_{0}-s) + k_{4}(RH)} \dots /5-55/$$

$$(H0 \cdot) = \frac{G_{W}I}{k_{2}(s) + k_{2}^{*}(s_{0}-s) + k_{5}(RH)} \dots /5-56/$$

$$(R \cdot) = \frac{G_{0}I}{k_{3}(s) + k_{3}^{*}(s_{0}-s) + k_{6}(RH)} \dots /5-57/$$

The steady state values of (H•), (H0•) and (R•) (/5-55/, /5-56/ and /5-57/) are substituted into Eq. /5-54/. The radicals react as readily with the transformed sulfide molecules as with the sulfide in its original form. Thus these are assumed: $k_1 \circ k_1$, $k_2 \circ k_2$ and $k_3 \circ k_3$

$$-\frac{d(S)}{dt} = \frac{k_1(G_wI + G_0I)}{k_1(S_0) + k_4(RH)} + \frac{k_2G_wI}{k_2(S_0) + k_5(RH)} + \frac{k_3G_0I}{k_3(S_0) + k_6(RH)}$$
(S)

In pure water, (RH) = 0, $G_0I = 0$

$$-\frac{d(s)}{dt} = \frac{2G_{W}I}{(s_{o})}$$
(s)

When t = 0, (S) = (S_0)

$$\ln(S) = \ln(S_0) - \frac{2G_W}{(S_0)}$$
 It

Where It = D(Dose)

This indicates that there is a linear relationship of logarithmic sulfide concentration and radiation time(t) for the gamma radiolysis of sulfide at constant dose rate(I).

According to Eq. /5-58/, the degradation of sulfide in black liquor which usually contains high organic components, is expressed by Eq. /5-60/3

$$\frac{d(s)}{dt} = \sqrt{\frac{G_{w}I + G_{o}I}{(s_{o}) + \frac{k_{\mu}(RH)}{k_{1}}}} + \frac{G_{w}I}{(s_{o}) + \frac{k_{5}(RH)}{k_{2}'}} + \frac{G_{o}I}{(s_{o}) + \frac{k_{6}(RH)}{k_{3}'}} / (s)$$

$$\frac{G_{w} + G_{o}}{(s_{o}) + \frac{G_{w} + G_{o}}{(s_{o}) + \frac{G_{w}}{k_{1}'}}} + \frac{G_{v}I}{(s_{o}) + \frac{G_{v}I}{k_{3}'}} / (s)$$

$$\frac{G_{v} + G_{v}}{(s_{o}) + \frac{K_{\mu}(RH)}{k_{1}'}} + \frac{G_{v}I}{(s_{o}) + \frac{G_{v}I}{k_{2}'}} + \frac{G_{v}I}{(s_{o}) + \frac{G_{v}I}{k_{2}'}} / (s)$$

Where It = D(Dose).

It is also illustrated that the logarithm of sulfide concentration decreases linearly with radiation time(t) at constant dose rate(I). The presence of organic components give scavenging effect and reduce the yields of sulfide degradation.

In this study, the dose rate(I) is constant, so that the plot of logarithmic sulfide concentration versus irradiation time (t) is a straight line for sulfides in both pure water solutions (Tables 4.2, 4.3 and 4.5 as well as Figs 4.1, 4.2, and 4.3) and black liquors (Tables 4.6, 4.15, 4.16, 4.19, 4.20, 4.21, 4.22, and 4.25 as well as Figs. 4.3, 4.12, 4.13, 4.17, 4.18, 4.19, 4.20, 4.26, 4.27 and 4.28).

5.4 Effect of Gamma Radiation on Black Liquor pH

The pH of black liquor is little changed when black liquor is irradiated at Gammacell ambient temperature (Tables 4.6 and 4.12). However, a significant decrease in the pH of black liquor was observed for both control and gamma irradiated samples (Table 4.10) as the solution temperature was increased from room temperature to 115° C (under 50 psi initial oxygen pressure). Decrease of pH with the irradiated samples was greater than that the control samples under similar oxygen pressure. On the other hand, the temperature effect on the pH change was not significant for either irradiated and control samples of carbonated black liquor (Table 4.11).

In gamma radiolysis of the oxygenated black liquor, the oxygen molecules are considered to add to the organic radicals to form relatively stable peroxy radicals:

 $\operatorname{RO}_{2}^{\bullet}$ + $\operatorname{RH} \longrightarrow \operatorname{RO}_{2}^{\bullet}$ H + $\operatorname{Re}_{2}^{\bullet}$ + $\operatorname{Re}_{2}^{\bullet}$

The schemes presented in Eqs. /5-62/ and /5-63/ are chain reactions. Autooxidation proceeding in the above schemes also may be suspected due to heating the black liquor under oxygen pressure.

In addition, organic molecules in aqueous solution may be oxidized to CO_2 and H_2O when they are exposed to radiation for a sufficiently long time (91). Thus the pH of black liquor decreases by oxidation at elevated temperature with or without radiation. However, since gamma radiation can speed up the oxidation process of both carbohydrates and possibly the lignin fractions in black liquor, the pH is greatly decreased.

5.5 Oxidation of sulfides in black liquor

The gamma radiolysis of sodium sulfide solution at pH 12.46

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showed the lowest degradation rate (Fig. 4.1). When black liquor (3-1, pH 13.27) was irradiated in an open vessel in free contact with air, the consumption of silver nitrate $(AgNO_3)$ decreased rapidly to almost zero, as indicated by the inflection point "a" on potentiometric titration curve, whereas for the inflection point "b" it increased to a maximum and then decreased as shown in Table 4.14 and Fig. 4.11. These results are similar to those observed on black liquor oxidation by Murray et al. (142). They stated that oxidation of sulfide ions in black liquor proceeded in two steps. The first step involves oxidation of sulfide into an inorganic and/or organic polysulfide (inflection point "b"). The second step involves the oxidation of polysulfide ion to the final oxidation products (thiosulfate and elemental sulfur).

As for organic sulfides, the methyl mercaptide ion in black liquor is readily oxidized to dimethyl disulfide at ambient temperature in the presence of air. Extensive oxidation of dimethyl sulfide and dimethyl disulfide was also observed in black liquor (1-3) and carbonated black liquor (2-1). Under 50 psi initial oxygen pressure, the oxidation degradation rates of the organic sulfides increased greatly as the temperature was increased from 60 to 115° C (Figs. 4.7 and 4.8). At constant temperature (34°C), the rate of degradation of organic sulfides increased with increasing oxygen pressure from 25 to 100 psi (Figs. 4.9 and 4.10).

5.6 Applications

This pioneering research for treatment of sulfate pulp mill effluents to eliminate pollution and recover polysulfide from green liquor may find useful applications in various ways.

5.6.1 Treatment of digester and blow relief, and evaporator condensates

The sulfate pulp mill relief condensates contain malodorous sulfur compounds such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, and various volatile organic compounds formed during the course of pulping, along with minor amounts of black liquor and fibres (95, 120, 125). The amount of condensates is about one cubic meter per air-dry ton of pulp. The BOD load is mainly attributed to the presence of high methanol content (173).

Gamma radiolysis of aerated digester and blow relief condensates will reduce the toxicity and BOD load because methanol in the condensate is readily oxidized to aldehyde and formic acid by gamma radiation (85).

Amount of evaporator condensates is about 4 to 7 cubic meters per air-dry ton of pulp (173). Though it does not contribute to BOD to a large extent, it contains poisonous sulfides. With respect to purity, of course, the condensates can be recycled in pulp mills for preparing the cooking liquor, but only half the available amount of total condensates is required for this purpose.

The toxicity of the evaporator condensates can be greatly reduced by gamma radiolysis of the aerated solution before it is discharged to sewers.

5.6.2 High sulfidity and polysulfide recovery processes

Carbonation of high sulfidity black liquor and stripping of hydrogen sulfide before combustion will reduce the emissions of sulfur dioxide and hydrogen sulfide from the combustion furnace, as well as reduce the ratio of smelt sulfur to sodium oxide (S/Na_0) . According to the method of Gray <u>et al</u>. (79), black liquor is carbonated with lime kiln and flue gases under pressure, followed by vacuum stripping of hydrogen sulfide. This process can recover 55 to 65% of black liquor total sulfur. By gamma radiolysis of the aerated, acidified black liquor, the residual sulfides compounds in the carbonated black liquor are stable enough for further treatment such as condensation.

The treated sulfate black liquor is fermentable with yeast; the recoverable thiolignin has no obnoxious smell.

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The regenerated hydrogen sulfide in carbonated black liquor may be either absorbed in white liquor for the preparation of conventional sulfate cooking liquor or pressurized in green liquor and irradiated to form polysulfide.

Regeneration of polysulfide from gamma radiolysis of green liquor can be effected by acidification either with carbon dioxide or hydrogen sulfide. Hydrogen sulfide acidification usually gives higher efficiency of polysulfide formation than carbon dioxide.

The regenerated polysulfide, containing carbonate, can be causticized by calcium oxide or calcium hydroxide, as practiced with conventional green liquor causticization for sulfate cooking (194).

6.0 CONCLUSION

The work contained herein describes new, improved methods of total sulfide analysis of adequate sensitivity and quantitative reproducibility required to describe gamma radiation initiated changes in sulfide energetics occurring in sulfate black liquors and carbonated black liquors. Model experiments were run for the investigation of variables influencing the rate of sulfide stabilization in aqueous solutions. The information gathered from these model experiments was used in formulating a proposal for an industrial black liquor stabilization process, based on the radiolytic oxidation of sulfides in aqueous solution in the presence of excess oxygen.

6.1 Sulfide Analyses

Sulfate and polysulfide black liquor analysis by silver nitrate potentiometric titration shows two equivalent end points. It is shown that the two equivalence points arise from two different forms of sulfide; namely, the first inflection point (-430 mv) is considered to be monosulfide, the second inflection (-250 mv) is due to presence of organic and inorganic polysulfides. The organic polysulfide is formed by the reaction of methyl mercaptide ion with elemental sulfur. Inorganic polysulfide is generated by the oxidation of sulfide ions.

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In black liquor, methyl mercaptan can not be directly analyzed by potentiometric titration due to its low concentration. However, the quantitative determination is afforded by acidification of the black liquor sample to pH 6.5 with suspensions of boric acid in carbon tetrachloride and analysis of the organic layer with gas liquid chromatography (GLC).

Dimethyl sulfide and dimethyl disulfide in black liquor can be determined by carbon tetrachloride liquid/liquid extraction and GLC analysis.

Residual sulfides in carbonated black liquor, such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, may be quantitatively determined by GLC following adjustment of the sample pH to 6.5 with boric acid and low temperature extraction with carbon tetrachloride (liquid/liquid extraction.

6.2 Gamma Radiolysis of Sulfides in Aqueous Solution

Part of the products resulting from the gamma radiolysis of sulfide model compounds in aqueous solution have been identified. Polysulfide and sulfate are formed from radiolysis of sodium sulfide, dimethyl disulfide and sulfate from methyl mercaptan. An amorphous substance was obtained from dimethyl sulfide, and sulfate from dimethyl disulfide. This indicates that oxidation of sulfides is the most important reaction of gamma radiolysis of sulfides in aqueous solution.

The apparent degradation yields of sodium sulfide $(G(-Na_2S))$ in aqueous solution are pH dependent. In sulfide solutions at pH 8.38, $G(-Na_2S)$ is 7.5, gradual reduction in degradation yields $(G(-Na_2S) = 5.0)$ is observed with solutions at strongly alkaline (pH 12.46) condition. The apparent degradation yields of sodium methyl mercaptan are also greatly affected by solution pH; $G(-CH_3SNa)$ values of 2.5, 11.3 and 15.4 were calculated corresponding to solution pH values of 13.54, 12.54 and 10.70, respectively. Again, degradation of this compound shows the same trend as above.

The apparent degradation yields of dimethyl sulfide (G(-CH₃SCH₃)) and dimethyl disulfide (G(-CH₃SSCH₃)) in alkaline solutions (pH 13.12) were obviously higher than in black liquor (pH 13.14). The degradation yields of dimethyl sulfide and dimethyl disulfide correspond to 0.73 and 0.89 for aqueous alkaline solutions and only 0.50 and 0.43 for black liquor. Further, lower solution pH and lignin concentration, increased temperature and oxygen pressure promoted development of higher degradation yields.

In gamma radiolysis of sulfate black liquor, sodium sulfide concentration is generally decreased as it is converted to polysulfide. In this study, maximum polysulfides were obtained about 1 Mrad at 34⁰C, and then degraded for further radiation.

The apparent degradation yields of dimethyl sulfide (0.001-0.003) and dimethyl disulfide (0.002-0.085) were significantly correlated with their initial concentration in black liquors (pH 12.85-13.40).

Degradation yields of hydrogen sulfide (0.015-3.427), methyl mercaptan (0.006-0.230), dimethyl sulfide (0.003-0.020) and dimethyl disulfide (0.004-0.035) in the sulfate and polysulfide carbonated black liquors (pH 8.20-9.15) were also shown to be significantly correlated with their initial concentration.

The presence of oxygen in the sulfide enriched carbonated black liquor (pH 7.50) increased the radiolytic degradation yields of hydrogen sulfide (16.7), methyl mercaptan (28.0), dimethyl sulfide (0.74). The higher degradation yields of hydrogen sulfide and methyl mercaptan are considered to be due to chain reactions.

Degradation of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide by gamma radiation in aqueous solution and carbonated black liquor is exponential with dose. Similarly, the exponent with dose was also found to characterize the degradation of dimethyl sulfide and dimethyl disulfide in the

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various unacidified black liquors.

In radio-chemical reactions of oxygenated black liquors and carbonated black liquors, the degradation of malodorous sulfides is considered to be oxidation, polyaddition and combination of oxidation and polyaddition products. The volatile malodorous sulfides are thus stabilized in the black liquor after gamma radiation treatment. Advantages of these reactions in processing of black liquor are proposed to relate to abatement of air pollution from sulfate pulp mills.

Gamma radiation induced oxidation of sulfide and mercaptide ions, and organic components in the aerated sulfate pulp mill effluent, is further expected to reduce toxicity and biological oxygen demand (BOD) of pulp mill effluents. Thus, the radiation treatment is also proposed to reduce major problems of water pollution.

Polysulfide can be generated by gamma radiation of carbon dioxide or hydrogen sulfide acidified sodium sulfide and sulfate green liquors. The apparent yields of polysulfide excess sulfur (G(S)) were 2.96 and 4.92 for acidification with carbon dioxide (120 psi) and hydrogen sulfide (270 psi), respectively. However, further optimization of the reaction condition to obtain higher yields of polysulfide is necessary for industrial polysulfide cooking liquor regeneration.

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Mill	50 ₂	H ₂ S	снзен	сн ₃ scн ₃	снзеснз	Total	Ref.
* (Batch)			0.070	0.081	0.080	0.231	15
Kopmanhoimen* (Batch)			0.450	0.044	0.008	0.502	15
Norrsundet [*] (Continuous)			0.049	0.021		0.070	15
* Lovholmen (Continuous)			0.118	0.045	0.001	0.164	15
(Batch)		0.01-0.12	0.002-0.004	0.40-2.50	0.20-1.50	0.72-4.	12 90
Brown Stock Washers	0.01-0.02	0.01-0.12	0.10-0.25	0.01-0.02	0.01-0.02	0.14-0.	43 90

Table 2.1 Release of volatile sulfur compounds from digester; and washers.

Release 1b/air-dry ton of pulp.

* From condensate (turpentine and blow condensates) only.

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	so ₂	H ₂ S	CH ₃ SH	CH3SCH3	CH3SSCH3	Total
Oxidation tower	0-0.01	0.01-0.02	0.05-0.10	0.02-0.08	0.05-0.15	0.13-0.35
Multiple effe evaporators	ct					
A. B.	$0 - 0 \cdot 01$ $0 - 0 \cdot 01$	0.10 - 3.0 0.01 - 0.02	0.10 - 1.5 0.10 - 0.30	0.05-0.08 0.05-0.15	0.01-0.02	0.26-4.61 0.21-0.63
Contact Evaporators A. B.	2.0-8.0	5.0-30.0	0.50-2.50	0.10-0.30	0.10-0.40	7.70-41.20
	200-000	0.10-2.00	0.09-0.2		0.01-0.20	~•17=10•99
furnace	10.0-15.0	1.0-5.0	0.1-0.10	0.01-0.02	0.01-0.02	11.03-20.14
Smelt tank	0.0-0.01	0.02-0.05	0.02-0.05	0.01-0.02	0-0.01	0.05-0.14
Lime kiln	No data a	available.				

Table 2.2 Release of volatile sulfur compounds from sulfate recovery systems (90). Release, 1b/air-dry ton of pulp

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A. Unoxidized black liquor,

B. Oxidized black liquor

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Compound	Boiling point, °C	Explosive conc. range in air, % (54)	Dissociation const. at 100°C (169)	Odor threshold in ambient air ppm (114)
H ₂ s	-61.80	4.3-45.5	$K_1 = 2 \cdot 1 \times 10^{-7} (A)$ $K_2 < 10^{-14} (B)$	0.00047
сн _з ѕн	7.6	2.2-9.2	$K = 4.3 \times 10^{11} (C)$	0.0021
сн sch 3 3	37.0-38.0	3.9-21.8		0.001
CH3SSCH3	109-111		No data available	
A. $H_2 S \stackrel{K_1}{\underset{\sim}{\longleftarrow}}$	HS +	H ⁺ /2-1	1/.	
B. HS $\leftarrow K_2$:s - +	H ⁺ ····/2-12	2/	
с. сн ₃ sн z	k→ CH ₃ s	+ H ⁺ /2-13	/ .	

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Table 2.3 Physical characteristics of sulfate pulp mill malodorous sulfides.

Code No.	Company	Location	Wood Species	Sulphidity %	Kappa No.
1 - 1	Weyerhaeuser	Everett	Douglas-fir	30	26.7
1 - 2	Weyerhaeuser	Longview	Douglas-fir	19.2	22.7
1 - 3	Weyerhaeuser	New Bern	65% Loblolly pine	9	21.0
		N•C•	35% Pond pine	S	•
1 - 4	Weyerhaeuser	Springfield	Douglas-fir	21.4	50.0
2 - 1	Canadian Forest	Port Mellon			
	Products	в.с.			
3 - 1	Forest Products	Vancouver	Spruce		
	Laboratory	B.C.			
4 - 11	Pulp Paper Res.	Montreal			
	Inst. of Can.	P.Q.			
4 - 1V	Pulp Paper Res.	Montrea1			
	Inst. of Canada	P.Q.			

Table 3.1 Sulfate and polysulfide black liquor sources.

Table 3.2 Effect of inflection point "a" and "b" in potentiometric titration curves on calculation of hydrogen sulfide in black liquor.

		T. 61 +	 	
Sources	pt "a"	pt "b"	g/1	%
1 - 1	4.25	4.76	0.50	11.8
1 - 2	0.95	1.50	0.55	57.3
1 - 3	3.42	3.84	0.42	12.3
1 - 4	2.42	2.86	0.44	18.2
2 - 1	2.63	3.19	0.56	21.3
3 - 1	1.71	2.83	1.12	65.2
4 - 1L	8.80	9.41	0.61	7.0
4 - 1V	0.81	1.72	0.91	111.7

 H_2 S Calculation, g/1

	<u></u>	Added	, mg		Found, mg				
Source	№ ₂ S	CH ₃ SNa	Thio- lignin	Na S inflect. 2 pt "a"	• %	Bound Na- mer- captan inflect. a - b	Free Na- mercap- tan	Total	A©ĉ't for %
	10.0	66.5	-	9•3	93.0	19.1	45.1	64.2	96•5
Na ₂ S									
Solution*	10.0	67.7	1%	9.8	98.0	21.2	44.5	65.7	97.0
	19.9	56.8	-	19.9	100	23.1	35.7	58.8	103.5
White	22.6	55.1	-	18.7	82.7	40.3	16.1	56.4	102.3
Liquor	19.9	57.8	-	19.5	98.0	37.7	20.1	57.8	100.0 ¹
(1-3)									

Table 3.3 Accuracy of potentiometric titration of sulfide in alkaline solution in the presence of methyl mercaptan.

* Reagent grade Na₂S in 1N NaOH Solution,

;# ;* 1

1

1 ;

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	Tab1e 3.4	Interpretation of the potentiometric titration curve as
		affecting the accuracy of sulfide determination by
`		addition of methyl mercaptan.

Add	led		· 1	Found		
Na ₂ S, mg	Thiolignin, %	Na ₂ S inflection	Error, %	Na ₂ S inflection	Error	4
		pt "a", mg		pt "b", mg		
10.0	-	9•3	-7	22.1	+120.5	
10.0	-	10.7	+7	22.9	+129.1	
10.0	1.0	9.8	-2	22.0	+119.7	
10.0	1.0	9.8	-2	22.4	+124.4	12
		······				213

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2

Table 3.5	Determination addition of e alkaline sulf thiolignin as	of su xcess ide so addi	ulfid of Na plutio tive.	e and a-merc on wi	bound captai th and	l mero n to o l witl	captan oxidiz nout	ı by 2ed
	Oxidation**							
With 1%	time, min.	0	5	10	20	50	70	80
thiolignin	Na ₂ S, g/1*	9.8	9.3	8.8	6.2	1.2	0.4	
	Bound							
	Na-mercap- tan, g/1*	21.2	37.6	27.4	20.5	17.8	17.4	
Without 1% thiolignin	^{Na} 2S, g/1* Bound	12.4		10.0	9.0	5.5		4.0
	Na-mercap- tan, g/1*	22.8		29.4	20.9	19.5]	10.9

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*n = 2.

**0 flow rate = 44 ml/min in 400 ml liquor sample.

Table 3.6 Potentiometric titration of methyl mercaptan in alkaline solution in the presence of elemental sulfur.

4.

			•				
Sin	CH SNa	11.22	11.22	11.22	11.22	11.22	11.22
Sample	Elemental Sulfur	0	4.0	8.0	20.0	38.4 4	157.0
*mg	Approx. Mercap. S/So	0	2.8	1.4	0.6	0.3	0.02
	Apparent Sulfid	e 0	0.51	0	1.01	1.11	1.41
S Found	Bound S	0	3.62	6.83	10.42	11.24	11.22
	Total	0	4.13	6.83	11.82	12.43	12.62
	%	0	103.3	85.4	59.1	32.1	2.8
	Bound Mercap- tan	0	3.62	4.42	11.22	11.24	11.22
Mercap-	Apparent Mercaptan S	11.22	7.21	6.83	0	0	0
tan S	Total	11.22	10.83	11.25	11.22	11.64	11.22
Found mg	%	100.0	96.5	100.3	100.0	103.7	100.0

*pH = 13.3 - 13.6.

n=2.

Liquor	Sulfur con	npound added	<u>Sulfur</u>	Sulfur compound found				
	CH3SCH3	CH3SSCH3	CH_SCH	%	CH3SSCH3	%		
	×10 ⁻³ g	x10 ⁻³ g	x10 ⁻³ g		x10 ⁻³ g			
White 1:	iguor (pH =	13.6)						
	0.845	1.057	0.766 0.766 0.769	90.7 90.7 91.0	0.825 0.835 0.826	78.1 79.0 78.1		
	91	f0	0.764	90.4	0.825	78.0		
	Average		0.766	90.7	0.828	78.3		
·	0.423 "	0.529	0.400 0.390	94.6 92.2	0.427 0.415	80.7 78.4		
	Average		0.395	93.4	0.421	79.6		
	0.212	0.264 "	0.200 0.195	94 .3 92.0	0.215 0.206	81.4 78.0		
	Average		0.198	93.4	0.211	79•9		
Black 1i	iquor (pH =	13.1)						
	0.845	1.057	0.774 0.780	91.5 92.3	0.805 0.855	76.2 80.9		
	Average		0.777	91.9	0.830	78.5		
	0.423 "	0•529 "	0.405 0.394	95•7 93•1	0.421 0.430	79.6 81.4		
	Average		0.400	94.6	0.426	80.5		
	0.212	0.264	0.190	89.6	0.208	78.8		

89.6

94.3

92.0

0.190

0.200

0.195

88

Average

n

0.206

0.207

78.8

78.0

78.4

Efficiency of 5 x 10 ml carbon tetrachloride liquid/liquid extraction of the organosulfides from 5 ml sulfate white and black liquors. Table 3.7

Table 3.8 Efficiency of 20ml carbon tetrachloride liquid/ liquid extraction of organic sulfide compounds from 5 ml boric acid (1.0g) treatment carbonated black liquor (1-1).

Organosul	Organosulfides added		Organosulfides found					
сн ₃ scн ₃	сн _з sscн ₃	сн _з scн _з сн _з sscн _з						
x 10 ⁻³ g			x	10 ⁻³ g				
0.212	0.264	0.198	93.6%	0.234	88.6%			
.,	"	0.191	90.1%	0.222	84.1%			
ft .	11	0.201	95.0%	0.232	87.9%			
								

Average

0.197 92.9% 0.229 86.9%

4

						S	ulfides,	x 10 ⁻³	g/1
Source	рН	Solids, % (n=4)	Density g/ml, 25 ⁰ C (n=3)	Lignin g/1 (n=2)	H ₂ S (n=4)	Сн ₃ SH (n=3)	CH3SCH3 (n=3)	"X" (n=3)	CH ₃ SSCH ₃ (n=3)
1 - 1	13.21	20.1	1.0953	37.5	4254.8	53•57	0	6.49	7.58
1 - 2	12.87	12.4	1.0657	33.9	953.1	14.90	1.10	10.73	6.53
1 - 3	13.07	13.4	1.0706	44.3	3419.6	49.67	0	8.10	3.00
1 - 4	12.85	14.1	1,0727	37.0	2422.8	34.07	0.25	0.36	0.44
2 - 1	13.25	13.3	1.0695	35.7	2625.1	50.43	0.56	102.00	17.08
3 - 1	13.27	12.6	1.0668	30.3	1714.6	12.87	0.20	85.00	2.10
4 - 1L	13.40	14.1	1.0744	48.6	8796.5	83.67	0.39	50.21 ;	39.71
4 - 2V	13.22	5.5	1.0304	18.6	811.5	11.23	0	4.48	5.06

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Table 4.	1 Char	racteristics	of	sulfate	and	polysu	1fide	e black	liquors,
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Dose	Na2S	Molecu.	pН	Poly-S*	Na S	Molecu.	$\mathbf{p}\mathbf{H}$	Poly-S*
Mrad	g/1	x10 ²⁰		x10 ⁻² g/1	g/1	x10 ²⁰		x10 ⁻³ g/1
0.0	3.37	260.2	8.38	16.3	3.19	246.4	12.46	0.0
0.1	3.29	254.2	8.73	16.9	3.17	244.6	12.48	0.5
0.3	3.13	241.5	8.49	17.5	3.03	234.0	12.46	3.5
0.5	3.03	233.7	8.59	18.9	2.96	228.4	12.52	5.1
0.7	2.87	221.6	8.84	21.8	2.88	221.9	12.42	6.1
0.9	2.76	213.2	8.89	22.0	2.75	212.0	12.49	7.6
1.5	2.61	201.2	9.32	26.3	2.80	216.2	12.49	11.6
2.0	2.49	191.5	8.71	30.1	2.79	214.9	12.53	14.7
2.5	2.39	184.3	8.80	32.8	2.70	208.3	12.44	16.00
3.0	2.29	176.5	9.03	34.0	2.66	205.1	12.49	16.5
3.5	2.21	170.5	9.25	34.2	2.64	204.5	12.51	18.5
4.0	2.16	166.8	9.07	39.0	2.62	202.1	12.47	19.0
4.5	2.05	158.4	9.14	41.6	2.60	201.7	12.33	20.2

Replications, n=2. * Polysulfide excess sulfur.

Table 4.3	Effect of solution pH on gamma radiation
	degradation yield (G)* of sodium sulfide and
	sodium methyl mercaptan and yield (G)* of
	polysulfide excess sulfur.

Initial pH#	8.38	12.46	
Na_2S conc., $\# g/1$	3.37	3.19	
$G(-Na_2S)^+$	7.5	5.0	
G(S) ⁺	1.1	0.1	
Initial pH#	10.70	12.54	13.54
CH_3SNa conc., $\#$ g/	1 6.59	7.46	8.61
$G(-CH_3SNa)^+$	15.4	11.3	2.5

* Apparent G, Molecules/100 ev.

From Tables 4.2 and 4.4.

+ G calculated from initial slope of curve in Figs 4.1 and 4.2.

G(S) Yield of polysulfide excess sulfur.

Dose Mrad										
CH ₃ SNa, g/1	8.61	8.60	8.59	8.55	8.51	8.47	8.45	8.48	8.21	8.26
Molecu. x 10 ²⁰	740.0	739.4	737.7	734.3	731.3	727.9	726.4	728.2	705.5	709.8
сн _з sscн ₃										
$x 10^{-3} g/1$	6.67	9.25	11.35	13.60	15.15	15.90	17.00	17.47	18.58	20.47
рН	13.54	13.55	13.53	13.•53	13.54	13.55	13,48	13.46	13.42	13.35
CH ₃ SNa, g/1	7.46	7.16	7.09	6.76	6.71	6.51	6.42	6.45	6.27	6.21
Molecu. $x 10^{20}$	641.3	614.8	608.8	580.8	576.5	559.2	551.2	554.2	538.7	533•5
рН 	12.54	12.46	12.45	12.42	12.43	12.35	12.37	12.34	12 . 32	12.27
CH ₃ SNa, g/1	6.59	6.42	6.03	6.17	5.64	5.26	5.13	5.21	4.80	4.48
Molecu. $x 10^{20}$	566.2	551.2	535.2	530.0	484.9	451.7	441.1	447.9	412.6	385.0
рH	10.70	10.85	10.93	10.95	11.03	11.10	11.24	11.41	11.48	11.57

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Table 4.4 Gamma radiolysis of sodium methyl mercaptan in various pH solutions at Gammacell temperature (34°C).

Replications, n=2.

	CI	I, SCH,	CH3SSCH3					
Dose <u>M</u> rad	x10 ⁻³ g/1	Molecu.x10 ²⁰	$x 10^{-3} g/1$	Molecu.x10	20 pH			
0.0	91.0	8.82	163.6	10.46	13.12			
0.1	86.5	8.38	153.3	9.81	13.15			
0.3	78.2	7.58	136.5	8.73	13.13			
0.5	69.8	6.76	125.0	8.00	13.13			
0.7	59•5	5.77	117.0	7.48	13.15			
0.9	51.5	4.99	105.5	6.75	13.17			
1.5	36.3	3.52	84.1	5.38	13.15			
2.0	30.2	2.93	75.8	4.85	13.16			
2.5	24.0	2.32	61.9	3.96	13.15			
3.0	21.2	2.05	52.9	3.38	13.17			
3.5	16.0	1.55	47.8	3.05	13.15			
4.0	10.5	1.01	42.1	2.69	13.14			
4.5	6.3	0.61	33.5	2.14 .	13.13			

Replications, n=4.

Table 4.6 Gamma radiolysis of dimethyl sulfide and dimethyl disulfide in sulfate black liquor (2-1) at Gammacell temperature (34°C).

_	CI	H3 SCH3	C		
Dose Mrad	x10 ⁻³ g/1	Molecu.x10 ²⁰	x10 ⁻³ g/1	Molecu.x10 ²⁰	pH
0.0	171.8	16.65	207.5	13.27	13.14
0.1	171.4	16.61	203.6	13.02	13.14
0.3	169.3	16.42	202.9	12.97	13.14
0.5	162.5	15.77	200.6	12.83	13.14
0.7	161.0	15.61	195.8	12.52	13.14
0.9	135.8	13.16	180.1	11.52	-
1.5	127.9	12.40	178.6	11.42	13.14
2.0	121.9	11.82	169.8	10.86	-
2.5	117.5	11.40	145.3	9.29	13.12
3.0	99.8	9.67	140.6	8.99	-
3.5	94.0	9.11	133.9	8.56	13.12
4.0	89.0	8.63	128.6	8.18	-
4.5	82.8	8.0	117.8	7•53	13.10

Replications, n=4.

Table 4.7 Gamma radiation degradation yields(G)^{*} of dimethyl sulfide and dimethyl disulfide in alkaline aqueous solution and black liquor (2-1).

Sources.	G(-CH ₃ SCH ₃)	G(-CH ₃ SSCH ₃)		
Aq. Solution	0.73	0.89		
(pH 13.12)				
Black liquor	0.50	0.43		
(pH 13.14)				

* Apparent G, Molecules/100ev.

G Calculated from initial slope of curves in Fig. 4.3.

Table 4.8	Effect sulfide	of sol and d	lution limethy	pH on yl disu	gamma. 1fide.	radiol	ysis (3 Mrad	l) of d	limethy	1	
Initial pH	0.5	2.5	4.4	5.5	6.5	7.5	8.4	9•7	10.1	11.5	13 . Ő	13.5
CH ₃ SCH ₃ , x	10 ⁻³ g/1	. .										
Initial Conc.	91.0	91.0	91.0	91.0	91.0	88.0	80.0	75.0	75.0	75.0	75.0	75.0
Final conc.	8.0	16.0	22.5	25.5	24.2	26.0	29.0	29.5	33. 0'	35.0	37.0	42.0
Decomp., %	91.2	82.4	75•3	72.0	73•5	70.5	63.8	60.7	56.0	53.3	50.7	44.0
G*	0.43	0.39	0.30	6 0.34	0.35	5 0.32	2 0.26	0.24	0.22	0.21	0.20	0.17
#* G/Co	203.5	266.2	245.7	232.1	238.9	226.0	201.9	198.8	182.3	174.0	165.7	140.9
u/ 00	~) / • /											
Initial pH	1.5	2.5	4.4	5.5	7.0	8.4	9.7	10.1	11.5	12.5	13.0	13.5
Initial pH CH_SSCH, x	1.5 10 ⁻³ g/1	2.5	4.4	5.5	7.0	8.4	9.7	10.1	11.5	12.5	13.0	13.5
Initial pH CH SSCH , x 3 3 Initial	1.5 10 ⁻³ g/1 165.0	2.5 170.0	4.4	5.5 182.0	7.0	8.4	9.7 160.0	10.1 160.0	11.5 160.0	12.5 160.0	13.0	13.5
Initial pH CH SSCH, x 3 3 Initial conc. Final conc.	1.5 10 ⁻³ g/1 165.0 29.0	2.5 170.0 26.5	4.4 178.0 32.5	5.5 182.0 36.0	7.0 184.0 44.5	8.4 170.0 50.0	9.7 160.0 54.5	10.1 160.0 56.0	11.5 160.0 47.5	12.5 160.0 44.0	13.0 160.0 42.0	13.5 160.0 47.0
Initial pH CH SSCH , x 3 Initial conc. Final conc. Decomp., %	1.5 10 ⁻³ g/1 165.0 29.0 82.4	2.5 170.0 26.5 84.4	4.4 178.0 32.5 81.7	5.5 182.0 36.0 80.2	7.0 184.0 44.5 75.8	8.4 170.0 50.0 70.6	9.7 160.0 54.5 65.9	10.1 160.0 56.0 65.0	11.5 160.0 47.5 70.3	12.5 160.0 44.0 72.5	13.0 160.0 42.0 73.8	13.5 160.0 47.0 70.6
Initial pH CH SSCH , x 3 3 Initial conc. Final conc. Decomp., % G*	1.5 $10^{-3} g/1$ 165.0 29.0 82.4 0.47	2.5 170.0 26.5 84.4 0.49	4.4 178.0 32.5 81.7 0.50	5.5 182.0 36.0 80.2 0 0.50	7.0 184.0 44.5 75.8 0 0.48	8.4 170.0 50.0 70.6 3 0.41	9.7 160.0 54.5 65.9 0.36	10.1 160.0 56.0 65.0	11.5 160.0 47.5 70.3 5 0.38	12.5 160.0 44.0 72.5 0.40	13.0 160.0 42.0 73.8 0.40	13.5 160.0 47.0 70.6 0.39

* Molecules/100ev.

** Molecules/Mol. 100ev.

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g/1	0.0	10.0	30.0	50.0	70.0	100.0	120.0
1.5 Mrad, CH ₃ SCH ₃	initia	l conc.	, Co=1	65.0 x	10-3	g/1	
CH ₃ SCH ₃ ,x10 ⁻³ g/1	105.8	119.6	131.3	133.3	126.1	-	128.7
Decomp., %	35.88	27.52	20.42	19.21	23.58	-	22.00
G*(-СН ₃ SCH ₃)	0.61	0.47	0.35	0.33	0.40	-	0.38
3.0 Mrad							
CH3 SCH3, x10 ⁻³ g/1	69.0	85.0	96.0	95.0	88.0	82.0	81.1
Decomp., %	58.18	50.00	41.82	42.42	46.67	50.31	50.91
G(-CH ₃ SCH ₃)	0.50	0.41	0.36	0.36	0.40	0.43	0.44
1.5 Mrad, CH ₃ SSCH		al conc	., Cø=	190.0 :	×10 ⁻³ g	/1	
CH ₃ SSCH ₃ ,x10 ⁻³ g/1	102.5	139.0	140.0	139.0	145.0	135.0	130.0
Decomp., %	46.05	26.84	26.31	26.85	23.68	28.95	36.84
G(-CH3SSCH3)	0.60	0.35	0.34	0.35	0.31	0.38	0.47
3.0 Mrad							
CH ₃ SSCH ₃ ,x10 ⁻³ g/1	75.00	104.0	102.0	96.0	90.0	86.0	91.5
Decomp., %	60.35	45.26	46.23	49.47	52.63	54.74	51.84
G(-CH SSCH ₃)	0.39	0.29	0.30	0.32	0.33	0.36	0.34
Average G**	0.53	0.38	0.34	0.34	0.36	0.39	0.41
pH 3 Mrad	13.12	13.07	12.81	12.10	10.90	10.12	9.08

*Molecules/100ev.

** Average G value of dimethyl sulfide and dimethyl disulfide.

Table 4.10 Effect of temperature on gamma radiolysis of dimethyl sulfide and dimethyl disulfide in black liquor (1-3) under 50 psi initial oxygen pressure.

Max Temp. ^o C.	60	77	83	103	115	
3 Mrad, CH ₃ SCH ₃ init	tial conc	., Co=1	.60.00×10 ⁻³	g/1		
CH ₃ SCH ₃ ,x10 ⁻³ g/1	75.83	60.00	53.08	50.42	36.08	
Decomp., %	52.88	62.50	66.83	68.28	77.45	
G*C-CH3SCH3)	0.44	0.52	0.55	0.57	0.64	
Control, 305 min, Cl	H ₃ SCH in	tial co	onc., Co=16	0.00x10	-3 _{g/1}	
CH ₃ SCH ₃ ,x10 ⁻³ g/1	104.55	87.08	73•75	71.76	70.00	
Decomp., %	34.79	45.58	53.91	55.21	56.25	
3 Mrad, CH ₃ SSCH ₃ in:	itial con	Co=	130.00x10	³ g/1		<u>,</u>
CH ₃ SSCH ₃ ,x10 ⁻³ g/1	36.42	13.50	1.77	0.60	0.00	
Decomp., %	71.98	89.62	98.64	99•54	100.00	
G*(-CH ₃ SSCH ₃)	0.34	0.42	0.46			
Control, 305 min, Cl	H SSCH i	nitial	conc., Co=	130.00x:	10 ⁻³ g/1	
CH3SSCH3, x10 ⁻³ g/1	56.17	45.00	34.92	36.47	21.75	
Decomp., %	56.79	65.38	73.14	71.95	83.27	
3 Mrad	12.51	12.26	11.18	11.11	10.00	
Control	12.67	12.61	12.45	12.47	11.42	

Replications, n=3 * Molecules/100ev.

Table 4.11 Effect of temperature on gamma radiolysis of dimethyl sulfide and dimethyl disulfide in carbonated black liquor (2-1) under 50 psi initial oxygen pressure.

Max. Temp. ^o C.	77	83	103	115		
3 Mrad, CH ₃ SCH ₃ initial conc., $Co=54.17 \times 10^{-3} g/1$						
сн ₃ sch ₃ , x10 ⁻³ g/1	22.08	16.25	11.92	6.67		
Decomp., %	59.24	70.00	78.00	87.68		
G*(-CH SCH)	0.17	0.20	0.22	0.25		
Control, 299 min, CH	3 ^{SCH} 3 init	ial conc.	, Co=54.17x1	.0 ⁻³ g/1		
CH ₃ SCH ₃ ,x10 ⁻³ g/1	35.83	29.13	23.08	21.37		
Decomp., %	33.86	46.22	57.39	59.22		
3 Mrad, CH ₃ SSCH ₃ ini	3 Mrad, CH_3SSCH_3 initial conc., $Co=97.92 \times 10^{-3} g/1$					
CH ₃ SSCH ₃ ,x10 ⁻³ g/1	45.21	10.25	4.09	2.16		
Decomp., %	53.82	89.53	95.82	97•79		
G*(-CH3SSCH3)	0.18	0.29	0.31	0.34		
Control, 297 min, CH_3SSCH_3 initial conc., $Co=97.92 \times 10^{-3} g/1$						
CH3 SSCH3, x10 ⁻³ g/1	62.50	38.33	25.67	20.71		
Decomp., %	36.17	60.80	73.78	78.86		
Mrad	7.94	8.12	8.07	7.92		
Control	8.19	8.00	8.14	8.10		

Replications, n=3 *Molecules/100ev. Table 4.12 Effect of oxygen pressure on gamma radiolysis of dimethyl sulfide and dimethyl disulfide in black liquor (2-1) at Gammacell temperature (34°C).

Oxygen Pressure psi	25	50	75	100		
3 Mrad, CH SCH initial $3 3$	conc., Co=0	63.01x10 ⁻³ 6	g/1			
CH ₃ SCH ₃ ,x10 ⁻³ g/1	31.50	11.17	7.51	3.95		
Decomp., %	50.00	81.70	87.99	93•73		
G*(-CH ₃ SCH ₃)	0.16	0.27	0.29	0.31		
Control, 294 min, CH_3SCH_3 initial conc., $Co=63.01 \times 10^{-3} g/1$						
CH ₃ SCH ₃ ,x10 ⁻³ g/1	45.58	35.17	23.17	18.08		
Decomp., %	22.90	44.18	63.23	71.31		
3 Mrad, CH_3SSCH_3 initial conc., $Co=43.63 \times 10^{-3} g/1$						
CH ₃ SSCH ₃ ,x10 ⁻³ g/1	19.08	12.25	6.00	4.58		
Decomp., %	56.26	71.92	86.25	89.50		
G*(-CH ₃ SSCH ₃)	0.08	0.11	0.13	0.14		
Control, 294 min, CH_3SSCH_3 initial conc., $Co=43.63 \times 10^{-3} g/1$						
CH ₃ SSCH ₃ ,x10 ⁻³ g/1	35.42	27.68	22.25	9•71		
Decomp., %	18.79	36.56	49.00	77.74		

Replications, n=3. * Molecules/100ev. Table 4.13 Effect of oxygen pressure on gamma radiolysis of dimethyl sulfide and dimethyl disulfide in carbonated black liquor (2-1) at Gammacell temperature (34°C).

Oxygen pressure psi	25	75	100
3 Mrad, CH ₃ SCH ₃ initi	al conc.,	Co=54.17x	$10^{-3}g/1$
CH ₃ SCH ₃ ,x10 ⁻³ g/1	18.33	10.27	6.67
Decomp., %	66.16	81.04	87.67
G*(=CH3SCH3)	0.21	0.26	0.28
Control, 294 min, CH ₃	SCH ₃ init	ial conc.,	Co=54.17x10 ⁻³ g/1
CH ₃ SCH ₃ ,x10 ⁻³ g/1	38.28	26.00	23.07
Decomp., %	29.33	52.00	57.41
3 Mrad, CH ₃ SSCH ₃ init	ial conc.	, Co=97.92	x10 ⁻³ g/1
CH ₃ SSCH ₃ , x10 ⁻³ g/1	52.17	38.64	21.67
Decomp., %	46.72	60.72	77.87
G*(+CH3SSCH3)	0.16	0.20	0.26
Control, 294 min, CH ₃	SSCH ₃ ini	tial conc.	, Co=97.92x10 ⁻³ g/2
сн ₃ ssch ₃ , x10 ⁻³ g/1	68.33	64.17	42.08
Decomp., %	30.22	34.47	57.03

Replications, n=3.

*Molecules/100ev.

Table 4.14	Potentiometric titration of mono- and polysulfide
	in 4 ml gamma irradiated black liquor (3-1).

	Consumpti	Consumption of 0.05N AgNO3, m1				
Dose Mrad	Monosulfide ^a	Polysulfide ^b	pH			
0.0	7.24	4.52	13.32			
0.06	6.64	4.60	13.32			
0.12	6.56	4.65	13.32			
0.24	6.42	4.96	13.31			
0.37	5.20	5.12	13.31			
0.49	4.40	5.46	13.32			
0.61	2.74	6.14	13.32			
0.92	0.32	6.80	13.31			
1.22	0.26	5.85	13.29			
1.52	0.19	4.05	13.29			
1.83		3.64	13.30			
2.13		2.79	13.25			
2.44		1.87	13.25			

Replications, n=2.

Radiolysis at Gammacell temperature (34°C) a. Inflection "a" of potentiometric titration curve. b. Inflection "b" of potentiometric titration curve.

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polysulfide black liquors.						
Dose Mrad	0.0	1.0	2.0	3.0	4.0	5.0
1-2 СH ₃ SCH ₃ ,x10 ⁻³ ,g/1	1.10	0.96	0.73	0.60	0.46	0.37
Molecu.x10 ^{±7}	106.6	93.4	70.8	57.8	44.6	36.2
1-4 СH ₃ SCH ₃ ,x10 ⁻³ ,g/1	0.25	0.21	0.11	0.06	0.01	
Molecu.x10 ¹⁷	24.2	20.4	10.3	3.5	1.0	-
²⁻¹ CH ₃ SCH ₃ ,x10 ⁻³ ,g/1	0.56	0.45	0.30	0.19	0.14	0.07
Molecu.x10 ¹⁷	54.6	43.6	29.1	18.4	13.6	6.5
3-1 CH ₃ SCH ₃ ,x10 ⁻³ ,g/1	0.20	0.09	0.06	0.02	<u></u>	
Molecu. $x10^{17}$	19.4	12.0	5.8	2.3	-	-
4-1L CH ₃ SCH ₃ ,x10 ⁻³ ,g/1	0.39	0.31	0.21	0.07	0.04	0.01
Molecu.x10 17	38.1	29.1	20.4	6.8	3.6	1.0

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Table 4.15 Gamma radiolysis of dimethyl sulfide in sulfate and

Replications, n=3.
Dose Mrad	0.0	1.0	2.0	3.0	4.0	5.0
1-1 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	7.58	4.30	3.44	2.96	1.71	1.06
18 Molecu.x10	48.5	27.5	22.0	18.7	10.9	6.8
1-2 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	6.53	5.00	3.67	2.90	1.03	0.71
Molecu.x10 ¹⁸	19.2	15.4	9.3	5.1	4.4	3.1
1-3 CH ₃ SSCH ₃ ,×10 ⁻³	3.00	2.41	1.41	0.81	0.69	0.49
Molecu.x10 ¹⁸	41.8	32.1	23.0	18.5	6.6	4.5
1-4 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	0.44	0.27	0.15	0.09	0.03	0.01
Molecu.x10 ¹⁸	2.8	1.8	1.0	0.6	0.2	0.1
²⁻¹ CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	17.08	15.42	11.36	9.15	7.65	5.58
Molecu.x10 ¹⁸	109.3	98.6	72.7	58.5	48.9	35.7
3-1 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	2.10	0.69	0.44	0.27	0.16	0.07
Molecu.x10 ¹⁸	13.4	4.4	2.8	1.7	1.0	0.4
4-1L CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	39.71	35.90	30.29	23.87	21.15	18.66
Molecu.x10 ¹⁸	253.9	229.6	193.7	152.8	135.3	119.3
4-2V CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	5.06	4.63	3.16	2.27	1.34	0.52
Molecu.x10 ¹⁸	32.4	29.6	20.2	14.5	8.6	3.3

Table 4.16 Gamma radiolysis of dimethyl disulfide in sulfate and polysulfide black liquors.

Replications, n=3.

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Table 4.17 Gamma radiolysis of unidentified sulfur compound (X) in sulfate and polysulfide black liquors at Gammacell temperature (34°C)

Dose Mrad	0.0	1.0	2.0	3.0	4.0	5.0	
¹⁻¹ X,x10 ⁻³ ,g/1	6.49	5.11	3.58	1.91	0.64	0.28	
1-2 X,x10 ⁻³ ,g/1	10.73	6.98	4.38	2.30	1.08	0.69	
1-3 X,x10 ⁻³ ,g/1	8.10	6.37	1.31	0.36	0.22	0.11	
$x^{1-4}, x^{10}^{-3}, g/1$	0.36	0.21	0.09	0.05	0.02	0.01	
2-1 X,x10 ⁻³ ,g/1	102.00	92.15	79.12	69.38	62.50	59.17	
3-1 X,x10 ⁻³ ,g/1	85.00	56.10	47.39	33.50	24.51	20.34	
4-1L X,x10 ⁻³ ,g/1	50.21	44.58	25.63	23.33	18.54	12.17	
4-2V X,x10 ⁻³ ,g/1	4.48	2.67	1.63	1.05	0.78	0.53	

Replications, n=3.

Quantitative determination from dimethyl sulfide calibration curve.

Sources	G(-CH ₃ SCH ₃)	G(-CH ₃ SSCH ₃)	
1-1	· · · · · · · · · · · · · · · · · · ·	0.034	· · · · · · · · · · · · · · · · · · ·
1-2	0.003	0.006	
1-3		0.016	
1-4	0.001	0.002	
2-1	0.002	0.045	
3-1	0.001	0.014	
4-1L	0.002	0.085	
4-2 V		0.005	

Table 4.18 Gamma radiation degradation yield(G)* of dimethyl sulfide and dimethyl disulfide in the various sulfate and polysulfide black liquors.

* Apparent G, Molecules/100ev.

G Calculated either from initial slope of curves in Figs. 4.12, 4.13 or estimated from Table 4.15. Table 4.19

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Gamma radiolysis of hydrogen sulfide in carbonated sulfate and polysulfide black liquors at Gammacell temperature (34°C).

Mrad	0.0	1.0	2.0	3.0	4.0	5.0
H_2^{1-1} , x10 ⁻³ , g/1	116.44	34.65	15.45	7.00	2.21	0.69
Molecu.x10 ¹⁹	205.8	61.2	27.3	12.4	3.9	1.2
1^{-2} H ₂ S,x10 ⁻³ ,g/1	0.89	0.42	0.23	0.15	0.10	0.04
Molecu.x10 ¹⁹	1.6	0.7	0.4	0.3	0.1	0.1
1-3 H ₂ S,x10 ⁻³ ,g/1	182.19	94.71	30.93	16.10	8.00	2.04
Molecu.x10 ¹⁹	322.0	167.4	54.7	28.5	14.1	3.6
H_2^{1-4} , x10 ⁻³ ,g/1	2.57	0.74	0.42	0.23	0.13	0.08
Molecu.x10 ¹⁹	4.5	1.3	0.7	0.4	0.2	0.1
H_2^{2-1} , g/1	16.23	9.28	2.79	1.67	0.59	0.30
Molecu.x10 ¹⁹	28.7	16.4	4.9	3.0	1.0	0.5
$\frac{3-1}{H_2^{5,x10^{-3}},g/1}$	2.87	1.00	0.54	0.41	0.20	0.13
Molecu.x10 ¹⁹	5.1	1.8	1.0	0.7	0.3	0.2
4-1L H ₂ S,x10 ⁻³ ,g/1	265.20	159.45	131.40	81.19	15.42	6.99
Molecu.x10 ¹⁹	468.7	281.8	232.2	143.5	27.3	12.3
$\frac{4-2v}{H_2s,x10^{-3},g/1}$		1.18	0.56	0.41	0.18	0.14
Molecu.x10 ¹⁹	5.5	2.1	1.0	0.7	0.3	0.3
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Replications, n=3.

Table 4.20 Gamma radiolysis of methyl mercaptan in carbonated sulfate and polysulfide black liquors.

Dose Mrad	0.0	1.0	2.0	3.0	4.0	5.0
1-1 CH ₃ SH,x10 ⁻³ g/1	4.13	1.70	0.65	0.46	0.30	0.17
Molecu.x10 ¹⁸	51.8	21.3	8.2	5.7	3.7	1.4
1-2 CH ₃ SH,x10 ⁻³ g/1	1.57	0.70	0.35	0.18	0.08	0.04
Molecu.x10 ¹⁸	19.6	8.6	4.1	2.3	1.0	0.5
1-3 CH ₃ SH,x10 ⁻³ g/1	28.70	17.25	11.05	8.00	3.63	1.22
Molecu.x10 ¹⁸	359.3	216.0	138.4	100.1	45.5	15.3
1-4 CH ₃ SH,×10 ⁻³ g/1	7.30	4.16	1.55	0.67	0.36	0.19
Molecu.x10 ¹⁸	91.4	52.1	19.5	8.4	4.5	2.4
²⁻¹ CH ₃ SH,x10 ⁻³ g/1	13.15	7.84	4.27	1.40	0.67	0.35
Molecu.x10 ¹⁸	164.7	98.2	53.5	17.5	8.4	4.2
3-1 CH ₃ SH,x10 ⁻³ g/1	1.25	0.59	0.33	0.19	0.10	0.05
Molecu.x10	15.7	7.4	4.1	2.4	1.2	0.6
4-1L CH_SH,x10 ⁻³ g/1	73.87	49.75	32.73	22.55	10.38	6.80
Molecu.x10 ¹⁸	925.0	623.0	409.9	282.4 1	29.9	85.1
4-2v CH ₃ SH,x10 ⁻³ g/1	0.48	0.21	0.10	0.06	0.03	0.01
Molecu.10 ¹⁸	6.0	2.6	1.3	0.8	0.4	0.1
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Replications, n=3.

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Table 4.21	Gamma radiolysis of dimethyl sulfide in carbonat	;ed
	sulfate and polysulfide black liquors.	

Dose Mrad	0.0	1.0	2.0	3.0	4.0	5.0
1-1 CH ₃ SCH ₃ ,x10 ⁻³	1.16	0.90	0.49	0.23	0.07	0.03
Molecu.x10 ¹⁷	112.1	87.6	47.5	22.6	6.8	2.9
1-2 CH ₃ SCH ₃ ,x10 ⁻³	5.22	3.96	2.64	1.97	1.20	0.81
Molecu.x10 ¹⁷	506.0	383.9	255.9	191.0	116.0	79.5
1-3 CH ₃ SCH ₃ ,x10 ⁻³	1.62	0.91	0.69	0.46	0.31	0.13
Molecu.x10 ¹⁷	156.7	88.5	67.2	44.6	30.4	12.6
1-4 CH ₃ SCH ₃ ,x10 ⁻³	0.60	0.42	0.19	0.13	0.04	0.02
Molecu.x10 ¹⁷	58.2	40.7	18.4	12.6	4.2	1.6
2-1 CH ₃ SCH ₃ ,x10 ⁻³	1.62	1.05	0.66	0.54	0.31	0.23
Molecu. $x10^{17}$	156.7	108.3	63.7	52.3	30.4	22.0
³⁻¹ сн ₃ sсн ₃ , x10 ⁻³	3.27	2.48	1.83	1.10	0.79	0.69
Molecu.x10 ¹⁷	313.4	240.1	177.7	106.3	76.3	66.6
4-1L CH ₃ SCH ₃ ,x10 ⁻³	4.53	3.32	2.15	0.94	0.61	0.49
$Molecu.x10^{17}$	439.5	321.5	205.2	90.8	59 .1	47.5
$\frac{4-2V}{CH_3SCH_3, x10^{-3}}$	0.95	0.76	0.42	0.17	0.08	0.04
Molecu.x10 ¹⁷	92.1	73•7	40.7	16.5	7.8	3.9

Replications, n=3.

Table 4

.22	Gamma r	adiolysis	of dime	ethyl (disulfide	in	carbonated
	sulfate	and poly	sulfide	black	liquors.		

Dose						
Mrad	0.0	1.0	2.0	3.0	4.0	5.0
1-1 -3	• -					
CH ₃ SSCH ₃ ,x10,g/1	4.81	2.40	1.65	1.35	0.65	0.39
Molecu.x10 ¹⁷	307.4	153.7	105.5	86.3	41.6	25.2
1-2 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	1.03	0.60	0.38	0.25	0.16	0.10
Molecu.x10 ¹⁷	65.7	38.6	24.1	15.6	10.1	6.6
1-3 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	2.06	1.43	1.04	0.55	0.28	0.15
Molecu.x10 ¹⁷	131.7	91.4	66.5	34.3	18.1	9.6
1-4 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	1.80	0.92	0.48	0.26	0.12	0.06
Molecu.x10 ¹⁷	114.9	59.0	30.5	16.8	7.7	3.6
²⁻¹ CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	9.11	5.70	4.80	3.93	2.83	1.65
Molecu.x10 ¹⁷	582.5	364.5	306.9	251.1	181.2	105.5
3-1 CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	1.11	1.09	0.62	0.33	0.26	0.14
Molecu.x10 ¹⁷	105.9	69.9	39.6	27.1	15.1	8.7
4-L CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	8.00	4.72	2.68	1.83	1.53	1.03
Molecu.x10 ¹⁷	511.6	301.8	171.4	116.8	98.1	65.9
4-2V CH ₃ SSCH ₃ ,x10 ⁻³ ,g/1	2.93	1.62	1.12	0.64	0.35	0.21
Molecu.x10 ¹⁷	187.6	103.6	71.8	40.7	22.4	13.4

Replications, n=3.

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Dose Mrad	0.0	1.0	2.0	3.0	4.0	5.0
1-1 X, x10 ⁻³	0.47	0.32	0.14	0.06	0.03	0,01
x^{1-2} , x^{10}^{-3}	1.38	0.60	0.38	0.17	0.02	0.06
x^{1-3} , x^{10}^{-3}	6.22	4.28	3.78	2.95	2.25	1.18
x^{1-4} , x^{10}^{-3}	0.36	0.18	0.12	0.08	0.04	0.01
x^{2-1} , x^{10}^{-3}	3.70	2.47	1.42	1.27	0.90	0.44
3-1 X, x10 ⁻³	2.88	1.89	1.08	0.73	0.32	0.11
4-1L X, x10 ⁻³	18.15	14.38	10.00	5.23	3.79	3.01
4-2v X, x10 ⁻³	1.31	0.94	0.44	0.20	0.14	0.06

Table 4.23 Gamma radiolysis of unidentified sulfur compound (X) in carbonated sulfate and polysulfide black liquors.

Replications, n=3.

Quantitative determination from dimethyl sulfide calibration curve.

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Table 4.24 Gamma radiation degradation yields(G)* of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide in the various carbonated black liquors.

Sources	pH [#]	$G(-H_2S)$	G(-CH ₃ SCH)	G(-CH3SCH3)	G(-CH3SSCH3)
1-1	8.20	2.720	0.049	0.004	0.025
1-2	8.50	0.015	0.018	0.020	0.004
1-3	8.75	3.147	0.230	0.010	0.007
1-4	8.45	0.051	0.063	0.003	0.009
2-1	9.00	0.306	0.107	0.008	0.035
3-1	8.50	0.053	0.013	0.012	0.006
4-1L	9.15	3.427	0.518	θ.020	0.034
4-2V	8.20	0.055	0.006	0.003	0.014

* Apparent G, Molecules/100ev.

- G Calculated either from initial slope of curves in Figs. 4.17, 4.18, 4.19 and 4.20, or estimated from Tables 4.19, 4.20, 4.21, and 4.22.
- # Initial pH.

Table 4.25 Effect of nitrogen, air, and oxygen atmospheres on gamma radiolysis of sulfides in carbonated black liquor(1-1).

Dose Mrad	0.0	0.5	1.0	2.0	3.0	<u> </u>
H_2 s, x10 ⁻³ g/1	L					
N_2 -atmo.	607.50	472.50	342.00	146.92	105.00	
Molecu.x10 ²⁰	107.4	83.5	60.4	26.0	18.6	
Air-atmo.	387.00	256.00	109.33	8.45	2.93	
Molecu.x10 ²⁰	68.4	45.3	19.3	1.5	0.5	
0 ₂ -atmo.	247.75	21.34	14.68	6.99	1.93	
Molecu.x10 ²⁰	43.8	3.8	2.6	1.2	0.3	
CH ₃ SH, x10 ⁻³ g/	1					
N ₂ -atmo. 1	1935.00	1741.50	1665.00	1135.50	1035.00	
Molecu.x10 ²⁰	242.3	218.1	208.5	142.2	129.6	
Air-atmo. 1	645.00	1246.50	976.50	335.50	98.25	
Molecu.x10 ²⁰	206.0	156.1	122.3	42.0	12.3	
0 ₂ -atmo.	967.50	481.50	323.25	229.95	32.41	
Molecu.x10 ²⁰	121.2	60.3	40.5	28.8	4.1	
CH ₃ SCH ₃ ,x10 ⁻³	g/1					
$N_2 - a tmo$.	108.00	103.25	95.45	86.40	81.90	
Molecu.x10 ¹⁹	104.7	100.1	92.5	83.8	79.4	
Air-atom.	107.40	85.95	80.35	58.80	52.88	
Molecu.x10 ¹⁹	104.1	83.3	77•9	57.0	51.3	
$0_2 - a tmo$.	106.25	81.45	75.55	54.00	38.82	
Molecu.x10 ¹⁹	103.0	79.0	73.2	52.3	37.6	
CH3SSCH3, x10	³ g/1					
N_2 -atmo. 2	295.00	2340.00	2070.00	1752.00	1305.50	
Molecu.x10 ²⁰	146.8	149.6	132.4	112.0	83.5	3
Air-atom. 2	565.00	2835.00	2695.00	2272.50	1287.00	
Molecuax10 ²⁰	164.0	181.3	172.3	145.3	82.3	_
$0_2 - a tmo$. 3	217.50	3195.00	2835.00	2137.50	967.50	-
Molecu.x10 ²⁰ Replications.	$\frac{205.7}{n=2}$	204.3	181.3	136.7	61.9	

Initial pH 7.50

Table 4.26 Effect of nitrogen, air and oxygen atmospheres on gamma radiation degradation yield(G)* of hydrogen sulfide, methyl mercaptan and dimethyl sulfide in the carbonated black liquor(1-1).

Atmospheres	$G(-H_2S)$	G(-CH ₃ SH)	G(-CH ₃ SCH ₃) 0.19 0.43	
Nitrogen	8.5	10.2		
Air	9•7	18.5		
Oxygen	16.7	28.0	0.74	

* Apparent G, Molecules/100ev.

G Calculated from initial slope of curves in Figs. 4.26, 4.27 and 4.28.

	liquor.					
Treatment	Initial	Dose	Poly-S		H ₂ SO4	
	Na ₂ S,g/1	Mrad	g/1	G(S)	g/1	G(H ₂ SO ₄)
CO ₂ , 120 ps	si during i	rradiat	ion, Na ₂ 5	solutio	n.	
A.	20	11.8	0.875	2.23	0.218	0.18
5 min*	20	11.8	0.975	2.49	0.189	0.16
B.	20	11.8	0.575	1.47	0.222	0.19
в.	20	1.2	0.060	1.53		-
в.	20	5•9	0.310	1.58	0.240	0.40
CO ₂ , 120 ps	si during i	rradiat	ion, Na ₂ 9	solutio	n.	
1 hr.*	20	5.9	0.375	1.91	0.188	0.31
2 hr.*	20	5.9	0.525	2.68		
3 hr.*	20	5•9	0.515	2.63		
4 hr.*	20	5.9	0.580	2,96	0.160	0.27
5 hr.*	20	5.9	0.375	1.91	0.182	0.30
A .	20	5.9	0.485	2.48	0.183	0.31
H ₂ S, 270 ps	si during i	rradiat	ion, ^{Na} 2 ^S	solution	n.	
1 hr.*	80	11.8	1,200	3.06		
в.	80	11.8	1.550	3.95		
В.	40	17.2	2.450	4.92	0.118	0.07
B.	80	70.8	9.400	4.09	0.540	0.08
H ₂ S, 270 ps	i during i	rradiat:	ion, gree	n liquor	(1-2)	
в.	35.1	30.0	3.800	3.81	0.204	0.07
В.	35.1	60.0	6.625	3.34	0.197	0.03
A : Non-pre	irradiatio	n stirr	i ng			·····

Table 4.27 Gamma radiolysis of carbon dioxide and hydrogen sulfide acidified sodium sulfide and sulfate green

A : Non-preirradiation stirring.B : Stirring during irradiation.

* : Pre-irradiation stirring only.

G : Molecules/100ev.

Figure 2.1 The spectrum of electromagnetic radiation(163)



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Figure 3.2 Potentiometric titration curves of sodium sulfide solution, sulfate white liquor(WL,1-3) and black liquor(BL,1-2) and added methyl mercaptan.



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Figure 3.3 Potentiometric titration curves of sulfide in sulfate white liquor(WL, 1-2) and black liquor(BL, 1-2) in the presence of methyl mercaptan.



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Figure 3.4 Potentiometric titration curves of sodium polysulfide in presence of methyl mercaptan.



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Potentiometric titration curves of sodium sulfide in 1% thiolignin containing Figure 3.5 alkaline solution with and without oxidation and addition of sodium methyl mercaptan.







Figure 3.7 Potentiometric titration curves of methyl mercaptan with and without added elemental sulfur in alkaline solution.



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CONCENTRATION, g, $x10^9$

The calibration curves for hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide Figure 3.8 in carbon tetrachloride.



-254-

Figure 3.10 Steps of carbon tetrachloride liquid/liquid extraction of dimethyl sulfide and dimethyl disulfide from white liquor(WL) and black liquor(BL).

CH3SSCH3 0-0105.7



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Figure 3.11 Effect of solution pH on the efficiency of carbon tetrachloride liquid/liquid extraction.



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Figure 3.13 Gas liquid chromatography(GLC) of carbon tetrachloride extracts of acidified and unacidified black liquor(2-1) samples.



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Figure 3.15 Calibration curve for spectroscopic determination of polysulfide excess sulfur in 3M NaCl and 0.01M NaOH solution.







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Figure 3.17 Calibration curve of thiolignin concentration versus absorbance at 213nm.

Figure 3.18 Relationship of black liquor(BL) pH and carbon dioxide volume bubbled.



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Figure 3.20 Schematic drawing of high pressure and temperature irradiation apparatus.



A. Gas supply B. Reducing valve C. Gas release system a-valve b-gas trap(NaOH, 20%) D. Blow-out assembly E. Pressure gage F. Flexible tube G. Pressure vessel and heating mantle H. Temperature recording a-thermocouple b-ice bottle c-recorder I. Temperature control a-powerstat

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b-power supply



Figure 3.21 Relationship of powerstat setting and pressure vessel temperature.



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Figure 4.1 Gamma radiolysis of sodium sulfide aqueous solution and formation of polysulfide excess sulfur at Gammacell temperature(34°C).

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Figure 4.2 Gamma radiolysis of various pH sodium methyl mercaptan solutions at Gammacell temperature(34°C).

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Gamma radiolysis of dimethyl sulfide and dimethyl disulfide in aqueous Figure 4.3 alkaline solution and black liquor(2-1) at Gammacell temperature.



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Effect of solution pH on gamma radiolysis(3 Mrad) of dimethyl sulfide and Figure 4.4 dimethyl disulfide.



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Figure 4.5 Effect of solution pH on ratios of gamma radiation(3 Mrad) degradation yield(G) and initial concentration(Co).



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Figure 4.6 Effect of lignin concentration on gamma radiolysis of dimethyl sulfide and dimethyl disulfide in aqueous alkaline solution.



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Potentiometric titration of mono- and polysulfide in 4 ml gamma irradiated black liquor(3-1).



Figure 4.11



Figure 4.12 Gamma radiolysis of dimethyl sulfide in sulfate and polysulfide black liquors at Gammacell temperature(34°C).

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Figure 4.13 Gamma radiolysis of dimethyl disulfide in sulfate and polysulfide black liquors at Gammacell temperature(34°C).

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Figure 4.14 Gamma radiolysis of an unidentified sulfur compound(X) in sulfate and polysulfide black liquors at Gammacell temperature(34°C).



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Figure 4.15 Relation of initial concentration and gamma radiation yields of dimethyl sulfide in black liquors.



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Figure 4.16

Relation of initial concentration and gamma radiation degration yields of dimethyl disulfide in black liquors.



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Figure 4.17 Gamma radiolysis of hydrogen sulfide in carbonated sulfate and polysulfide black liquors at Gammacell temperature(34°C).

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Figure 4.18 Gamma radiolysis of methyl mercaptan in carbonated sulfate and polysulfide black liquors at Gammacell temperature(34°C).

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Figure 4.19 Gamma radiolysis of dimethyl sulfide in carbonated sulfate and polysulfide black liquors at Gammacell temperature(34°C).





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Figure 4.22 Relation of initial concentration and gamma radiation degradation yields of hydrogen sulfide in carbonated black liquors.



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Figure 4.23 Relation of initial concentration and gamma radiation degradation yields of methyl mercaptan in carbonated black liquors.

Figure 4.24 Relation of initial concentration and gamma radiation degradation yields of dimethyl sulfide in carbonated black liquors.



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Figure 4.25 Relation of initial concentration and gamma radiation degradation yields of dimethyl disulfide in carbonated black liquors.

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Figure 4.26 Effect of nitrogen, air and oxygen atmospheres on gamma radiolysis of hydrogen sulfide in carbonated black liquor(1-1) at Gammacell temperature (34°C).



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Figure 4.27 Effect of nitrogen, air and oxygen atmospheres on gamma radiolysis of dimethyl sulfide in carbonated black liquor(1-1) at Gammacell temperature (34°C).



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Figure 4.28 Effect of nitrogen, air and oxygen atmospheres on gamma radiolysis of methyl mercaptan and dimethyl disulfide in carbonated black liquor(1-1) at Gammacell temperature(34°C).



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Figure 5.1 Formation of malodorous sulfides from sulfate cooking.

CH3SSCH3 H₂S CH3 SH H,0 02 Lignin OCH3 Lignin-OCH₃ HS 02 CH3SCH3 58

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Figure 5.2 Proposed radio-chemical reactions in gamma radiolysis of sulfate black liquor.

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