Mechanism for the Formation of Elemental Sulfur from Aqueous Sulfide in Chemical and Microbiological Desulfurization Processes

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Mechanism for the Formation of Elemental Sulfur from Aqueous Sulfide in Chemical and Microbiological Desulfurization Processes

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A detailed reaction mechanism is proposed for the formation of crystalline elemental sulfur from aqueous sulfide by oxidation with transition-metal ions like V^V, Fe^{III}, Cu^{II}, etc. The first step is the formation of $HS^•$ radicals by one-electron oxidation of HS^- ions. These radicals exist at pH values near 7 mainly as $S^{•-}$. Their spontaneous decay results in the formation of the disulfide ion S_2^{2-}. The further oxidation of disulfide either by $S^{•-}$ radicals or by the transition-metal ions yields higher polysulfide ions from which the homocyclic sulfur molecules S_6, S_7, and S_8 are formed. In water these hydrophobic molecules form clusters which grow to droplets of liquid sulfur (sulfur sol). Depending on the composition of the aqueous phase, crystallization of the liquid sulfur as either α- or β-S_8 is rapid or delayed. Surfactants delay this solidification, while certain cations promote it. All these reactions are proposed to take place in desulfurization plants working by the Stretford, Sulfolin, Lo-Cat, SulFerox, or Bio-SR processes. In addition, the sulfur produced from sulfide by oxidizing sulfur bacteria is formed by the same mechanism, which now explains many observations made previously (including the formation of the byproducts thiosulfate, polythionates, and sulfate).

Introduction

The removal of sulfide ions (HS^-) from aqueous solutions by oxidative reactions is one of the most important desulfurization processes (Dalrymple et al., 1989). Gases containing H_2S in low concentration may first be scrubbed by alkaline solutions, resulting in aqueous sulfide. There are a number of oxidants to transform the sulfide into elemental sulfur: the Stretford and the Sulfolin processes use vanadium(V) (Hammond, 1986; Heisel and Marold, 1987; Weber, 1986; Wilson and Newell, 1984; The Stretford, 1994), in the Lo-Cat process iron(III) is applied (Ullmann, 1994), and in microbiological processes (Buisman et al., 1989, 1990; Kuenen and Robertson, 1992) sulfur bacteria are active which contain enzymes like cytochromes; these also contain metals (Cu^{2+}, Fe^{3+}) as primary electron acceptors (Fischer, 1984; Takakuwa, 1992; Henkel et al., 1995). The overall process of sulfide oxidation may be represented by eq 1 in which M is a metal capable of cycling between two different oxidation states:

$$HS^- + 2M^{n+} \rightarrow S^0 + H^+ + 2M^{(n-1)+} \qquad (1)$$

The reduced metal ion is then oxidized by dioxygen and therefore just serves as a catalyst:

$$4M^{(n-1)+} + O_2 + 2H^+ \rightarrow 4M^{n+} + 2OH^- \qquad (2)$$
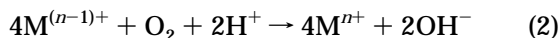
The overall reaction is therefore given by eq 3:

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad (3)$$
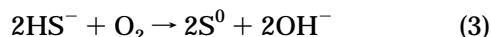
The elemental sulfur formed in reaction (1) is designated as S^0 to indicate the oxidation state of ±0. However, the extreme simplification of eq 1 does not allow a real understanding of the chemistry of such processes. The sulfur formed will consist mainly of cyclic S_8 molecules which have to be built up step-by-

step from precursor molecules or ions. After S_8 has been formed, it has to be transformed into crystals of the right shape and size which can be collected either by flotation or by other separation techniques. A detailed knowledge of the molecular processes going on in these various steps is a prerequisite for optimizing the operating conditions, for minimizing the byproducts, and for obtaining an optimum product quality.

In this paper a detailed mechanistic scheme is presented which explains the formation of solid sulfur from sulfide ions using the Stretford process as an example. However, reference to the other processes will be made whereever appropriate.

In the Stretford process H_2S is stripped from the feed gas by washing with a sodium carbonate solution containing vanadate. From the absorber the rich liquor flows through a delay or reaction tank to the oxidizer tank. Air is pumped into this tank, resulting in formation of a sulfur froth which is separated by flotation. The liquor is pumped to a balance tank to which chemicals and/or water may be added, and the lean liquor is recycled into the absorber. The sulfur froth is collected in a slurry tank, and the elemental sulfur is finally isolated by centrifugation and melting in a separator. The liquid sulfur is pure enough to be sold.

Results

The Catalysts. The Stretford process operates at pH values of between 8.5 and 9.5. A sodium carbonate/hydrogen carbonate buffer is used to maintain the pH in this range. Sodium metavanadate ($NaVO_3$) is added as a catalyst. However, by [51]V NMR spectroscopy it has been shown that under these conditions the vanadium-(V) exists mainly as $[H_nV_2O_7]^{(4-n)-}$ and $[V_4O_{12}]^{4-}$ ions which are in equilibrium (Vermaire and de Haan, 1988):

$$2[H_2V_2O_7]^{2-} \rightleftharpoons [V_4O_{12}]^{4-} + 2H_2O \qquad (4)$$
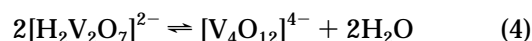
The dinuclear species dominates at higher alkalinities (e.g., 0.57 M Na_2CO_3). The Stretford process was

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introduced in 1959; other processes using vanadium(V) to oxidize H_2S are the Sulfolin (Heisel and Marold, 1987; Weber, 1986) and the Unisulf (Gowdy et al., 1987; Dalrymple et al., 1989) processes.

To assist the reoxidation of V^{IV} to V^V by molecular oxygen, diethanolamine (DEA) is sometimes added, although reoxidation in the absence of DEA is as efficient if the alkalinity is increased (Vermaire and de Haan, 1988). DEA forms complexes with vanadate anions (Crans, 1994). As the reoxidation step is the rate-determining step in this process, it is important to establish the most favorable conditions to facilitate the reoxidation of the reduced liquor. Another means toward this goal is the addition of anthraquinone disulfonic acid (ADA; a mixture of the 2,6- and 2,7-isomers) (Vermaire and de Haan, 1988) which rapidly oxidizes V^{IV} and is regenerated by reaction with molecular oxygen:

$$+ \ 2 \ V^{IV} \ + \ H_2O \longrightarrow \qquad (5)$$

$$+ \ 2 \ V^V \ + \ OH^-$$

$$+ \ O_2 \longrightarrow$$

$$+ \ H_2O_2 \qquad (6)$$
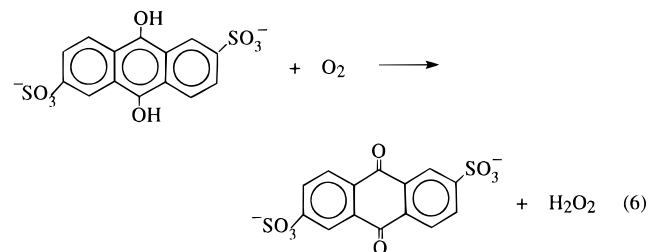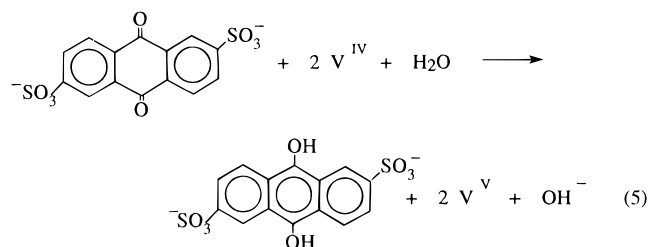
The hydrogen peroxide formed in reaction (6) also helps to oxidize V^{IV} to V^V:

$$2V^{IV} + H_2O_2 \rightarrow 2V^V + 2OH^- \qquad (7)$$
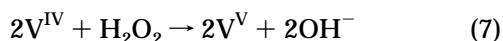
The Lo-Cat and the SulFerox processes use chelate complexes of iron(III) ($500-1500$ g/m^3) as catalysts to oxidize HS^- to S^0. The Fe^{2+} is reoxidized by blowing air into the solution. Similarly, in the Bio-SR processes $Fe_2(SO_4)_3$ is used to oxidize sulfide to S^0, while the reoxidation of the $FeSO_4$ by air is performed by *Thiobacillus ferrooxidans* bacteria (Bio-SR, 1995). The Hyperion process (Dalrymple et al., 1989) applies a hydroquinone iron chelate to oxidize HS^- to S^0.

The above-mentioned transition-metal compounds are all one-electron oxidants, i.e., they take up just one electron at a time from a substrate. This fact is important for the following discussion of the likely intermediates in the transformation of HS^- to S_8.

There is evidence that iron(III) chelate complexes react with H_2S and thiols in water of pH = 6.5 to give mononuclear (thiols) or dinuclear compounds which may be precursors of the electron-transfer process (Philip and Brooks, 1974). In the case of vanadium(V), however, there is no such evidence and it is not likely that the highly oxophilic V^V forms sulfide complexes in water at pH values near 7. However, in strongly alkaline solutions of $NaVO_3$ and HS^-, several thiovanadates have
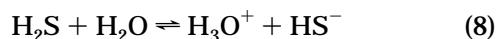
Table 1. First and Second Dissociation Constants of H_2S_n Molecules ($n = 1, ..., 5$) in Water at 20 °C, 0.1 M KCl (Given as pK_a Values) (Giggenbach, 1971; Schwarzenbach and Fischer, 1960)

	pK_1	pK_2
H_2S	7.0	17
H_2S_2	5.0	9.7
H_2S_3	4.2	7.5
H_2S_4	3.8	6.3
H_2S_5	3.5	5.7

been observed by UV and NMR spectroscopy (Hayden and Edwards, 1986).

The enzymes used by sulfur bacteria to oxidize HS^- to S^0 are also one-electron oxidants. Numerous types of sulfur bacteria are capable of carrying out this reaction producing S^0 which is deposited either intra- or extracellularly (Trüper, 1984). As far as the enzymes involved have been characterized, they have been classified as cytochromes (Takakuwa, 1992). These contain iron ions as part of heme groups in which the oxidation state of Fe may cycle between +2 and +3. In cytochrome *c* oxidase the primary electron acceptor is Cu^{2+}, but this enzyme also contains iron (Henkel et al., 1995).

Aqueous Sulfide. In water H_2S is a weak acid which at pH = $7-12.5$ exists predominantly as hydrogen sulfide anion:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad (8)$$

The pK_a values of H_2S and the oligomeric sulfanes H_2S_n are listed in Table 1. The extremely low second dissociation constant of H_2S is responsible for the fact that the S^{2-} ion can only be a minority species in water. The Stretford process and the other desulfurization processes mentioned above operate at pH values near 8.5; therefore, HS^- is the major sulfur species prior to oxidation.

The Oxidation. If HS^- ions are subjected to a one-electron oxidation, free radicals are formed:

$$HS^- \rightarrow HS^\bullet + e^- \qquad (9)$$

In the vapor phase the $HS^\bullet$ radical has been well characterized by UV spectroscopy (Huber and Herzberg, 1979). In solution $HS^\bullet$ has been observed by UV and ESR spectroscopy after pulse radiolysis of aqueous H_2S (Karmann et al., 1967; Mills et al., 1987) as well as on Co-60 irradiation of aqueous sulfide (Zhu et al., 1991). The pK_a value of $HS^\bullet$ is not known, but it has been suspected to be smaller than 7 (Mills et al., 1987; Zhu et al., 1991). If this is so, the radical anion $S^{\bullet-}$ will be the major reactive form rather than $HS^\bullet$ at pH $\geq$ 7:

$$HS^\bullet \rightleftharpoons S^{\bullet-} + H^+ \qquad (10)$$

The sulfur radical anion has been shown to spontaneously react both by dimerization

$$2S^{\bullet-} \rightarrow S_2^{2-} \qquad (11)$$

and by addition to HS^- (Karmann et al., 1967; Mills et al., 1987; Zhu et al., 1991):

$$S^{\bullet-} + HS^- \rightleftharpoons HSS^{\bullet 2-} \qquad (12)$$

The pK_a values of $HSS^{\bullet 2-}$ and its protonated form $HSSH^{\bullet-}$ are not known. But these radical ions rapidly

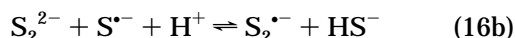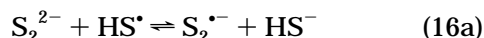decay by the following reactions, resulting in more disulfide formation (Mills et al., 1987):

$$2HSSH^{\bullet-} \rightarrow H_2S_2 + 2H_2S \qquad (13)$$

$$HSSH^{\bullet-} + HS^{\bullet} \rightarrow H_2S_2 + HS^- \qquad (14)$$
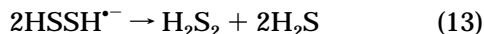
As the data in Table 1 show, H_2S_2 is a much stronger acid than H_2S and at pH values of 8−9 exists basically as disulfide dianion:

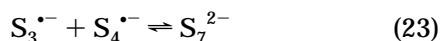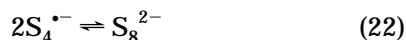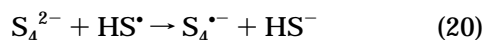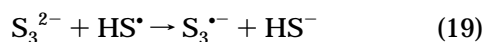$$H_2S_2 \rightleftharpoons H^+ + HS_2^- \rightleftharpoons 2H^+ + S_2^{2-} \qquad (15)$$
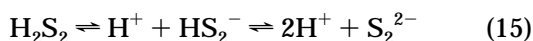
The monoprotonated anion given in eq 15 is a natural intermediate in the dissociation of H_2S_2 but it should be pointed out that species of type HS_n^- ($n > 1$) have never been observed. The disulfide anion formed in eq 15 contains the first sulfur−sulfur bond needed to make S_8 from HS^-. As a 2-fold negative ion, S_2^{2-} will easily give off one electron from its highest-occupied molecular orbital which is of antibonding character (Steudel, 1975). On the other hand, the $HS^{\bullet}$ radical has a high electron affinity (223 kJ mol^{-1} in the vapor phase: Lias et al., 1988). Therefore, the oxidation of S_2^{2-} by $HS^{\bullet}$ or $S^{\bullet-}$ is likely to be exothermic, shifting the equilibrium of reactions (16a,b) to the right.

$$S_2^{2-} + HS^{\bullet} \rightleftharpoons S_2^{\bullet-} + HS^- \qquad (16a)$$

$$S_2^{2-} + S^{\bullet-} + H^+ \rightleftharpoons S_2^{\bullet-} + HS^- \qquad (16b)$$

The disulfide radical ion $S_2^{\bullet-}$ is a well-known species which has been observed in various nonaqueous solvents, in salt melts, and in alkali-metal halide crystals after heating with elemental sulfur (Chivers, 1977; Clark et al., 1983; Fabian and Fischer, 1989). In water $S_2^{\bullet-}$ will either dimerize to tetrasulfide or combine with $S^{\bullet-}$ radicals to form trisulfide:

$$2S_2^{\bullet-} \rightarrow S_4^{2-} \qquad (17)$$

$$S_2^{\bullet-} + S^{\bullet-} \rightarrow S_3^{2-} \qquad (18)$$
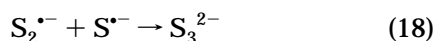
By a number of analogous reactions, larger and larger polysulfide anions are formed. The anions S_3^{2-} and S_4^{2-} can be oxidized by $HS^{\bullet}$ or $S^{\bullet-}$ radicals and thus form hexa-, hepta-, and octasulfide:

$$S_3^{2-} + HS^{\bullet} \rightarrow S_3^{\bullet-} + HS^- \qquad (19)$$

$$S_4^{2-} + HS^{\bullet} \rightarrow S_4^{\bullet-} + HS^- \qquad (20)$$

$$2S_3^{\bullet-} \rightleftharpoons S_6^{2-} \qquad (21)$$

$$2S_4^{\bullet-} \rightleftharpoons S_8^{2-} \qquad (22)$$

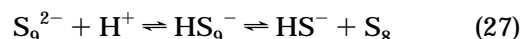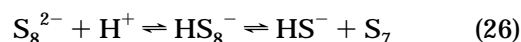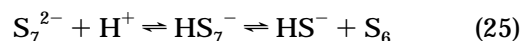$$S_3^{\bullet-} + S_4^{\bullet-} \rightleftharpoons S_7^{2-} \qquad (23)$$

The trisulfide radical anion $S_3^{\bullet-}$ has been observed in aqueous and nonaqueous solutions by UV, ESR, and resonance Raman spectroscopy (Chivers, 1977). Polysul-

fide anions are known to be in equilibrium with each other, and these equilibria are established very rapidly:

$$2S_6^{2-} \rightleftharpoons S_5^{2-} + S_7^{2-} \qquad (24)$$
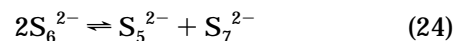
The pH value of the solution determines which species dominate, and as a general rule the chain length n of S_n^{2-} is as larger as the pH value is lower (Giggenbach, 1972). Near or below pH = 7 the formation of elemental sulfur is observed, which can be explained by reactions (25−27):

$$S_7^{2-} + H^+ \rightleftharpoons HS_7^- \rightleftharpoons HS^- + S_6 \qquad (25)$$

$$S_8^{2-} + H^+ \rightleftharpoons HS_8^- \rightleftharpoons HS^- + S_7 \qquad (26)$$

$$S_9^{2-} + H^+ \rightleftharpoons HS_9^- \rightleftharpoons HS^- + S_8 \qquad (27)$$

On acidification of polysulfide solutions H_2S and elemental sulfur are formed. Since the homocyclic molecules S_6 and S_7 are unstable under these conditions, the precipitated sulfur will mainly consist of S_8. However, it has been shown (Tebbe et al., 1982) that elemental sulfur in polar solvents exists as a mixture of S_8 (99% at 20 °C) with S_7 and S_6 (together 1%).

Reactions (25−27) are nucleophilic displacements in which one end of the chainlike HS_n^- ion attacks the other end with formation of a ring and extrusion of the HS^- ion. The removal of S_6, S_7, and S_8 from the equilibrium mixture by precipitation means that also S_7^{2-}, S_8^{2-}, and S_9^{2-} are removed and have to be resupplied by reactions of type (19−24). Finally, all sulfide is transformed this way into elemental sulfur.

At this stage it should be pointed out that some of the reactions just mentioned are not actually necessary to explain the formation of S_8. For example, if reactions (19−23) should not take place, the long-chain polysulfides needed for the ring formation in reactions (25−27) could be supplied by disproportionation of tri- and tetrasulfide formed in reactions (17) and (18):

$$2S_4^{2-} \rightleftharpoons S_3^{2-} + S_5^{2-} \rightleftharpoons S_2^{2-} + S_6^{2-} \qquad (28)$$
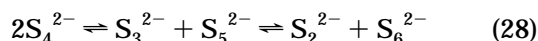
Furthermore, it is not necessary for the above reaction scheme to have an alkaline environment. Under acidic conditions the first step might be the one-electron oxidation of H_2S:

$$H_2S \rightarrow H_2S^{\bullet+} + e^- \qquad (29)$$
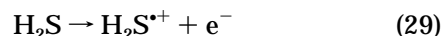
The radical cation $H_2S^{\bullet+}$ must be a much stronger acid than H_2S and therefore will immediately dissociate in water:

$$H_2S^{\bullet+} + H_2O \rightarrow H_3O^+ + HS^{\bullet} \qquad (30)$$
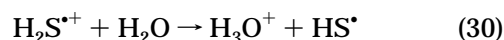
The $HS^{\bullet}$ radical then enters the reaction sequence (9−25). Under acidic conditions the polysulfides may exist as monoprotonated species, but this does not prevent the buildup of longer and longer chains and the following S_8 formation. Even the undissociated sulfanes H_2S_n are known to decompose in water spontaneously to H_2S and S_8 (Burton and Machmer, 1968).

In addition, it should be mentioned that some of the metal-containing catalysts may even be able to oxidize not only monosulfide (HS^-) but also polysulfide anions with formation of the radical anions $S_2^{\bullet-}$, $S_3^{\bullet-}$, $S_4^{\bullet-}$, etc., which then would dimerize to give the long-chain

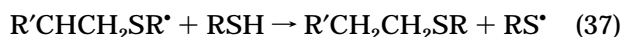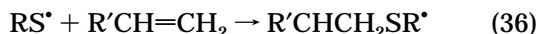polysulfides needed for the formation of the homocyclic molecules S_6, S_7, and S_8:

$$S_n^{2-} \rightarrow S_n^{\bullet -} + e^- \quad (n = 2, 3, ...) \tag{31}$$

$$2S_n^{\bullet -} \rightarrow S_{2n}^{2-} \tag{32}$$
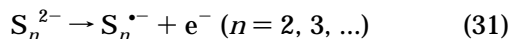
There is plenty of experimental evidence in support of the above mechanism, in particular for the formation of polysulfides from which the elemental sulfur molecules then can be split off. The electrochemical oxidation of aqueous sulfide (1 mM) at pH = 9.3 with exclusion of oxygen has been reported to yield first polysulfides and then elemental sulfur (Szynkarczuk et al., 1994). Although the authors did not discuss any reaction mechanism, it is likely that the observed products are formed by reactions (9−25). The autoxidation of thiols to disulfides is catalyzed by typical one-electron oxidants, e.g., Cu(II), Fe(III), Mn(III), and Co(III) (Misra, 1974; Sheldon and Kochi, 1981). These catalysts are usually employed to enhance the rate of oxidation. A number of studies of the interactions of metal compounds with thiols have been carried out. For example, stoichiometric oxidation of thiols by iron(III) octanoate proceeds via the following steps (Wallace, 1966), involving inner-sphere oxidation of RS^- by Fe-(III):

$$XFe^{III} + RS^- \rightarrow RSFe^{III} + X^- \tag{33}$$

$$RSFe^{III} \rightarrow Fe^{II} + RS^{\bullet} \tag{34}$$

$$2RS^{\bullet} \rightarrow RSSR \tag{35}$$

The intermediate thiyl radicals have been intercepted by olefins like 1-dodecene, resulting in the formation of sulfides via the following chain propagation sequence:

$$RS^{\bullet} + R'CH{=}CH_2 \rightarrow R'CHCH_2SR^{\bullet} \tag{36}$$

$$R'CHCH_2SR^{\bullet} + RSH \rightarrow R'CH_2CH_2SR + RS^{\bullet} \tag{37}$$

Hydrogen sulfide is oxidized by cationic Ru(III) complexes in deoxygenated water to give first a bright yellow solution (polysulfides), from which elemental sulfur precipitates (Diamond et al., 1980) (eqs 9−25). In a similar fashion aqueous sulfide (5 mM) produced polysulfides on shaking in air at a pH of 7.2 and in the presence of hemin (5.4 μg mL^{-1}; Sörbo, 1960). Absorption of H_2S by aqueous solutions of iron(III) chelated by nitrilotriacetic acid at pH = 8.5 resulted in formation of polysulfides and finally elemental sulfur (Clarke et al., 1994).
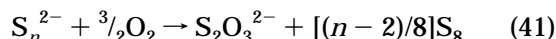
Certain sulfur bacteria using metal ion containing enzymes oxidize sulfide to polysulfides (Then and Trüper, 1983; van den Ende and van Gemerden, 1993), others oxidize thiols to organic disulfanes. For example, cytochrome c (containing Fe^{3+}) transforms glutathione GSH into GSSG, probably via the following reaction sequence which is analogous to reactions (9) and (11):

$$GSH \rightarrow GS^- + H^+ \tag{38}$$

$$GS^- + Fe^{3+} \rightarrow GS^{\bullet} + Fe^{2+} \tag{39}$$

$$2GS^{\bullet} \rightarrow GSSG \tag{40}$$
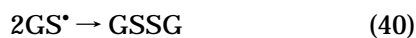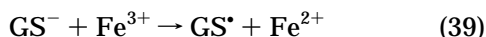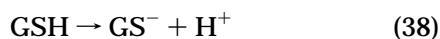
The formation of GS$^{\bullet}$ radicals from GSH by one-electron oxidation with either Cu^{2+} or Ce^{4+} ions has

been demonstrated (Gilbert et al., 1975). Since thiyl radicals RS$^{\bullet}$ cannot be observed by ESR spectroscopy due to line broadening, they have been intercepted by reaction with maleic acid, and the resulting sulfinyl radical $^{\bullet}$CH(CO$_2$H)CH(CO$_2$H)SR was detected by ESR spectroscopy.
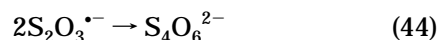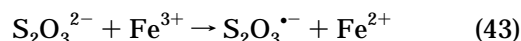
Sulfate, Thiosulfate, and Polythionate Formation. Sulfate and thiosulfate are unwanted products of most wet sulfide oxidation processes. Thiosulfate most probably originates from the autoxidation of the polysulfide anions, which is fairly rapid and can be quantitatively described by eq 41 (Steudel et al., 1986).

$$S_n^{2-} + {}^3/_2O_2 \rightarrow S_2O_3^{2-} + [(n-2)/8]S_8 \tag{41}$$

Thiosulfate is oxidized by certain metal ions to give tetrathionate; e.g.,

$$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow S_4O_6^{2-} + 2Fe^{2+} \tag{42}$$

This reaction is also performed by certain sulfur bacteria which produce metal-containing enzymes (cytochromes or HIPIP). Reaction (42) probably proceeds in two steps:

$$S_2O_3^{2-} + Fe^{3+} \rightarrow S_2O_3^{\bullet -} + Fe^{2+} \tag{43}$$

$$2S_2O_3^{\bullet -} \rightarrow S_4O_6^{2-} \tag{44}$$

Polythionates like $S_4O_6^{2-}$ will also be formed in the oxidizer of a Stretford or Sulfolin plant since vanadium-(V) is a powerful enough oxidant for the dimerization of thiosulfate. However, since hydrogen sulfide under alkaline conditions reacts rapidly with polythionates according to eq 45 (Klimmek et al., 1991), the concentration of $S_nO_6^{2-}$ will remain low. Polythionates can best be determined by ion chromatography (Steudel and Holdt, 1986).

$$S_nO_6^{2-} + 2HS^- \rightarrow S_{n-2}^{2-} + 2S_2O_3^{2-} + 2H^+ \tag{45}$$
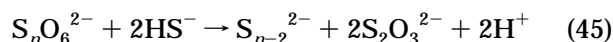
As can be seen, the latter reaction is another source of polysulfides. This reaction will take place mainly in the absorber where the concentration of HS^- is highest.

From the above it follows that the formation of thiosulfate can be suppressed if the presence of molecular oxygen is avoided in those parts of the plant where the polysulfide concentration is substantial (i.e., in the absorber and reaction tank). The formation of sulfate is probably due to a reaction of S$^{\bullet -}$ radicals with molecular oxygen. This reaction primarily yields SO$_2^{\bullet -}$ radical anions identical to those obtained by dissociation of the dithionite anion (Zhu et al., 1991):

$$S^{\bullet -} + O_2 \rightarrow SO_2^{\bullet -} \tag{46}$$

$$2SO_2^{\bullet -} \rightleftharpoons S_2O_4^{2-} \tag{47}$$
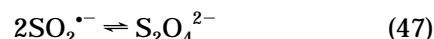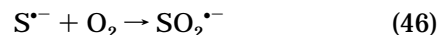
Dithionite is known to react rapidly with molecular oxygen and with hydrogen sulfide to give sulfite, thiosulfate, and sulfate, while polythionates are reduced by dithionite to thiosulfate, sulfite, and elemental sulfur (Münchow and Steudel, 1994). The alkaline hydrolysis of polythionates also produces sulfate and thiosulfate (Naito et al., 1975; Kurtenacker and Kaufmann, 1925).

Sulfur Precipitation. The homocyclic sulfur molecules formed in reactions (25−27) are hydrophobic as can be seen from the extremely low solubility of ortho-

rhombic α-sulfur (S_8) in water which amounts to only 5 × 10^{-6} g L^{-1} at 20 °C (Boulegue, 1978). If a hydrophobic molecule (S_8) is formed in water from a hydrophilic precursor (HS_9^-), it tends to escape the hydrophilic environment and to reduce the surface area exposed to the hydrophilic phase. Therefore, S_8 molecules form dimers, trimers, etc., and eventually clusters in which their combined surface area is smaller than the sum of the molecular surfaces of the single molecules. This process is driven by hydrophobic interaction and is the first step in the precipitation process:

$$S_8 + S_8 \rightarrow (S_8)_2 \xrightarrow{+S_8} (S_8)_3 \xrightarrow{+xS_8} (S_8)_n \qquad (48)$$
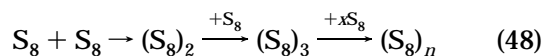
The cluster $(S_8)_n$ not only will grow from S_8 molecules but also will incorporate S_6, S_7, and other hydrophobic molecules present in the system (e.g., hydrocarbons). It therefore may be called a "dirty" sulfur cluster. As this submicroscopic cluster grows, it forms a liquidlike sulfur particle. Crystallization of this particle as α-S_8, the thermodynamically stable allotrope of sulfur at 20 °C/1.013 bar, is hindered for several reasons. The crystal structure of α-S_8 is quite complicated since the unit cell consists of not less than 16 molecules which have to be oriented in a special manner. This ordering process is hindered first by the impurities present in the dirty cluster and second by the high viscosity liquid sulfur must exhibit at 20 °C. Therefore, it is quite normal that the liquidlike cluster grows to a diameter of ca. 1 μm before it crystallizes. Sometimes the formation of monoclinic β-S_8 is observed; the unit cell of β-S_8 contains only six molecules.

This behavior is well-known from the study of synthetic sulfur sols. There are two types of sulfur sols: hydrophobic or Weimarn sol made from S_8 and hydrophilic or Raffo and Selmi sols. Raffo sols are prepared by acid decomposition of aqueous thiosulfate, while Selmi sols are obtained by reaction of aqueous sulfide with sulfite. Raffo and Selmi sols are hydrophilic due to the presence of long-chain polythionates which probably cover the surface of the sulfur particles (Steudel et al., 1988, 1989). For the understanding of the properties of elemental sulfur produced by oxidation of HS^- ions, the Weimarn sol is most important.

Weimarn Sulfur Sols. If a hot concentrated solution of S_8 in, for example, ethanol is poured into a large volume of pure water with moderate stirring, a clear solution is obtained which shows a bluish opalescence (von Weimarn, 1926). Within 10−20 min this mixture becomes turbid and then looks similar to milk; under the microscope droplets of liquid sulfur (diameter ca. 0.8 μm) can be observed (magnification 1000×). On standing of this sol without further stirring, a slow crystallization is observed: the first crystals (size 1−3 μm) occur after 3 days, and after 6 days all droplets usually have crystallized and form conglomerates which slowly settle to the bottom of the vessel. Only after 14 days is the supernatant completely clear (Zahn, 1990).

The lifetime of Weimarn sols can be increased or decreased by certain chemicals which are dissolved in the aqueous phase before the sulfur solution is added. The lifetime can be determined by the S_8 concentrations in the sol near the surface (the sol is contained in a test tube, and samples are drawn with a syringe from about 1 cm below the upper surface). Surfactants like sodium dodecyl sulfate (SDS), Triton X-100, or cetyltrimethylammonium bromide (CTAB) at a concentration of 1 mmol of surfactant/mmol of S_8 increased the lifetime.

Egg white had the same effect (Zahn, 1990). The molecules of these substances are probably adsorbed with their hydrophobic parts to the surface of the S_8 droplets, while the hydrophilic parts are directed toward the aqueous environment, making the droplets hydrophilic. In addition, the ionic surfactants adsorbed to the droplets make the latter equally, charged resulting in repulsion and thus stabilization of the sol. However, it has been observed that this stabilization works only as long as the sulfur particles are liquid. Once the droplet has crystallized, it forms aggregates and these settle to the bottom. It therefore seems that the hydrocarbon chains of the above-mentioned surfactants are "dissolved" in the liquid sulfur and are not as strongly attracted by the surface of *solid* sulfur particles. The mentioned substances therefore increase the lifetime of the *liquid* sulfur particles.

When Ca^{2+} or Mg^{2+} ions are added to the aqueous phase (1−2 mmol L^{-1}) the stabilizing effect of SDS disappeared, while Triton X-100 was still able to enhance the lifetime of the sol compared with that prepared from pure water. Pure Weimarn sols without surfactants are rather unstable in the presence of the mentioned cations and all sulfur precipitated within 6 h (compared to 14 days without these cations).

Sulfur Sols in Stretford Plants. Stretford and similar desulfurization plants occasionally suffer from operating problems like absorber plugging, production of sticky sulfur, separation (flotation) problems, and even the growth of hard sulfur layers on the walls of downstream pipes and other equipment. Most of these problems can be explained by the primary formation of sulfur sols. As outlined above, the sulfur formed by oxidation will first precipitate from the aqueous phase as *liquid* droplets. These droplets grow both by incorporation of more and more S_8 and by unification with other droplets with which they may collide. If the crystallization of these droplets is delayed, the following will occur:

(1) Droplets hitting the walls of the separator or other parts of the plant will crystallize on impact and grow to the surface.

(2) Droplets hitting crystals of sulfur will crystallize and form an aggregate, the shape of which will depend on the crystal's and droplet's size.

(3) Droplets well protected by a layer of surfactant-type molecules will not easily crystallize nor grow and will circulate in the plant as an emulsion of sulfur. They will neither float nor sink since their density will be well below that of pure liquid sulfur (ρ = 1.9 g cm^{-3}); see below.

(4) The sulfur emulsion together with crystalline sulfur may result in a sticky mixture in which the liquid sulfur plays the role of the glue.

To obtain a good sulfur quality, a rapid growth and rapid crystallization of the sulfur particles is desired. These crystals have to form aggregates in order to be able to include gas bubbles on airation to make them floating. "Bad" sulfur consists of either single solid sulfur particles which will not float or a mixture of solid sulfur in an emulsion of liquid sulfur in water. Such an emulsion, when not agitated, may be stable for days. It has been observed that sulfur emulsions of the type described here pass through filters of size G2; only very fine filters (G4) retain the liquid sulfur by initiating crystallization. The surfactant-type molecules stabilizing liquid sulfur droplets may originate from the feed gas or from sulfur bacteria.

Sulfur Bacteria. It is well-known that many Stretford and Sulfolin plants are inhabited by a variety of sulfur bacteria. Surprisingly, both oxidizing bacteria (*Thiobacilli, Pseudomonas*) and sulfate-reducing bacteria (SRB) have been found, the latter in pockets of the plant or under piles of elemental sulfur where molecular oxygen is depleted.

Sulfur bacteria are known to excrete surfactant-type molecules (Dees and Shively, 1982; Knoche and Shively, 1972; Beebe and Umbreit, 1971). In addition, when such bacteria die from mechanical, chemical, or thermal impact, the components of their cells like polysaccharides, phospholipids, and peptides are set free; all these compounds can probably serve as surfactants to increase the lifetime of sulfur sols. It is obvious that such materials will circulate in the plant and their concentration will even increase with time if bacterial growth is not controlled. Cell counts of up to 10^9 cm^{-3} have been reported in some cases. Foaming problems may also be caused by surfactant-type compounds originating from bacteria.

Thiobacilli oxidize sulfide, thiosulfate, and tetrathionate with formation of sulfate which the SRBs may reduce (to sulfide) using organic matter as a reductant. The bacteria may be controlled by biocides (Wilson and Newell, 1984) or by modifying the operation conditions (e.g., the salt concentration).

The production of liquid sulfur droplets at ambient temperature by oxidation of reduced sulfur compounds by bacteria has been known for more than 100 years and is well documented by microscopic photographs (Trüper, 1984). These droplets reach diameters of up to 1 μm and are deposited either inside or outside the bacterial cells. No crystallization occurs for days. In some cases the sulfur droplet ("globule") has been shown to be covered by a protein layer (Brune, 1995). This may serve the same function as the surfactants mentioned above. The density of globules produced by *Chromatium vinosum*, a phototrophic organism oxidizing sulfide, has been determined as 1.4 g cm^{-3} which was interpreted as "hydrated sulfur" (for a review on bacterial sulfur globules, see Steudel, 1989). Obviously, the protein attracts a layer of water which reduces the overall density.

Conclusions

The chemical model for the oxidative desulfurization of aqueous sulfide solutions presented here explains many of the observations made during Stretford and Sulfolin plant operations. The primary intermediate HS• or S•$^-$ triggers the formation of chain- and ringlike polysulfur compounds: polysulfide anions, radical anions, and finally sulfur homocycles. To avoid the formation of sulfate and thiosulfate, no molecular oxygen should come into contact with these radicals and anions which are subject to rapid autoxidation. If the feed gas contains alkenes, these may react with HS•/S•$^-$ to give organic sulfides, possibly resulting in odor problems.

The precipitated sulfur first forms an emulsion, the lifetime of which depends on the presence of surfactant-type molecules (which stabilize the sulfur sol) and of salts (which destabilize). The surfactants may result from bacterial activity, which therefore has to be controlled. Foaming problems also are related to bacterial contamination of the liquor. Sulfur bacteria can be controlled by biocides, but these degradate in the Stretford liquor. Therefore, other means should be

considered like limiting their essential nutrients (e.g., phosphate). The constant removal of sulfur as a froth or a slurry from the plants also removes some of the surfactants (which are adsorbed to the sulfur). Therefore, low bacterial cell counts are not causing major problems, but 10^8–10^9 cells cm^{-3} can usually not be tolerated.

Further research is needed to find out how the sulfur in emulsions can be crystallized despite the presence of surfactants and bacteria.

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