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**The Chemical Reactions of Sulfur
in the Citrate Process
for Flue Gas Desulfurization**

**By W. N. Marchant, S. L. May, B. W. Moore,
and W. W. Simpson**



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THE CHEMICAL REACTIONS OF SULFUR IN THE CITRATE PROCESS FOR FLUE GAS DESULFURIZATION

by

W. N. Marchant,¹ S. L. May,² B. W. Moore,³ and W. W. Simpson⁴

ABSTRACT

The Bureau of Mines performed chemical research to elaborate details of sulfur chemistry pertaining to the citrate flue gas desulfurization process in which sulfur dioxide (SO_2), absorbed (as bisulfite ion) in a buffered sodium citrate solution, is reduced by hydrogen sulfide (H_2S) according to the overall reaction $2\text{H}_2\text{S} + \text{HSO}_3^- + \text{H}^+ \rightarrow 3\text{S} + 3\text{H}_2\text{O}$. The rate-limiting step in the process was shown to be the reduction by H_2S of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) that is formed as an intermediate. Pseudo first-order kinetic measurements were made at room temperature to retard the reaction sufficiently that adequate analysis was possible. These measurements showed the rates of the following net processes to be

$$-d[\text{SO}_2]/dt \text{ (pH 4.5)} = (0.409 \pm 0.050) \text{ min}^{-1} [\text{SO}_2];$$

$$d[\text{S}_2\text{O}_3^{2-}]/dt \text{ (pH 4.5)} = (0.199 \pm 0.017) \text{ min}^{-1} [\text{SO}_2];$$

$$-d[\text{S}_2\text{O}_3^{2-}]/dt \text{ (pH 4.0)} = (0.0437 \pm 0.0265) \text{ min}^{-1} [\text{S}_2\text{O}_3^{2-}]^{\sim 1};$$

$$-d\text{H}_2\text{S}/dt \text{ (pH 3.9)} = (21.6 \pm 3.0) \text{ mmoles/min-atm} [\text{H}_2\text{S}]_g^{1.4},$$

where $[\text{H}_2\text{S}]_g$ is the partial pressure of H_2S in the gas phase, in atmospheres, and the rate describes the consumption of H_2S , in millimoles per minute;

$$d[\text{S}]/dt \text{ (pH 4.0)} = (38.0 \pm 3.4) \text{ min}^{-1} [\text{H}_2\text{S}]_1,$$

where $[\text{H}_2\text{S}]_1$ is the concentration of H_2S in solution. Hydrogen ion consumption during the slow phase of regeneration was shown to occur at (2.1 ± 0.5) times

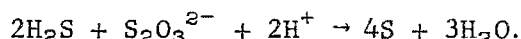
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the rate of thiosulfate consumption, which is interpreted as evidence for the following as the rate-limiting reaction:



A scheme consisting of five sequential general reactions is proposed to account for sulfur formation.

INTRODUCTION

The Bureau of Mines undertook flue gas desulfurization (FGD) research as part of a broad program designed to minimize the objectionable effects of minerals-processing operations upon the environment, and to produce technology that would contribute to a healthy domestic minerals economy. The citrate FGD process is a product of that research; however, unlike many FGD processes presently in use or advocated, the citrate process is regenerable, yields a desirable end product (elemental sulfur), and produces very little waste that requires disposal. The process has been successfully demonstrated in the laboratory and in two pilot-scale tests; however, reports describing these tests generally have emphasized process operation and overall test results (15).⁵ This report is an attempt to elaborate details of the sulfur reactions occurring in the citrate process, including reaction rates where they could be measured.

The gross chemical changes that occur when SO_2 and H_2S are combined in water were first reported by the German apothecary, Wackenroder, in 1845 (14), and the complex solution that results has been known historically as "Wackenroder's liquid." The nature of these changes has been called "a 'classical' problem in inorganic chemistry..." with "no experimentally proved mechanism known for the formation of sulfur and the sulfane disulfonic acids [polythionates]" (16). Other authors, writing of the reaction between sulfide and sulfite in solution, have said that "there can be no value in suggesting a detailed mechanism for the reactions occurring in such a complicated system, since the possibilities are numerous and there seems to be no way of determining which are important (12)." Bureau of Mines research has confirmed that H_2S and SO_2 in solution form an extremely complex system comprising at least 11 simultaneous reactions, many of which include a great number of related reactions that vary only in the number of sulfur atoms in the reactants. It has not been possible to prove a mechanism for sulfur formation; nevertheless, this research has determined which reactions are most important in sulfur production, which are merely side reactions, and a reasonable reaction sequence to explain the changes that occur in the process.

Briefly, the citrate process consists of three principal operations. First, SO_2 is absorbed from a cleaned (SO_3^- and dust-free) and cooled waste-gas stream into a solution of citric acid and sodium citrate. Citrate buffers the absorber solutions against the pH decrease that would otherwise accompany SO_2 dissolution and severely limit its solubility. Second, the absorber

⁵Underlined numbers in parentheses refer to items in the list of references at the end of this report.

solution containing dissolved SO_2 is reacted with gaseous H_2S to produce elemental sulfur. Hydrogen sulfide for this step is produced in a separate unit operation by reacting elemental sulfur with steam and a reducing agent (natural gas, carbon monoxide, methanol, coal, etc.) at about 650°C (15). Finally, sulfur is separated from regenerated absorbent solution by flotation. The float product is subsequently separated from entrained absorbent by autoclave heating to about 135°C , which melts the sulfur, forming a lower liquid phase from which absorbent solution comprising the upper phase is withdrawn for recycle. Part of the molten sulfur is diverted to the H_2S generator section, and the balance is cast into blocks for storage, sale, or other use.

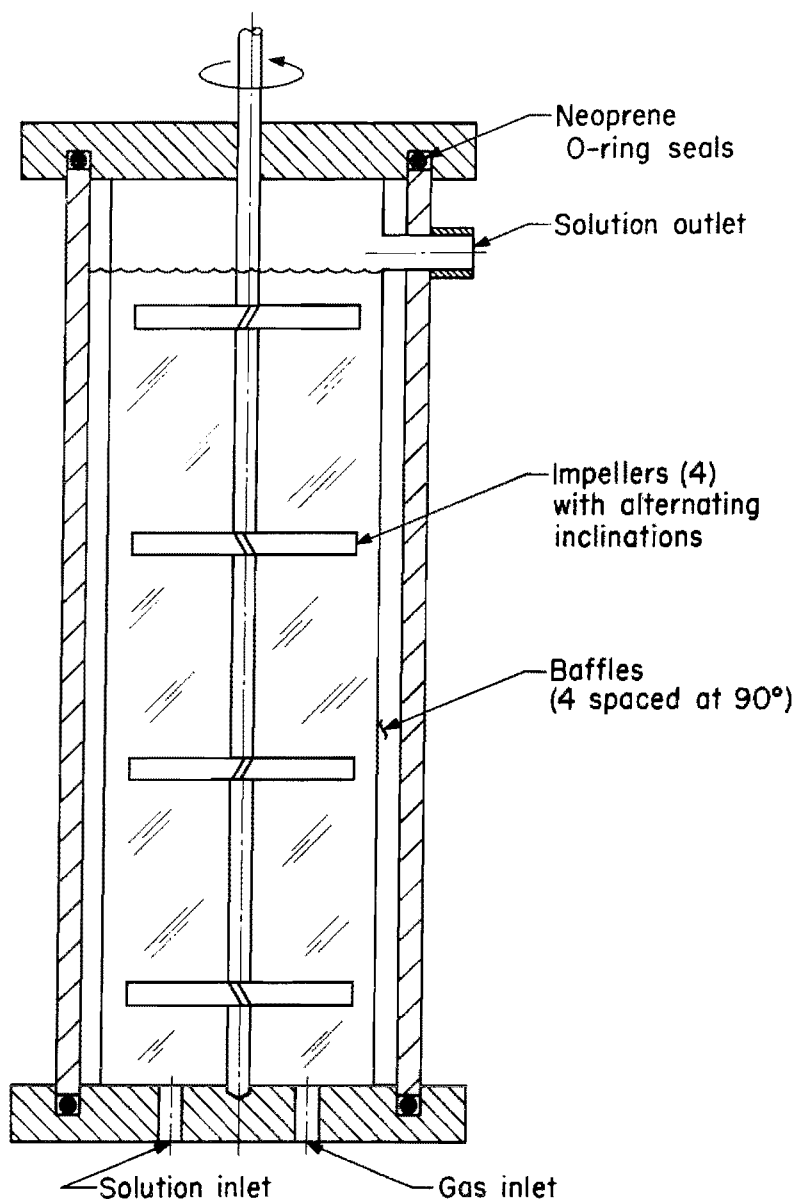


FIGURE 1. - Schematic diagram of continuous-flow kinetic study reactor.

Citric acid was among the first organic buffers tested in the absorbent solution, and the process has become identified with "citrate"; however, the nature of the buffer is not critical, and process chemistry is unaffected by substitution of other buffers. The desirable properties of a candidate buffer are (1) a maximum buffer capacity near pH 4 to 5, which is the region in which both absorption and regeneration proceed at useful rates, and (2) a sufficiently high buffer capacity that a reasonable buffer concentration substantially increases SO_2 solubility. Citric acid is particularly well suited for use in the process because it satisfies both of the preceding requirements and because it exhibits a linear buffer response for acid concentrations varying between about pH 3 and 6.

EQUIPMENT AND PROCEDURES

Batchwise reactions were conducted in a 1-liter glass reaction flask with four side indents (baffles). The flask was fitted with a gastight stirrer bearing, a pH electrode, a thermometer,

and a reflux condenser through which unreacted gas exited to be trapped or flared in a bunsen burner flame. The reaction was stirred by means of a hollow-shaft stirrer through which the reactant gas was admitted. Samples were withdrawn through a neck in the flask top that was closed with a ground-glass stopper when not needed. When required, the reactor was heated by means of electrical heating tape. Continuous-flow experiments were conducted in a 225-milliliter-capacity acrylic reactor shown schematically in figure 1. The impellers were turned at 2,700 rpm. Nominal liquid retention time for all runs was 2.25 minutes or greater. Mixing effectiveness was evaluated by injecting an intense dye into the reactor and timing the interval between injection and apparent homogeneity. Complete mixing was achieved in less than 5 seconds. Because this interval was brief compared with that of the minimum liquid retention time, homogenization of gas and liquid was assumed to be instantaneous. Effluent pH was monitored and samples were obtained immediately downstream from the solution outlet. For those tests in which a solution of NaHS was used in lieu of gaseous H_2S as the sulfide source, the SO_2 -rich absorbent feed and the NaHS feed were combined immediately before entering the reactor, and the pH of the combined stream was adjusted to the desired value with concentrated citric acid, phosphoric acid, or sodium hydroxide solution metered upon demand by a Mettler DK-10/DK-11 automatic titrimeter operating in the pH-stat mode.⁶ Gas and solution analyses were performed as described in companion Bureau of Mines publications (3, 11). Gas flow rates were measured with conventional ball-in-tube or hot wire ("mass flow") flowmeters. Solution flows were measured with ball-in-tube flowmeters calibrated against the solution being used.

SULFUR REACTIONS

Absorbent that is treated successively with SO_2 and H_2S in a batchwise experiment undergoes reproducible pH changes that provide useful indications of the processes occurring. Figure 2 shows a typical plot of solution pH as a function of time in contact with SO_2 and H_2S for such an experiment. Segment A-B corresponds to dissolution of SO_2 in the absorbent and shows the pH decrease caused by absorption of 0.21M SO_2 at point B. Between points B and E, H_2S bubbled into the SO_2 -rich absorbent causes the additional pH changes shown.

Completely regenerated absorbent is pale yellow and transparent; however, H_2S treatment of SO_2 -loaded absorbent causes two visible changes: between B and C the solution remains clear. At C, essentially all SO_2 has been consumed by reaction, and the solution becomes opalescent indicating incipient sulfur precipitation, although no gross sulfur is visible. At D, which marks the lowest pH attained during a cycle, sulfur flocs become observable. The reactions responsible for these changes are discussed in the following sections.

Absorber Reactions

Citrate absorbent that has been used in process operation always contains thiosulfate. Thus, chemical changes that occur during SO_2 absorption (between

⁶Reference to specific companies or brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

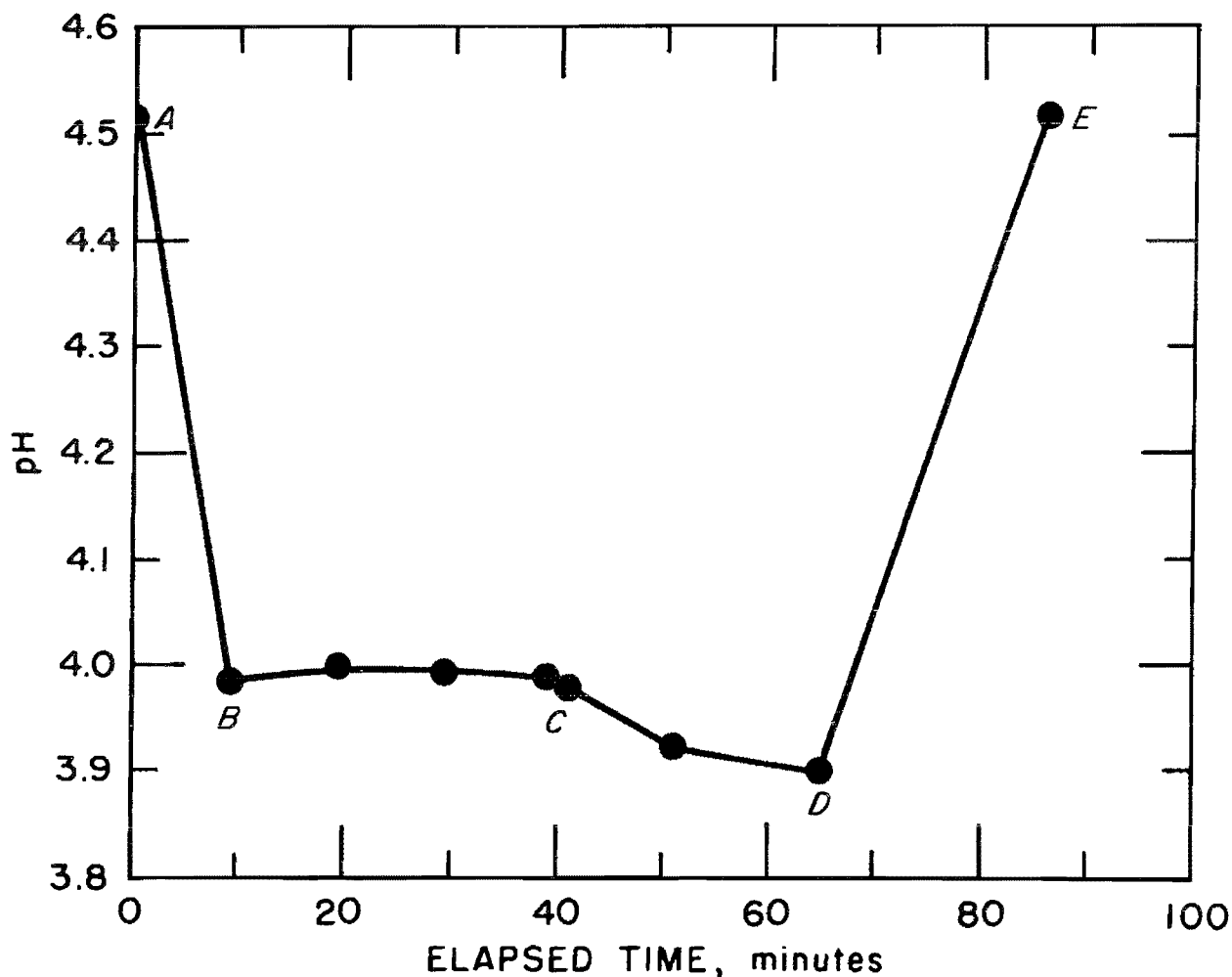
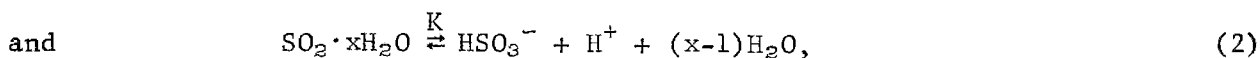
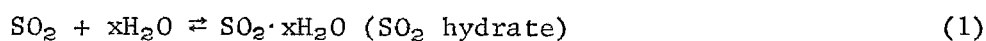


FIGURE 2. - Typical changes in pH during SO₂ loading and H₂S regeneration.

points A and B) include those involving thiosulfate. The following reactions are known to occur:



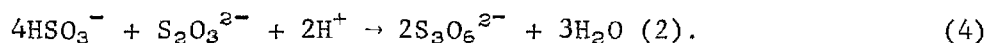
where

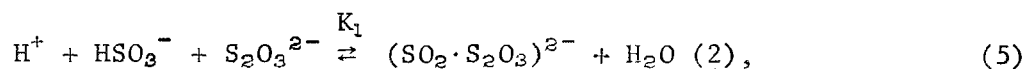
$$K = \frac{[\text{HSO}_3^-] [\text{H}^+]}{[\text{Total dissolved SO}_2] - [\text{HSO}_3^-] - [\text{SO}_3^{2-}]} = 1.3 \times 10^{-2} \quad (4).$$



where

$$K = 7 \times 10^{-2} \text{ mole}^{-1} \quad (4).$$



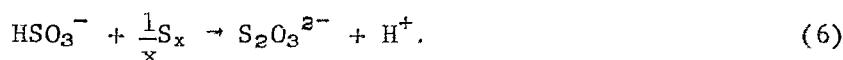


where
$$K = K_1 \frac{[\text{H}^+]}{[\text{H}_2\text{O}]} = \frac{[(\text{SO}_2 \cdot \text{S}_2\text{O}_3)^{2-}]}{[\text{HSO}_3^-] [\text{S}_2\text{O}_3^{2-}]}$$

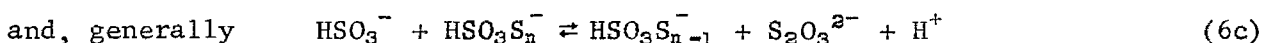
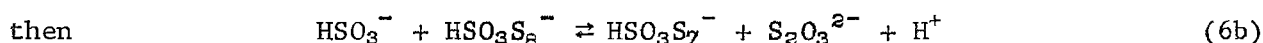
$$= (6.2 \pm 2.4) \times 10^{-2} \text{ liter mole}^{-1} \quad (2).$$

Reaction 5 is the reversible formation of a complex between SO_2 and thiosulfate that exhibits an ultraviolet absorption band at 293 nanometers. At high concentrations of SO_2 and $\text{S}_2\text{O}_3^{2-}$ this band overlaps the visible region, contributing to the distinctive yellow color of process solutions. The molar absorptivity, ϵ , reported for this complex is $(2.4 \pm 0.9) \times 10^3 \text{ liter mole}^{-1} \text{ centimeter}^{-1}$.

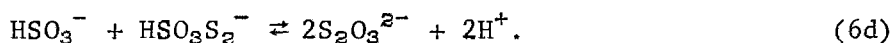
Thiosulfate is probably formed by



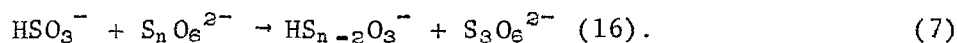
This reaction is the basis for at least one commercial process for thiosulfate production (10), and probably proceeds by way of



culminating in

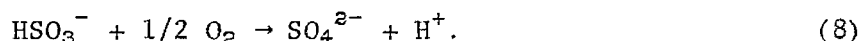


Polythionates ($\text{S}_n\text{O}_6^{2-}$, with $n \geq 3$) were first discovered in Wackenroder's liquid, and are always present in recycled citrate-process absorbent, although their concentration varies greatly depending upon the state of absorbent regeneration. They are known to undergo degradation by nucleophilic reagents such as cyanide or bisulfite (HSO_3^-) by



The sulfane monosulfonate fragments, HS_nO_3^- , produced by reaction 7, are reported to undergo mild oxidative dimerization to produce higher polythionates, $\text{O}_3\text{S}_{2n}\text{O}_3^{2-}$ (17). This reaction is analogous to the formation of tetrathionate, $\text{O}_3\text{S}_4\text{O}_3^{2-}$, during the iodometric titration of thiosulfate.

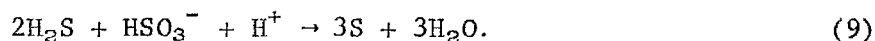
Finally, some SO_2 is oxidized to sulfate:



During phase A-B, the pH drop is attributable primarily to reaction 2, the ionization of hydrated SO_2 , although reactions 6 and 8 also contribute hydrogen ion. Reactions 4 and 5, which consume hydrogen ion, are minor reactions that exert little detectable effect upon the acid balance. For example, the reported equilibrium constant for reaction 5 can be used to show that for the SO_2 -rich absorbent in figure 2 only about 1.5 percent of the dissolved SO_2 is in the form of the complex. Similarly, the increase in $\text{S}_3\text{O}_6^{2-}$ during SO_2 absorption is barely perceptible, indicating that reaction 4 is a relatively unimportant mode of hydrogen ion consumption.

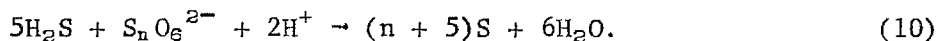
Regeneration Reactions

It is in the regeneration reactor that those reactions occur that are most complex and also most important in sulfur production. The following reactions are known to occur during H_2S treatment of SO_2 -rich absorbent:



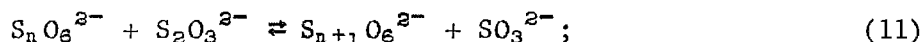
This is the overall reaction for sulfur formation; however, it is a gross simplification and indicates nothing about possible intermediates.

Reaction 10 is the reduction of polythionates by H_2S :



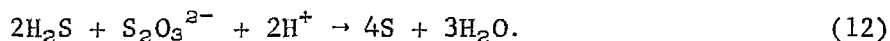
These ions are susceptible to nucleophilic degradation by H_2S in a manner analogous to the previously cited bisulfite degradation (reaction 7).

Foss (7) reported a kinetic rate constant for the reaction



however, Schmidt (16) argued, without including evidence, that this reaction does not take place. Reaction 11 is included, despite conflicting arguments in the literature, as a possible explanation for the presence of high-molecular-weight polythionates.

Reaction 12 has been proposed by others (9, 13) as rate limiting in the regeneration process:



Bureau of Mines data confirm that reaction 12 is rate limiting, and establish the critical role of thiosulfate in the system.

To test the proposition that thiosulfate reduction by reaction 12 is of primary importance in sulfur production, a "sham" regeneration experiment was conducted. Figure 3 depicts the pH changes that resulted from treating typical SO_2 -loaded citrate absorbent batchwise with H_2S in a control test and a sham experiment in which citrate absorbent containing only thiosulfate was prepared to simulate the control test solution composition at point D and then

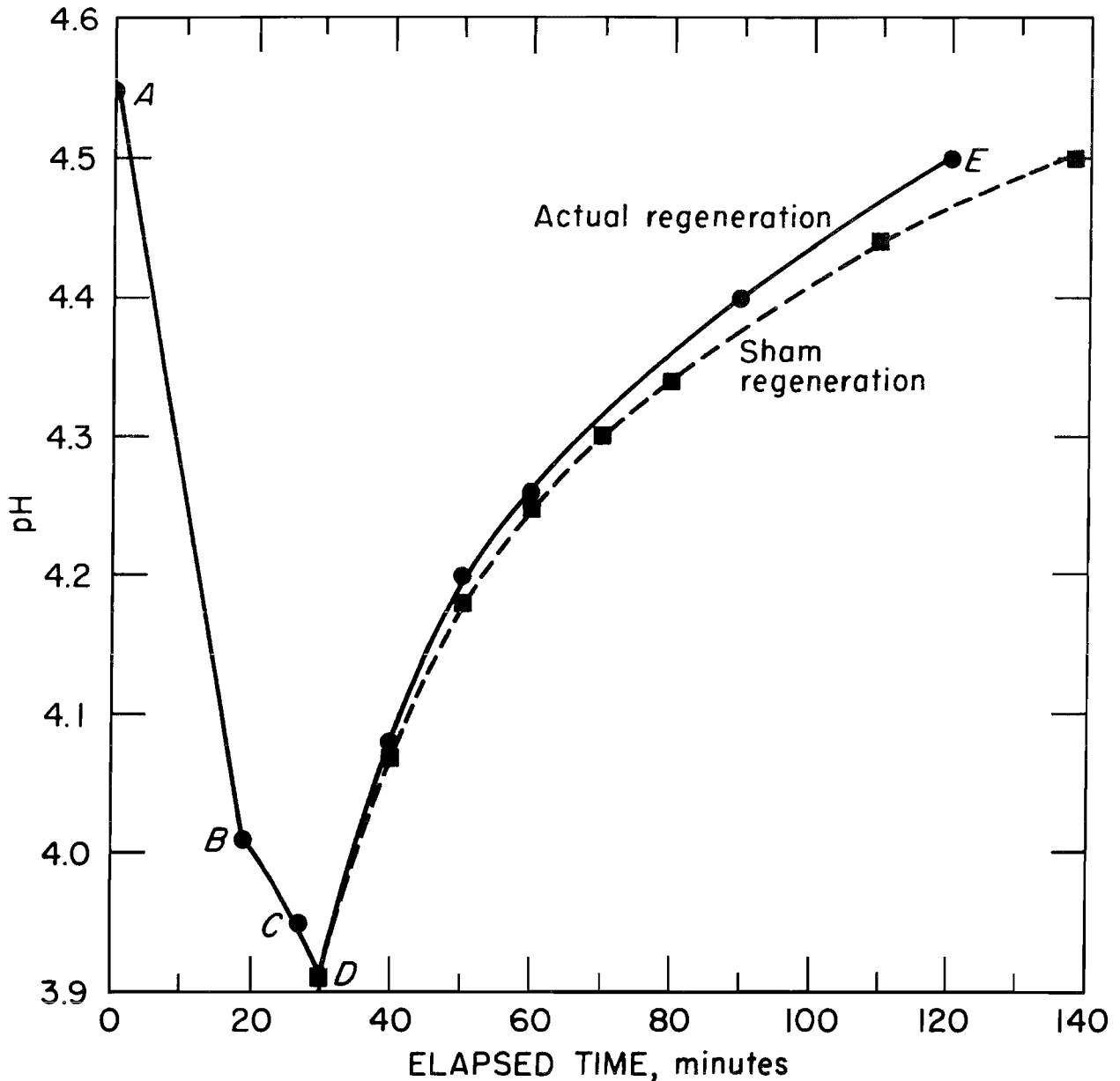


FIGURE 3. - Changes in pH during H_2S treatment of SO_2 -loaded absorbent and a simulated solution containing only thiosulfate.

treated with H_2S . The control solution, initially 0.10 M in thiosulfate, pH 4.55 (point A) was loaded to 0.22 M SO_2 (point B). Treatment with H_2S produced the familiar initial pH decrease to D at which point the SO_2 and thiosulfate concentrations were 0.004 M and 0.19 M , respectively. The sham solution, which included no polythionates, was 0.19 molar thiosulfate prior to H_2S treatment. It is significant that both the shape of the "regeneration" curves (D-E) and the time consumed are similar, indicating that similar processes are occurring. In the control test, 6.9 grams of thiosulfate was consumed between D and E; whereas, in the sham test 10.5 grams was consumed. A reason for this difference will be proposed later.

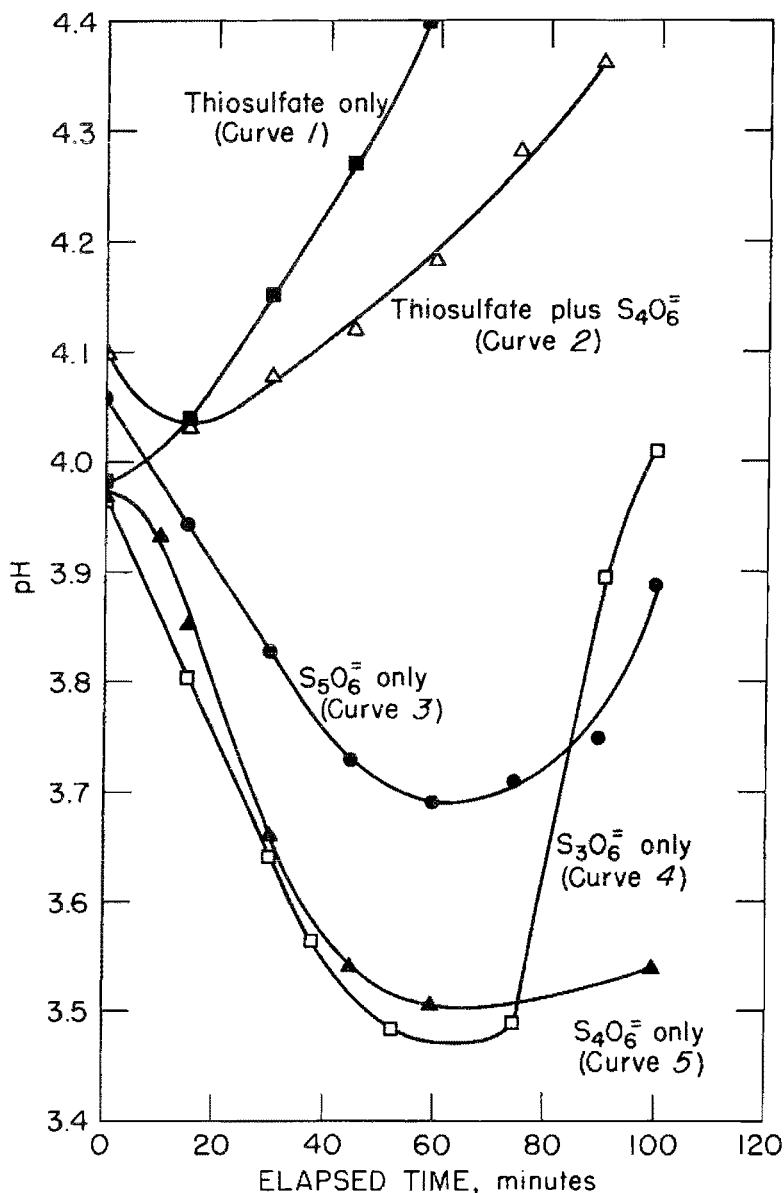


FIGURE 4. - Changes in pH during simulated regeneration of solutions containing thiosulfate or polythionates.

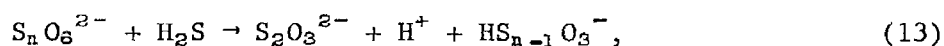
the pH drop observed in a typical batchwise regeneration experiment (fig. 2, portion C-D) was attributable to the reaction of polythionates with H_2S . Curve 2 (fig. 4) shows the reaction course for sham regeneration of 0.25M thiosulfate also containing 0.03M tetrathionate. The pH drop during the first 15 minutes of H_2S treatment resembles that occurring between points C and D during actual load-regeneration batch tests, and supports the proposal that polythionates formed early during regeneration are decomposed immediately prior to the beginning of the pH increase (D-E) that accompanies absorbent regeneration. Ideally, all of the solutions for figure 4 would have had exactly the same initial pH; however, as the pH of a solution containing thiosulfate is decreased below about 4.5, thiosulfate undergoes decomposition

Polythionates with as many as 60 sulfur atoms per molecule have been reported (12). Because the bond angles and bond lengths between sulfur atoms comprising the $-S_n-$ portion of the molecule are similar to those between atoms in the S_8 ring of rhombic sulfur, polythionates have been considered as possible precursors of elemental sulfur. Sham regeneration tests resembling that depicted in figure 3 for thiosulfate were run in which individual polythionates were used during the simulation. Figure 4 shows the course of these tests. Simulated absorbent solution containing 0.25M $S_nO_6^{2-}$ was adjusted to about pH 4 after which H_2S injection was begun. For the control test in this series a 0.25M thiosulfate solution containing no polythionates was used (curve 1). It is obvious that the reaction of H_2S with polythionates (curves 3-5) follows a course radically different from both ordinary regeneration (figs. 2-3) and other sham tests in which thiosulfate alone was treated with H_2S . The sharp decrease in pH for curves 3-5 suggested that

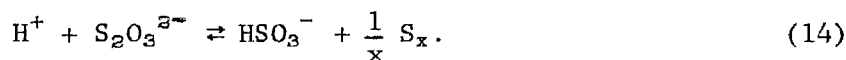
to produce elemental sulfur and HSO_3^- . Similar decomposition is usually evident in solutions presumed to contain only polythionates because of traces of thiosulfate present. Thus, pH adjustment must be done rapidly and H_2S injection begun as quickly as possible, precluding fine adjustments.

An important conclusion suggested by figure 4 is that polythionate degradation is not the principal reaction leading to sulfur formation. Clearly, if this were the case, regeneration, as indicated by increasing pH, would begin immediately upon treating a polythionate solution with H_2S .

Reaction 10, like others listed, is undoubtedly a simple statement of a complex process. As the reactions depicted by curves 3-5 (fig. 4) proceed, thiosulfate accumulates until each mole of polythionate initially present has been converted to 0.9 mole of thiosulfate with the liberation of about 0.8 mole of hydrogen ion. A reasonable explanation for these effects is the stepwise reaction of H_2S with a polythionate by nucleophilic degradation analogous to reaction 7:



followed by further reactions including reaction 12 and possibly the familiar acid decomposition of thiosulfate:



The present Bureau of Mines research did not produce evidence for the proposed intermediates HS_nO_3^- (the sulfanemonosulfonic acids); however, they have been prepared in nonaqueous solution (17), and Soviet workers claim to have isolated them as Nitron salts from the reaction of H_2S and SO_2 in acidic solution (8). They are reported to decompose rapidly in water to produce S, SO_2 , and thiosulfate. Davis (5) proposed a convincing mechanism for sulfur formation during the acid decomposition of thiosulfate that involves HS_nO_3^- ions increasing in size stepwise to HS_9O_3^- and concluding with intramolecular ring closure yielding S_8 and HSO_3^- .

Figure 5 shows another graph of sulfur species concentrations during H_2S regeneration of SO_2 -loaded absorbent. Beneath the graph is a photographic reproduction of a thin-layer chromatogram obtained for samples withdrawn at various times during regeneration. The elapsed time coordinate (X-axis) for the chromatogram and the graph coincide exactly, so that there is direct vertical correspondence between a sample on the chromatogram and solution composition depicted on the graph immediately above it. Points A through D on the chromatogram have the usual significance. The " ΔS " curve on the graph shows the concentration of dissolved sulfur that exceeds the sum of the SO_2 and thiosulfate concentrations determined by titration. Thus ΔS includes polythionates (the principal component), elemental sulfur, and any other soluble species that could not be identified or analyzed individually. The concentration of a species identified on the chromatogram is directly proportional to the area of the spot formed by that species upon visualization of the chromatogram.

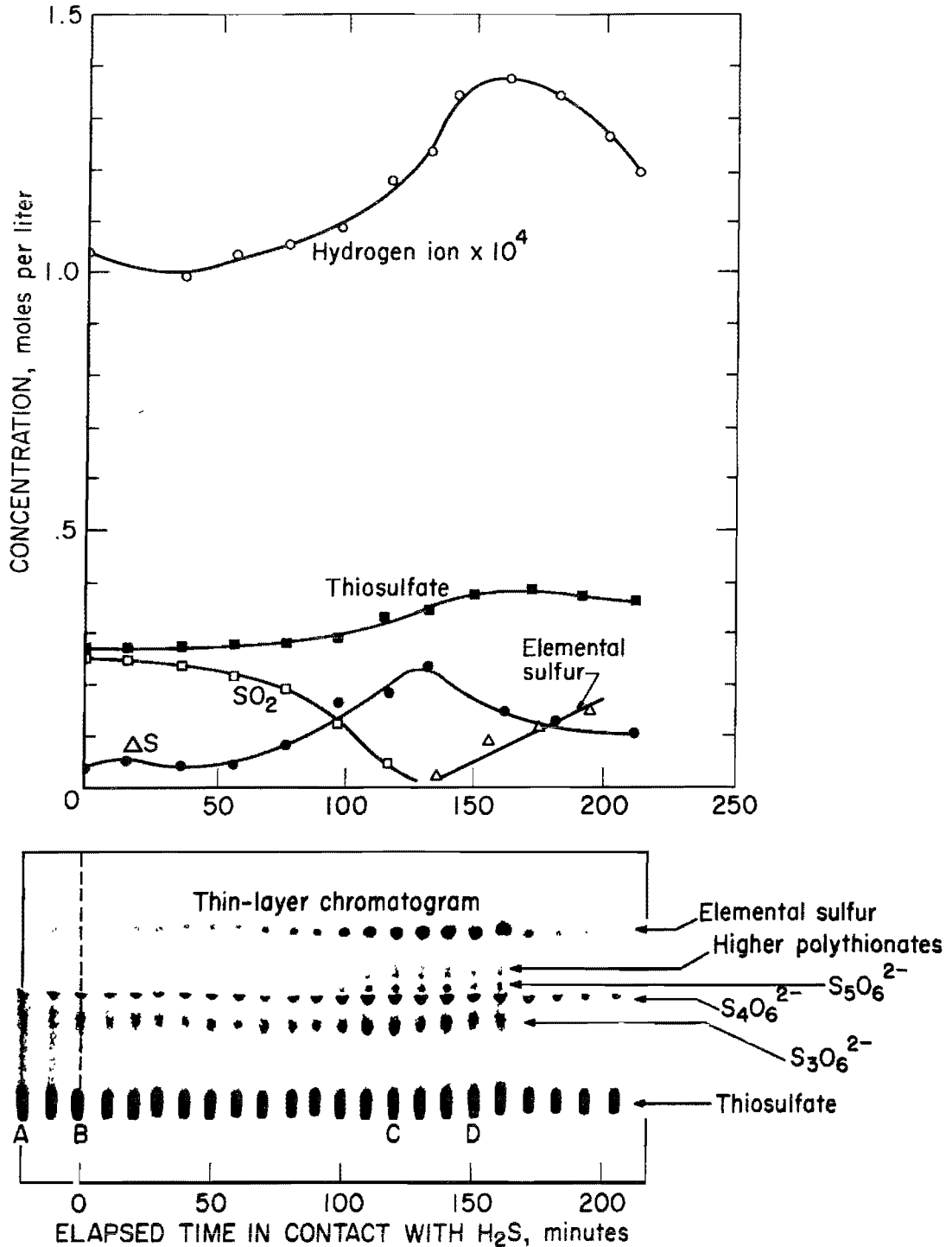


FIGURE 5. - Thin-layer chromatogram and corresponding graph of system changes during regeneration. NOTE.—“Elemental sulfur” on the graph refers to precipitated sulfur; on the chromatogram, it refers to dissolved sulfur.

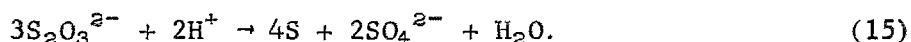
The test depicted in figure 5 was made using an extremely slow H₂S flow rate to retard the reaction and permit the analyses required. For this reason, complete regeneration (to point E) was not achieved within the available time; nevertheless, several noteworthy features of the regeneration process are evident:

1. Trithionate increased between A and B in accordance with reaction 4.
2. Tetrathionate was present throughout the test, even prior to H₂S treatment. (Tetrathionate is formed by mild oxidation of thiosulfate, and some tetrathionate is usually detectable in freshly made solutions of thiosulfate.)
3. Elemental sulfur existed in solution (either molecular or colloidal) more than 1 hour before point C at which the solution became opalescent, and nearly 2 hours before gross sulfur precipitated.
4. After sulfur precipitation began, the concentrations of dissolved elemental sulfur and polythionates other than S₄O₆²⁻ rapidly fell to near zero.
5. The maximum thiosulfate concentration occurred significantly later than the maximum polythionate concentration approximated by the ΔS curve. This observation correlates with the effects discussed in connection with figure 4. It also explains the different thiosulfate consumption in the "actual" and "sham" regeneration curves of figure 3. Polythionates formed during the actual test produced thiosulfate by reaction with H₂S during the D-E process (by reaction 13), causing the apparent thiosulfate consumption to be lower than during the sham test, which included no polythionates.

The formation or reaction of some citrate process components is highly pH dependent. Figure 6 shows the relative formation rates of sulfur species determined in a continuous flow test with absorbent at varying pH. Absorbent containing 0.2M SO₂ was treated with 11 percent H₂S (nitrogen diluent) metered at a rate of 1 mole H₂S per mole SO₂ entering the reactor. The pH plotted is the steady-state pH in the stirred reactor. The shapes of these curves were found to vary as conditions were changed. For example, 66 percent H₂S caused more sulfur to be formed at higher pH; however, the relative formation rates remained similar to those shown in the figure.

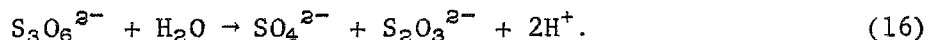
Melter Reactions

Two main reactions occur during the relatively high-temperature melting and decanting step. The principal reaction is thiosulfate decomposition:



This reaction is also a source of sulfate in the system.

A second melter reaction is trithionate hydrolysis:



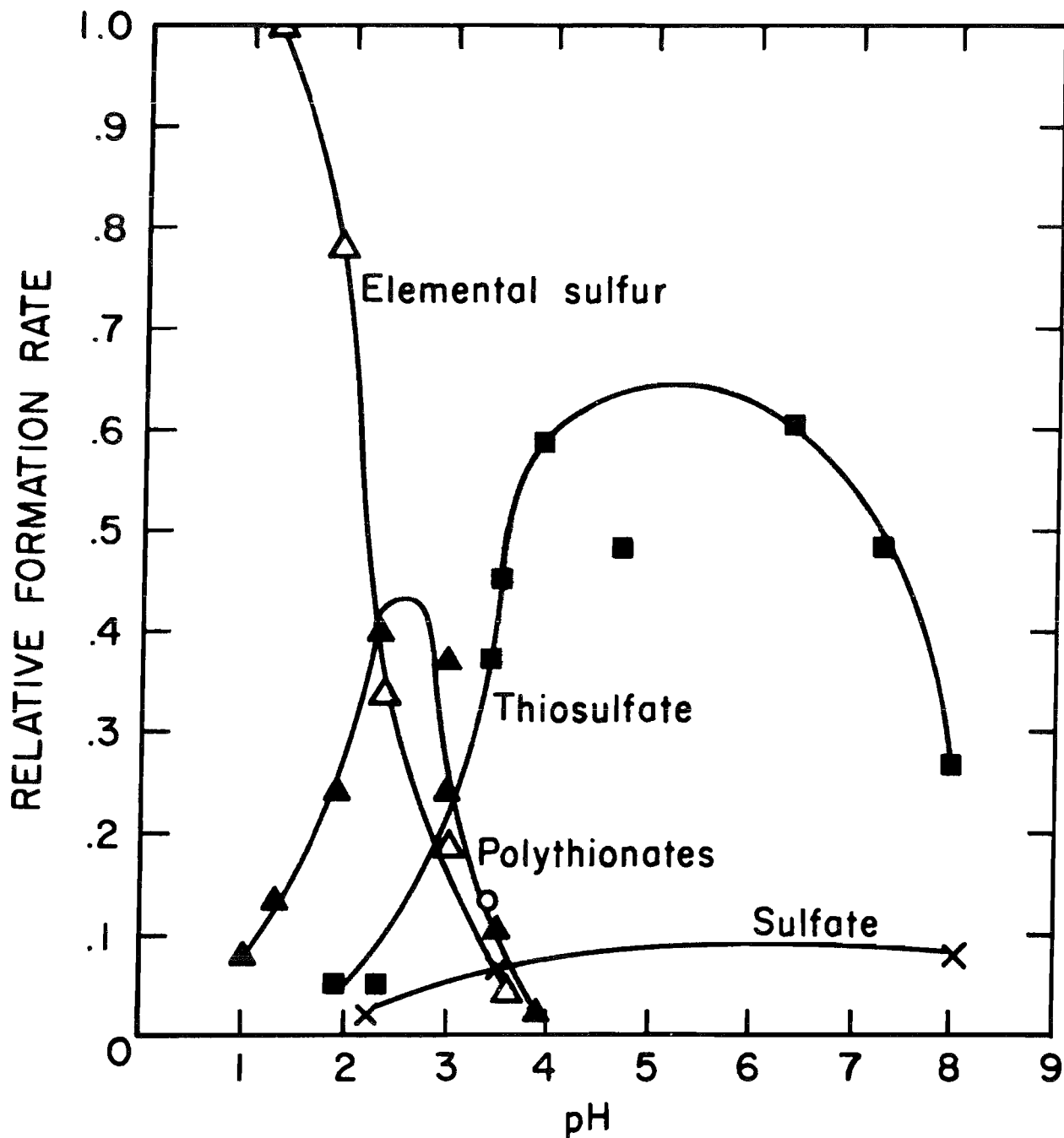


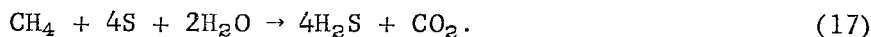
FIGURE 6. - Sulfur species formation rates at varying pH. Polythionates were determined as total $S_nO_6^{2-}$ and calculated as tetrathionate ($S_4O_6^{2-}$).

Any thiosulfate produced by reaction 16 would be expected to undergo further decomposition by reaction 15. The net pH increase observed during melting shows that the dominant process consumes acid according to reaction 15.

No rigorous kinetic measurements were made for the melter reactions; however, for an absorbent solution initially 0.5M in citrate, pH 4.5, and 0.25M in thiosulfate, decomposition of thiosulfate by reaction 15 at 135° C was 13.2 percent and 58.4 percent after 1 hour and 24 hours, respectively.

H₂S Generator Reactions

Proven commercial methods are the basis for H₂S generation in the citrate process. The overall reaction, with natural gas (principally methane) as the reductant is



Research by Bacon (1) indicates that complete conversion of sulfur to H₂S proceeds in stepwise fashion:



followed by



Carbonyl sulfide (COS) that appears in low concentrations in H₂S generator product gas arises from failure of reaction 17b to go to completion:



In practice, the product gas is about 76 to 78 percent H₂S, 18 percent CO₂, and 4 to 6 percent minor products consisting mainly of COS, unreacted methane, and nitrogen. Exhaustive tests were conducted in the Bureau of Mines laboratory and by an outside contractor to determine whether other potentially hazardous products are formed during H₂S generation. In these tests, minor amounts of CS₂ (about 0.4 percent) were detected as well as products tentatively identified as odorant added by the natural gas supplier.

REACTION RATE MEASUREMENTS

It must be emphasized that the reactions discussed in the foregoing sections do not occur singly. Rather, most of them are in progress simultaneously at any given time. For example, thiosulfate is formed by at least three different reactions (6, 7, and 13) and consumed by at least four others (4, 11, 12, and 14). Thus, a rate measured for thiosulfate formation or consumption is, at best, the net rate under a particular set of conditions. Furthermore, measurements were persistently complicated by the presence of liquid, solid, and gas phases during experiments. With this understanding, the approach used in the present work was to study the important net processes (such as thiosulfate formation, which occurs by means of several reactions) with the objective of measuring rates for them as they occur in citrate process operation.

The ionic strength in process solutions varies between about 1 and 2. No attempt was made during the present studies to provide constant ionic strength

because of the high concentrations of solutes already present. For all continuous-flow tests, an excess of H_2S was provided as evidenced by unreacted H_2S in the reactor offgas.

H_2S is soluble in the reaction solution only to the extent of about 2 grams per liter (0.06M). It reacts so rapidly that no method was found for determining the H_2S concentration in solution that could be correlated with other solute concentrations. Because excess H_2S was always available upon demand, the concentration in solution, where the reactions are presumed to occur, was assumed to be low but constant. Thus, H_2S concentration could be eliminated from the rate expressions in a manner analogous to pseudo first-order rate calculations.

SO₂ Consumption

The SO_2 consumption rate was measured at room temperature in the continuous-flow reactor. Citrate absorbent at pH 4.5 containing the indicated concentration of SO_2 was pumped into the reactor at 100 milliliters per minute. Table 1 shows the rate of change in SO_2 concentration and the corresponding pseudo first-order rate constant calculated for

$$\frac{-d[SO_2]}{dt} = k' [SO_2]. \quad (18)$$

TABLE 1. - Calculation of pseudo first-order rate constant for SO_2 consumption

$[SO_2]_0$, M	$\frac{-d[SO_2]}{dt}$, M min ⁻¹	k' , min ⁻¹
0.0457.....	0.0199	0.435
.0859.....	.0280	.326
.108.....	.0465	.431
.152.....	.0676	.445
Average.....	NAP	0.409±0.056

NAP Not applicable.

Thiosulfate Formation

The net thiosulfate formation rate was measured in the continuous-flow reactor under conditions identical to those used for SO_2 consumption measurements. Table 2 shows the net rates measured, together with the corresponding rate constants calculated by assuming first-order dependence upon SO_2 concentration for the process

$$\frac{d[S_2O_3^{2-}]}{dt} = k' [SO_2]. \quad (19)$$

TABLE 2. - Calculation of rate constant for thiosulfate formation

$[\text{SO}_2]_0, \text{ M}$	$\frac{d[\text{S}_2\text{O}_3^{2-}]}{dt}, \text{ M min}^{-1}$	$k', \text{ min}^{-1}$
0.0457.....	0.00919	0.201
.0859.....	.0168	.196
.108.....	.0193	.179
.152.....	.0336	.221
Average.....	NAp	0.199±0.017

NAp Not applicable.

Thiosulfate Consumption

At pH 4.5 the reactions consuming thiosulfate were slow and poorly reproducible; therefore, these processes were measured for thiosulfate feed solutions at pH 3.9 to 4.0, which approximates SO_2 -rich absorbent in the continuous-flow reactor. The rates for thiosulfate consumption are listed in table 3, together with rate constants calculated for the process

$$\frac{-d[\text{S}_2\text{O}_3^{2-}]}{dt} = k' [\text{S}_2\text{O}_3^{2-}]^n \quad (20)$$

for $n = 1$ and $n = 3/2$.TABLE 3. - Calculation of rate constants for thiosulfate consumption

$[\text{S}_2\text{O}_3^{2-}], \text{ M}$	pH	$\frac{-d[\text{S}_2\text{O}_3^{2-}]}{dt}, \text{ M min}^{-1}$	$k', \text{ min}^{-1}$ ($n = 1$)	$k', \text{ min}^{-1}$ ($n = 3/2$)
0.0624.....	3.9	0.00531	0.0851	0.332
.127.....	4.0	.00369	.0291	.0820
.142.....	3.9	.00667	.0470	.124
.205.....	3.9	.0142	.0693	.153
.256.....	4.0	.0111	.0434	.0854
.460.....	4.0	.0107	.0233	.0343
Average.....	NAp	NAp	.0437	.118
Standard deviation.....	NAp	NAp	.0265	.105

NAp Not applicable.

The order of this reaction with respect to thiosulfate is not established unequivocally by the data in table 3. Dinegar (6) reported the acid decomposition of thiosulfate to be proportional to $[\text{S}_2\text{O}_3^{2-}]^{3/2}$. Keller (9) stated that sulfur production from H_2S and SO_2 in solution is proportional to $[\text{S}_2\text{O}_3^{2-}]^{3/2}$. The Bureau of Mines data show that thiosulfate consumption is proportional to thiosulfate concentration, but with better correlation to the first power of thiosulfate concentration than to the 3/2 power. One reason for the scatter in these data is believed to be the limited gas-liquid contact time possible in the small reactor owing to rapid passage of the buoyant gas through even vigorously agitated liquid.

H₂S Consumption

The continuous-flow reactor must provide for free effluent flow to avoid elemental sulfur buildup. This requirement precludes accurate offgas sampling and renders the reactor unsuitable for H₂S consumption rate measurements. For this reason, these rates were determined in the batch reactor. Initial measurements showed that between points B and C all H₂S was consumed (that is, the offgas contained no H₂S) over a range of feed H₂S concentrations from 0.05 to 0.476 atmosphere and H₂S flow rates from 19.6 to 316 cubic centimeters per minute. At point D, where slower reactions predominate, H₂S consumption diminished, and the offgas contained from 2.3 to 36 percent H₂S. Thus, the H₂S consumption rates reported below are the rates corresponding to point D for citrate absorbent containing 0.3M thiosulfate, pH 3.9. These rates are not expressed in the customary units of change in concentration per unit time because, as discussed earlier, the instantaneous H₂S concentration in the liquid phase could not be determined. Rather, the rates reported here are millimoles of H₂S consumed per unit time, and are cited to show the dependence of these rates upon the H₂S concentration (partial pressure) in the feed gas. Attempts to determine the reaction rate dependence upon H₂S concentration in solution will be described later. The process assumed in the calculations is

$$\text{rate, } R \equiv \frac{-dH_2S}{dt} = k' [H_2S]_g^n, \quad (21)$$

where $[H_2S]_g$ refers to concentration in the gas phase, expressed in atmospheres, and k' includes contributions of other reaction partners and the influence of mass transfer of H₂S from the gas to the liquid phase. The value of n , 1.4, in the rate expression above was determined by plotting $\log R$ versus $\log [H_2S]_g$ and determining n from the slope of the line. Good linearity was obtained for this plot, which exhibited a correlation coefficient of 0.993. Table 4 lists the data together with k' calculated for $n = 1.4$.

TABLE 4. - Calculation of pseudo n-th order rate constant
H₂S consumption

$[H_2S]_g$, atmospheres	$R \equiv -dH_2S/dt$, mmoles min ⁻¹	k' , mmoles/min-atm
0.053.....	0.39	23.8
.080.....	.71	24.4
.094.....	.67	18.4
.15.....	1.44	20.5
.33.....	4.81	22.5
.43.....	5.19	16.9
.48.....	8.62	24.4
Average.....	NAP	21.6±3.0

NAP Not applicable.

Sulfur Formation

Sulfur formation rates were determined in the continuous-flow reactor by weighing the elemental sulfur contained in effluent samples. No satisfactory

correlation could be found between sulfur formation and SO_2 or thiosulfate concentrations or pH. In a series of 18 room-temperature measurements for feed solutions containing from 0M to 0.15M SO_2 only, and from 0M to 0.26M thiosulfate only, pH 3.9 to 4.5, and for H_2S gas concentrations from 0.52 to 1.0 atmosphere, the sulfur formation rate averaged (0.029 ± 0.012) moles per liter-minute. The lack of systematic variation in this rate indicates that sulfur formation is limited by mass transfer of H_2S into the liquid phase. A limited series of tests was run in the continuous-flow reactor in which the sulfide source was a solution of NaHS in place of gaseous H_2S . For a feed sulfide concentration of $6.3 \times 10^{-4}\text{M}$, varying the influent SO_2 concentration from 0.04M to 0.12M produced no significant change in the sulfur formation rate that averaged (0.023 ± 0.001) moles per liter-minute; however, varying the feed sulfide concentration from $6.3 \times 10^{-4}\text{M}$ to $1.89 \times 10^{-3}\text{M}$ with a constant feed SO_2 concentration of 0.04M caused a linear (first-order) increase in the sulfur formation rate from 0.024 to 0.072 mole per liter-minute. For all measurements, the rate constant, k' , calculated assuming pseudo first-order dependence upon sulfide concentration for the process

$$\frac{d[\text{S}]}{dt} = k' [\text{H}_2\text{S}]_1 \quad (22)$$

was $(38.0 \pm 3.4) \text{ min}^{-1}$, where $[\text{H}_2\text{S}]_1$ refers to the sulfide concentration in the feed solution.

An additional series of tests was conducted to determine the sulfur formation rate for solutions containing both SO_2 and thiosulfate. Figure 7 depicts the results of these room temperature, continuous-flow reactor tests, all of which were run with gaseous H_2S . Whereas, in earlier tests on solutions containing only SO_2 or thiosulfate the sulfur formation rate was essentially constant, as discussed earlier, in the tests represented by figure 7, the rate increased both in tests with varied SO_2 at constant thiosulfate and in those complementary tests with varied thiosulfate at constant SO_2 . Interestingly, the sulfur formation rate determined for tests at varied SO_2 exceeded the sum of the rates determined for solutions containing SO_2 or thiosulfate individually under similar conditions. For example, the sulfur formation rate for a solution containing only 0.15M SO_2 was 0.038 mole per liter-minute; the rate for a solution containing only 0.062 molar thiosulfate was 0.016 mole per liter-minute. The rate for a solution containing both 0.16M SO_2 and 0.062M thiosulfate was 0.15 mole per liter-minute, which is 2.7 times the sum of the individual rates. Clearly, SO_2 and thiosulfate interact to facilitate sulfur formation upon treatment with H_2S . Complex formation as in reaction 5 may be the first step in a sulfur-producing process analogous to that reported by Battaglia and Miller to occur when bisulfite (HSO_3^-) is depleted during the reaction of SO_2 and thiosulfate (2).

Hydrogen Ion Consumption

Between pH 3 and pH 6 citrate buffer solutions exhibit a linear pH response of 0.72 pH unit per mole of H^+ ion per mole of contained citrate. By using this buffer response value, it was possible to calculate the rate of hydrogen ion consumption during the D-E portion of batchwise actual and sham

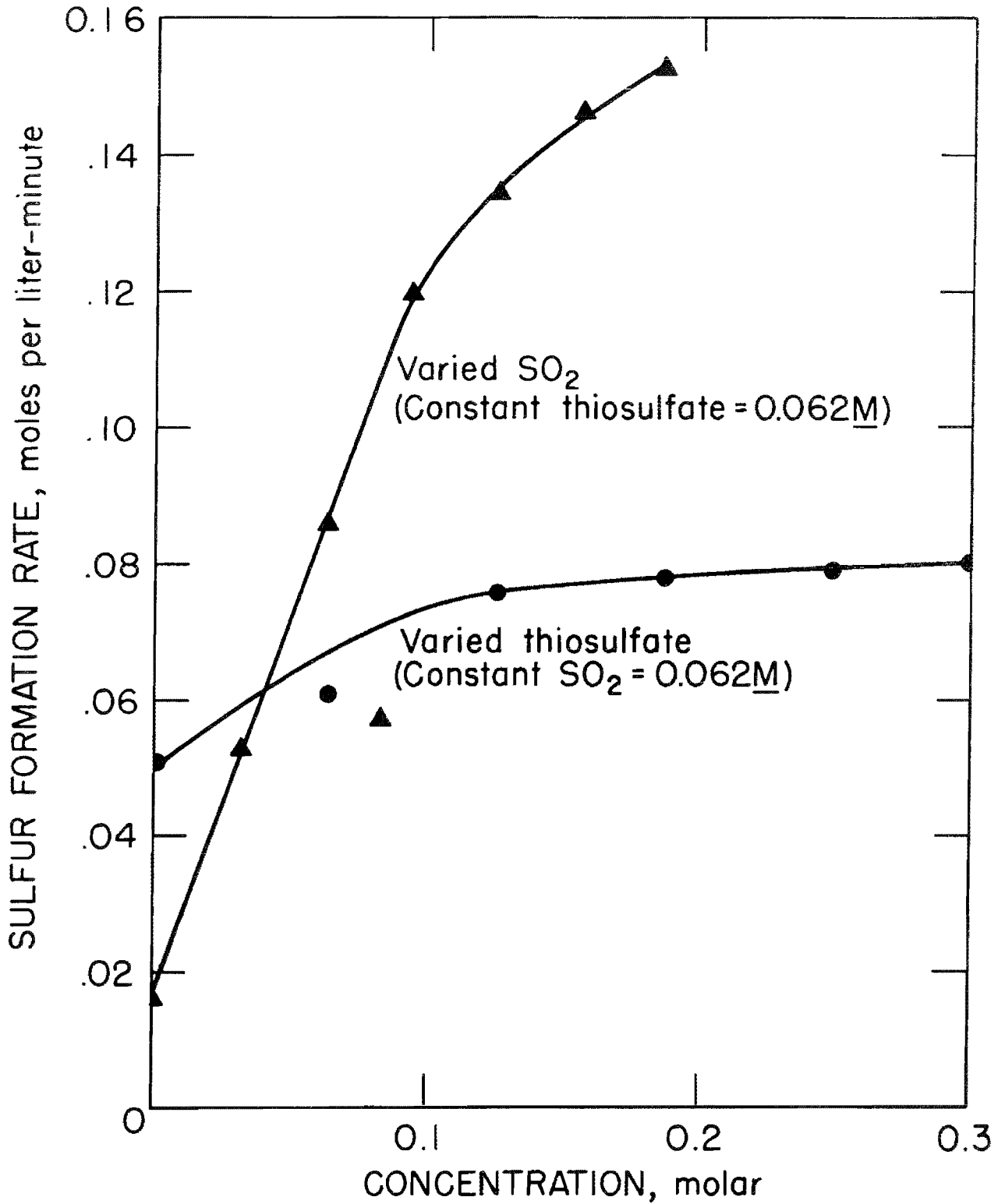


FIGURE 7. - Sulfur formation rates in absorbent containing both SO₂ and thiosulfate.

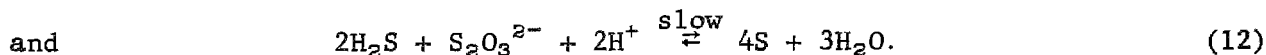
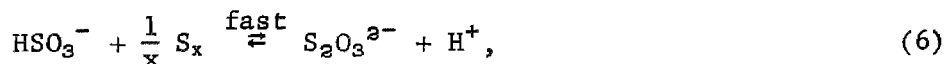
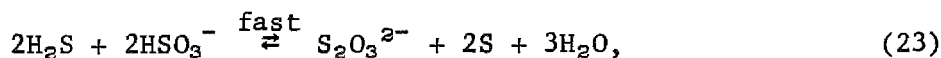
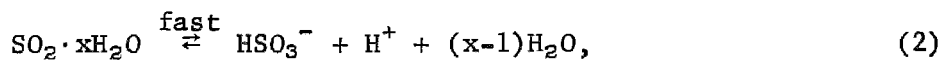
regeneration tests. The hydrogen ion and thiosulfate concentration differences between successive points along the D-E segment of the curve were correlated with the time elapsed between the points. The significant feature of these calculations is that for each mole of thiosulfate consumed along this segment of the regeneration curve two moles of hydrogen ion are consumed. Specifically, for 24 pairs of points during actual regeneration tests under widely varying temperature, H_2S partial pressure, and thiosulfate concentration the value for the ratio $\frac{-d[S_2O_3^{2-}]/dt}{-d[H^+]/dt} = (2.1 \pm 0.5)$. For 12 pairs of points obtained during sham regeneration tests (that is, for solutions containing only thiosulfate) the value for this ratio is (2.3 ± 0.6) . This observation provides substantial additional evidence that the important, rate-limiting process during absorbent regeneration is thiosulfate reduction by reaction 12.

CONCLUSIONS

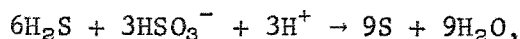
The precise, molecular-level mechanism for sulfur formation in citrate process operation remains unclear. Because of the complex array of simultaneous, competing, and sequential reactions known to occur in this system, it is unlikely that any single mechanism will be proven; nevertheless, the principal processes important in sulfur production are known, and a reasonable reaction sequence explaining them can be proposed. Prior to this, some observations from the foregoing discussion should be summarized:

1. Elemental sulfur is present in solution during regeneration of SO_2 -rich absorbent with H_2S before it is visible as a second phase.
2. No gross sulfur is visible during regeneration until essentially all SO_2 is consumed.
3. H_2S reacts with polythionates to produce thiosulfate and liberate hydrogen ion.
4. Polythionate concentrations increase until all SO_2 is consumed, then diminish.
5. The rate of hydrogen ion consumption during the final regeneration phase (D-E) is twice the rate of thiosulfate consumption.

The following scheme is proposed to account for the preceding observations, as well as sulfur formation in general:



Note that adding reactions 23, 6, and twice reaction 12 yields



which is simply three times the familiar overall reaction 9.

Elemental sulfur in solution during the early stages of regeneration is formed according to reaction 23; however, so long as HSO_3^- remains in solution, much of the sulfur is rapidly converted to thiosulfate by reaction 6 at a rate that slows with diminishing HSO_3^- .

Polythionates are produced in side reactions such as the dimerization of fragments, $\text{S}_n\text{O}_3^{2-}$, resulting from the stepwise reaction of HSO_3^- with elemental sulfur. Other, probably simultaneous, reactions producing polythionates include 4, 7, and 11.

Reaction 12, which is proposed as rate-limiting, requires the hydrogen ion to proceed. It is significant that in alkaline solution (above about pH 6) no elemental sulfur is produced and all H_2S and SO_2 are converted to thiosulfate. This is interpreted as additional evidence for reaction 12 as the critical step in absorbent regeneration.

Because H_2S utilization shows marked dependence upon the sulfide concentration in solution it is clear that the absorbent regeneration rate can be increased most effectively by increasing the solution sulfide concentration. This can be achieved by increasing the gas-liquid interfacial area through more vigorous agitation, or, as indicated by the H_2S consumption rates reported, by increasing the partial pressure of H_2S in the gas phase.

Finally, this report does not purport to answer all questions regarding the chemistry of this system. Additional tests to determine the exact temperature dependence of the various reactions discussed would be appropriate. Further insight could be gained by using radioactive sulfur compounds in rate studies. For example, the rate of conversion of oxidized sulfur to a reduced form could be measured by reacting H_2S with thiosulfate labeled on the inner (sulfate) sulfur ($\text{S}-\text{S}^*\text{O}_3^{2-}$) and determining the rate at which the labeled sulfur is found in either the outer position ($\text{S}^*-\text{SO}_3^{2-}$) or in other compounds in which the sulfur exists in a reduced formal oxidation state.

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