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DEVELOPMENT OF INSTRUMENTAL MEHTODS OF ANALYSIS OF SULFUR COMPOUNDS IN COAL PROCESS STREAMS

Quarterly Technical Progress Report for the Period October—December 1980

MASTER

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U. S. DEPARTMENT OF ENERGY

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DEVELOPMENT OF INSTRUMENTAL METHODS OF ANALYSIS OF
SULFUR COMPOUNDS IN COAL PROCESS STREAMS

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for the period
October-December 1980

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ABSTRACT

A synopsis of progress during October-December, 1980, is presented. This is the fifth quarter of a two-year contract renewal period. Recent work on the four tasks is reviewed.

TASK 1. EXTENSION AND REFINEMENT OF THERMODYNAMIC SURVEY AND CONSTRUCTION OF POURBAIX DIAGRAMS. Work is in progress on the preparation of a user-oriented computer software manual, for estimating sulfur speciation in aqueous coal process streams from a thermodynamic data base.

TASK 2. VOLTAMMETRIC METHODS DEVELOPMENT. Capabilities and limitations of sulfide and polysulfide analysis by differential pulse polarography at a dropping mercury anode are assessed critically.

TASK 3. ENTHALPIMETRIC METHODS DEVELOPMENT. Thallous nitrate used as the titrant reagent in a thermometric enthalpy titration yields the molar sum of monosulfide (HS^- , S^{2-}) and polysulfide (S_x^{2-} , $x = 2-5$).

TASK 4. APPLICATION AND TECHNOLOGY TRANSFER TO COAL CONVERSION PLANTS. Inorganic sulfur has been successfully speciated in coal conversion by-product water samples. A combination of differential pulse voltammetry, thermometric enthalpy titrations and classical methods was used. One hundred percent of the total sulfur present was quantitatively accounted for.

TABLE OF CONTENTS

	Page
Abstract	1
Objectives and Scope of Work	3
Task Descriptions	4
Progress Report Chart	6
Summary of Progress to Date	7
Description of Technical Progress	11
Task 1. Extension and Refinement of Thermodynamic Survey and Construction of Selected Condi- tional Pourbaix Diagrams	11
Task 2. Voltammetric Methods Development	11
Task 3. Enthalpimetric Methods Development	13
Task 4. Application and Technology Transfer to Coal Conversion Plants	15
Conclusions	19
Literature Cited	20
Acknowledgement	21

OBJECTIVES

The general objective is resource development in the analytical chemistry of sulfur compounds for the evolving new coal technologies. Based on fundamental considerations, judiciously selected methods of instrumental analysis will be developed for determining sulfur compounds in coal conversion process streams. Significant sulfur moieties will be identified with the aid of thermodynamic and kinetic criteria. Two discrete types of procedures will be developed for each and every such moiety, viz.,

- 1) an enthalpimetric method, which relies on the measurements of heats of reaction in adiabatic cells;
- 2) a voltammetric method, using glassy carbon indicator electrodes.

SCOPE OF WORK

Stability domains of all known sulfur compounds will be "mapped" as function of redox potential and pH. Characteristic abundance profiles will be determined, specifying the moieties which exist in every oxidation state of sulfur ranging from -2 (e.g., sulfide) to +8 (persulfate). Based on this information, the "occurrence probability" of potential sulfur contaminants in coal conversion streams will be assessed.

In the area of quantitative analytical methods development, specificity will be optimized by choice of selective reagents for the calorimetric determinations, and by using controlled potential scans and intrinsically selective techniques (such as differential pulse measurements) in voltammetry. Sensitivity will be maximized by reliance upon appreciably exothermic or endothermic reactions on the one hand, and the use of rotated disk electrodes on the other hand. Precision, accuracy and interferences will be assessed in simulated and actual coal conversion process stream samples.

TASK DESCRIPTIONS

TASK 1. EXTENSION AND REFINEMENT OF THERMODYNAMIC SURVEY AND CONSTRUCTION OF POURBAIX DIAGRAMS. (J.D. Stutts)

- a. Algorithms will be developed for evaluating "expectation values" for the concentrations of sulfur contaminants in process streams from experimentally determined values of pH, redox potential and total sulfur.
- b. Pourbaix Diagrams will be generated for nonaqueous solvents.
- c. "Conditional Pourbaix Diagrams" will be generated, taking into account the "freezing out" of selected equilibria by slow kinetics.

TASK 2. VOLTAMMETRIC METHODS DEVELOPMENT. (S.J. Ankabrandt, J.E. Yakupkovic)

- a. Hydrodynamic differential pulse voltammetry at rotated glassy carbon disk electrodes will be used for developing quantitative methods amenable to the determination of inorganic and organic sulfur moieties in coal conversion process streams and products.
- b. Interferences and precision will be assessed. Dependability will be checked by comparison with an independent enthalpimetric methods of analysis (cf., Task 3, below).

TASK 3. ENTHALPIMETRIC METHODS DEVELOPMENT. (J. Stahl)

- a. Direct injection enthalpimetry (DIE) will be used for developing quantitative methods for the determination of sulfur moieties in coal conversion process streams.
- b. Dependability will be checked by comparison with an independent voltammetric method of analysis (cf., Task 2, above).

TASK 4. APPLICATION AND TECHNOLOGY TRANSFER TO COAL CONVERSION PLANTS. (S.J. Ankabrandt, J. Stahl, J.E. Yakupkovic)

- a. Using representative samples of coal conversion process streams and products, relevant pH values, redox potentials and total sulfur concentrations will be determined.
- b. Using procedures developed in Task 1, expected concentrations of sulfur contaminants will be evaluated with the aid of appropriate algorithms.
- c. All sulfur moieties which appear significant on the basis of these predictions will be determined quantitatively by an appropriate enthalpimetric method (developed by Task 3) and by a discrete voltammetric method (developed in Task 2).

- d. Detailed information on the above general procedures will be disseminated to operators of coal conversion plants, for current and future use.

PROGRESS REPORT CHART

	1979	1980				1981		
	Oct. - Dec.	Jan. - Mar.	Apr. - Jun.	Jul. - Sept.	Oct. - Dec.	Jan. - Mar.	Apr. - Jun.	Jul. - Sept.
<u>Task</u>								
1) Extension and Refinement of Thermodynamic Survey and Construction of Selected Conditional Pourbaix Diagrams
2) Voltammetric Methods Development
3) Enthalpimetric Methods Development
4) Application and Technology Transfer to Coal Conversion Plants

Legend

SUMMARY OF PROGRESS TO DATE

This is the thirteenth Quarterly Technical Report since the project has been initiated on September 30, 1977, and subsequently renewed on September 30, 1979. A retrospective update of accomplishments during the forty months period, October 1977 - December 1980, is given below, complementing and recapitulating the corresponding summary page of FE-2710-12.

TASK 1. EXTENSION AND REFINEMENT OF THERMODYNAMIC SURVEY AND CONSTRUCTION OF POURBAIX DIAGRAMS. Thermodynamic parameters have been critically tabulated for selected inorganic moieties in aqueous solution. Standard heats of formation, third-law entropies and molar heat capacities have been compiled from the literature and/or appropriately evaluated for thirty significant solute species containing the elements sulfur, oxygen and/or hydrogen. Algorithms have been developed for the generation of abundance profiles and for delineating thermodynamic stability domains as function of pH, redox potential and temperature; and for predicting the relative concentrations of moieties containing the elements hydrogen, oxygen, and 1 to 5 atoms of sulfur per molecule. The algorithm is outlined in sufficient detail, and such generality, that computer programs can be written in any high level language and for moieties of any combination of elements for which the requisite thermodynamic data is available. Simple procedures have been developed for taking into account the "blocking" of specified reactions by slow kinetics. A software manual is in its final stages of preparation and will consolidate contributions from Task 1 and Task 4.

TASK 2. VOLTAMMETRIC METHODS DEVELOPMENT. Differential Pulse Voltammetric (DPV) methods have been developed for the determination of inorganic and organic sulfur moieties in aqueous and non-aqueous solvents. Rotated glassy carbon disk (RGCD) and dropping mercury (DM) electrodes were employed. Quantitation has been accomplished by correlating ($\Delta i/\Delta E$) peaks of differential pulse voltammograms with concentrations of electrooxidizable and electroreducible sulfur moieties. Selectivity was achieved by maintaining experimental conditions (solvents, supporting electrolytes, pH, potential domains) where specified electrode reactions proceed with 100% current efficiency. Work has been initiated on "wave equations" describing the analytic geometry of differential pulse voltammograms, applicable to irreversible electrooxidation processes. Preliminary findings suggest that differential pulse polarography may be amenable to quantitating the total sulfur present in formal oxidation states between -2 and zero, i.e., the sum of sulfides and polysulfides. The current status of the voltammetric capabilities developed to date is summarized below.

A. Determination of Sulfur Dioxide

Conditions: RGCD in aqueous solution

Electrode Reaction Employed: $\text{SO}_2 + 4\text{H}^+ + 4\text{e}^- = \text{S} + 2\text{H}_2\text{O}$ (electroreduction)

Status: Tested in gasification by-product water process streams.

B. Determination of Sulfite

Conditions: DM in aqueous solution

Electrode Reaction Employed: $\text{Hg} + 2\text{SO}_3^{2-} = \text{Hg}(\text{SO}_3)_2 + 2\text{e}^-$ (anodic depolarization)

Status: Sulfite selectively quantified in the presence of thiosulfate; tested in gasification by-product water process streams.

C. Determination of Thiosulfate

Alternative Method I:

Conditions: RGCD in aqueous solution

Electrode Reaction Employed: $2\text{S}_2\text{O}_3^{2-} = \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$ (electrooxidation)

Status: Dynamic range up to 0.001 M, phenol interferes in process stream samples.

Alternative Method II:

Conditions: DM in aqueous solution

Electrode Reaction Employed: $\text{Hg} + 2\text{S}_2\text{O}_3^{2-} = \text{Hg}(\text{S}_2\text{O}_3)_2 + 2\text{e}^-$ (anodic depolarization)

Status: Tested in actual process streams.

D. Determination of Sulfide

Conditions: DM in aqueous solution

Electrode Reaction Employed: $\text{Hg} + \text{S}^{2-} = \text{HgS} + 2\text{e}^-$ (anodic depolarization)

Status: Dynamic range up to 1.2×10^{-2} M.

E. Determination of Tetrathionate

Alternative Method I:

Conditions: RGCD in aqueous solution

Electrode Reaction Employed: $\text{S}_4\text{O}_6^{2-} + 2\text{H}_2\text{O} = 2\text{SO}_4^{2-} + 2\text{S} + 4\text{H}^+ + 2\text{e}^-$ (electrooxidation)

Status: Phenol interferes in process stream samples.

Alternative Method II:

Conditions: DM in aqueous solution

Electrode Reaction Employed: $\text{S}_4\text{O}_6^{2-} + 2\text{e}^- = 2\text{S}_2\text{O}_3^{2-}$ (electroreduction)

Status: Dynamic range studies in progress.

F. Determination of Dibenzothiophene (DBT)

Conditions: RGCD in acetonitrile

Electrode Reaction Employed: $2\text{DBT} = 9\text{-}[3\text{-dibenzothiophenyl}]\text{-dibenzothiophenium}^+ + 2\text{e}^- + \text{H}^+$ (electrooxidation)

Status: Tested in several coal liquefaction products; precision: 0.5%

G. Determination of Benzothiophene (BT)

Conditions: RGCD in acetonitrile

Electrode Reaction Employed: $2\text{BT} = \text{benzothiophenyl-benzothiophenium}^+ + 2\text{e}^- + \text{H}^+$ (electrooxidation)

Status: Dynamic range 3×10^{-6} M to 2×10^{-3} M; determination feasible in the presence of DBT.

TASK 3. ENTHALPIMETRIC METHODS DEVELOPMENT. Heats of 20 oxidation-reduction, acid-base, complexation and precipitation reactions of H_2S , SO_2 , and of related Bronsted acid-base moieties have been determined under rigorously defined experimental conditions of pH, ionic strength, etc. Corresponding formal (conditional) ΔH values in aqueous solutions at 25°C have been intercompared critically. Definitive ΔH assignments were made within specified precision limits on considerations of internal consistency. The conceptual and practical foundations have been laid for the non-separative quantitative analysis of a mixture of sulfate, bisulfite, (or SO_2 , or sulfite) and thiosulfate by direct injection enthalpimetry (DIE). Implementation involves the accurate measurement of heats evolved upon reacting aliquots of the mixture with excess barium chloride, potassium triiodide, formaldehyde, and hydroxymercury benzoate (HOMB). Under the relevant experimental conditions, the heat of precipitation of barium sulfate was invariant of pH in a range between 4 and 10. A precision and accuracy of 1% was attained in the determination of thiosulfate in aqueous samples. The dynamic range encompassed sample sizes between 10 and 20 micromoles. Formaldehyde was found to be a preferred enthalpimetric reagent for sulfur dioxide, bisulfite and sulfite. Quantitation of H_2S , HS^- and S^{2-} was accomplished using the reagent HOMB: the method has a dynamic range which corresponds to sodium bisulfide concentrations between 50 and 5000 ppm and a precision of 5%. Feasibility of the simultaneous determination of S_x^{2-} polysulfide is being explored.

Work has been initiated on developing a novel general approach to the determination of Bronsted base moieties (e.g., sulfate, sulfite, bisulfite, bisulfide and sulfide). The new concept involves simultaneous thermometric and potentiometric titrations with strong acid, using readouts from thermistors and glass electrodes immersed in an adiabatic cell. The technique has been successfully applied to the determination of sulfide (S^{2-}) or sulfite (SO_3^{2-}) in the presence of hydroxide (OH^-) and carbonate (CO_3^{2-}). By pretitrating with TlNO_3 to precipitate Tl_2S , a solution containing both sulfide and sulfite can be determined in a single aliquot. Thallous nitrate has been found to also precipitate polysulfides (S_x^{2-} , $x = 2-5$) quantitatively.

TASK 4. APPLICATION AND TECHNOLOGY TRANSFER TO COAL CONVERSION PLANTS. A user-oriented computer program (written in BASIC) has been developed for estimating "thermodynamic expectation values" of the mole-fractional abundances of thirty moieties containing the elements hydrogen, oxygen and 1-5 atoms of sulfur per molecule. Required inputs are pertinent Gibbs free energy of formation assignments (available in tabulations) plus three readily measurable variables, viz., the pH, the redox potential and the temperature of the process stream. The corresponding concentration of each sulfur moiety can be conveniently calculated if the total sulfur molarity is known. In four

gasification by-product water process stream samples, the actual concentrations of sulfide (H_2S , HS^- , S^{2-}) and sulfite (SO_2 , HSO_3^- , SO_3^{2-}) were significantly different from the thermodynamic expectation values. Evidently equilibrium did not prevail and the "expectation assignments" require refinements incorporating kinetic considerations. Generally, liquefaction by-product waters exhibit more negative redox potentials than gasification by-product water: corresponding thiosulfate/sulfide ratios encompassed a range between 0.01 (liquefaction) and 2000 (gasification). Differential pulse voltammetric techniques, developed in Task 2 and tested in actual coal conversion process streams, appear ready for in-plant use. Sulfur dioxide was successfully determined in coal gasification and liquefaction "by-product" water streams, using differential pulse voltammetry at a rotated glassy carbon disk cathode. Interference by sulfide (a common contaminant) was circumvented by prior precipitation as cadmium sulfide. Sulfide, thiosulfate, and sulfite were also successfully determined by DPV at a dropping mercury anode. As an alternative method for sulfide determination, sulfidic sulfur was successfully quantitated by thermometric enthalpy titrations in a wide variety of coal liquefaction and gasification by-product water samples. Standard solutions of hydroxymercury benzoate were used as reagent. With the aid of differential pulse voltammetry at a rotated glassy carbon disk anode, dibenzothiophene has been identified and quantitated in a variety of coal liquefaction products ranging from light distillates to SRC II stripper bottom fractions. Using a multipoint "standard addition calibration" procedures, the DBT content of the samples was found to range between 0.1 and 0.2 percent. Where comparable data are available, the differential pulse voltammetric assignments are in excellent agreement with results obtained independently by other analytical methods. H-Coal® "sour water" samples have been characterized in terms of pH and redox potentials. Depending on the latter, sulfur was present either entirely as sulfide, or as a mixture of sulfides, polysulfides and thiosulfate.

DESCRIPTION OF TECHNICAL PROGRESS

Task 1: Extension and Refinement of Thermodynamic Survey and Construction of Selected Conditional Pourbaix Diagrams. (J.D. Stutts)

Work on this task has been substantively completed. During the next three months (see Progress Report Chart, p. 6), a user-oriented manual (including appropriate computer programs) will be prepared, for estimating sulfur speciation in aqueous coal process streams from a thermodynamic data base. Input will include pH, redox potential, total sulfur, ionic strength and temperature. The manual will consolidate contributions from Tasks 1 and 4.

Task 2: Voltammetric Methods Development (S.J. Ankabrandt)

The procedures for the determination of sulfide by differential pulse polarography (DPP) using a dropping mercury anode have been described⁶. Use was made of the well-known anodic depolarization of mercury with sulfide, viz.,

which yielded peak currents proportional to the sulfide concentration up to 2.0×10^{-3} M. When this method was applied to H-Coal "sour water" specimens (see Task 4 below), the results shown in Table II.1 were obtained.

Table II.1

Comparison of Results Obtained by Classical Methods
and Differential Pulse Polarography (DPP)

(1) Sample ^(b)	Sulfur Speciation by Classical Methods ^(a) , g/l			(5) Sulfide by DPP(c), g/l
	(2) Sulfidic ^(d)	(3) Polysulfidic ^(e)	(4) (2) + (3)	
LO 2097	26.6	14.0	40.6	41.4
LO 2098	59.0	--	59.0	63.2

(a) Same data as in Table IV.2, expressed in gr per liter of sulfur.

(b) See Columns 1,2,3 of Table IV.1 below.

(c) Measured via anodic depolarization currents at dropping mercury electrode (peak potential = -0.61 volt vs. the saturated calomel electrode).

(d) $\text{CS}_2^- + 1/2\text{CS}_2 + 1/3\text{CS}_3 + \dots (= \sum_x 1/x \text{CS}_x^-)$

(e) $1/2\text{CS}_2 + 2/3\text{CS}_3 + 3/4\text{CS}_4 + \dots [= \sum_x (x-1)/x \text{CS}_x^-]$

A comparison of Columns 4 and 5 makes it apparent that the DPP signal was actually proportional to the sum of two quantities, viz.,

$$\text{"sulfidic sulfur"} = [S^{\bar{2}}] + [S_2^{\bar{2}}] + [S_3^{\bar{2}}] + \dots \quad (2.2)$$

$$\text{"polysulfidic sulfur"} = [S_2^{\bar{2}}] + 2[S_3^{\bar{2}}] + 3[S_4^{\bar{2}}] + \dots \quad (2.3)$$

Or, in general:

$$\text{Sulfidic sulfur} = \sum_x [S_x^{\bar{2}}] \text{ where } x = 1, 2, 3, 4, 5 \quad (2.4)$$

$$\text{Polysulfidic sulfur} = \sum_x (x-1)[S_x^{\bar{2}}] \quad (2.5)$$

The data in Columns 2 and 3 of Table II.1 were obtained by independent methods. "Sulfidic sulfur" (as defined in Equations 2.2 and 2.4) was determined by a classical iodometric titration¹. "Polysulfidic sulfur" (defined in Equations 2.3 and 2.5) was quantitated by gravimetric determination¹⁷ of the sulfur precipitated (upon acidification) via the Reaction

Thus, what transpires from Table II.1 is the remarkable finding that in mixtures of sulfides and polysulfides the DPP signal was proportional to

$$\text{Sulfidic} + \text{polysulfidic sulfur} = \sum_x x \cdot [S_x^{\bar{2}}] \quad (2.7)$$

i.e., to the total amount of sulfur which was present (in the relevant coal process stream samples) in a range of formal oxidation states between -2 and zero^{*}. That this may indeed be the case appears plausible in the light of previous pertinent work in the literature¹³⁻¹⁵. Analogous expressions to Equation 2.1 (e.g., Equation 2.8 below) account for faradaic currents proportional to the concentration of sulfidic sulfur:

However, it is not obvious why the observed DPP signals were also proportional to the non-sulfidic component $(x-1)S$. Work is in progress to elucidate this question.

*In this context, the formal oxidation state of sulfur in $S^{\bar{2}}$ is -2; in $S_2^{\bar{2}}$, -1; in $S_3^{\bar{2}}$, -2/3; in $S_4^{\bar{2}}$, -0.5; in $S_5^{\bar{2}}$, -0.4.

Task 3. Enthalpimetric Methods Development. (John Stahl)

Thallous nitrate has been found to be a promising reagent for the selective precipitation of sulfide as Tl_2S in its determination by thermometric enthalpy titration (TET)¹². Because of the occurrence of polysulfides in many coal conversion by-product waters, the possible reactions of thallium(I) with the polysulfides are also important.

Feigl reports a spot test for elemental sulfur which results in the formation of a thallium polysulfide¹⁶. That compound, Tl_2S_x ($x = 2,3,4,5$), unlike the monosulfide, Tl_2S , has the following chemical properties:

- (a) it is insoluble in strong acids,
- (b) it is not oxidized nor dissolved by H_2O_2 solution.

This difference in chemical properties suggests that one might conceivably differentiate between monosulfide and polysulfides by their titration with thallium(I) to a thermometric endpoint. This would be theoretically possible if there were appreciable differences in the heats and Gibbs free energies of the reactions:

A literature search for the relevant thermodynamic data is in progress. Preliminary relevant experiments are reported below.

An aqueous solution made up of 0.1 M NaOH, 0.008 M Na_2S , and containing 0.01 moles per liter of elemental sulfur was titrated with 0.326 M $TlNO_3$ in an adiabatic cell. The titrand solution is known to contain¹⁰ a mixture of the ions $S^{=}$, $S_2^{=}$ and $S_4^{=}$ (plus relatively small concentrations of $S_3^{=}$ and $S_5^{=}$). The thermometric titration is shown in Figure 3.1. Only one clearly defined endpoint was obtained, whose stoichiometry corresponded to $2Tl^+$ per mole of Na_2S used in preparing the solution. In other words, the titration with thallous nitrate did not discriminate between the $S^{=}$ and its complexed homologs $S_x^{=}$. Thus, the titration endpoint provided the molar sum

$$a = [S^{=}] + [S_2^{=}] + \dots + [S_5^{=}]$$

which is conventionally referred to as "sulfidic sulfur."

Fig. 3.1 Thermometric titration of 30.0 mls. of an aqueous polysulfide solution prepared by dissolving elemental sulfur (0.01 mole per liter) in 0.1 M NaOH plus 0.008 M Na_2S . The titrant was 0.326 M TiNO_3 . The endpoint corresponds to the total "sulfidic" sulfur content, viz., 0.008 M

Work is in progress for resolving the mixture. It is apparent in Figure 3.1 that the titration curve was not quite rectilinear. Such was not observed in thermometric titrations of pure Na_2S solutions with thallous nitrate (Reaction 3.1). Thus it is likely that the curvature in Figure 3.1 was due to the presence of polysulfides, which precipitated Tl^+ via Reactions 3.2 through 3.5.

In Task 4 of this report (v.i), results are presented on thermometric titrations of process stream samples with TlNO_3 . Aliquots were prepared by injecting 0.100 ml. of sample into 30.0 mls of 0.1 M NaOH containing 0.25 g of ascorbic acid in a Dewar flask which had been pre-equilibrated thermally. Nitrogen was kept flowing in the flask, and the ascorbic acid provided additional antioxidation protection. The aliquots were then titrated with 0.326 M TlNO_3 and the temperature change was monitored. The results obtained agreed with the classical iodometric determination of sulfidic sulfur¹⁷.

Task 4. Application and Technology Transfer to Coal Conversion Plants. (S.J. Ankabrandt, John Stahl, and J.E. Yakupkovic)

One hundred percent of the sulfur present has been speciated in two coal conversion by-product water samples made available by Hydrocarbon Research, Inc., Research and Development Center, Lawrenceville, NJ 08648. Both samples emanated from H-Coal* process streams, involving the high pressure hydrogenation of coal slurries suspended in so-called "internal recycle-oils" which are the products of prior coal liquefaction steps. A distinctive feature of the H-Coal process is the absence of water, of other sources of oxygen and of oxidizing agents (electron acceptors) in general. The two samples originated from analogous runs in September 1977 and September 1979, using different types of coal which are identified in Table IV.1. The tables list the pH, redox potential (E) and total sulfur content of the two samples, which were determined in the present work.

In a previous Quarterly Report¹² it was shown that $\text{pH} > 9$ and $E < -0.25$ volt were distinguishing characteristics of liquefaction by-product waters. Their gasification counterparts tended to be more acidic ($\text{pH} < 9$) and less reducing ($E > -0.2$). Thus columns 5 and 6 in Table IV.1 are in good agreement with the pH and redox potential patterns of other liquefaction scrubber waters. On the other hand, the processing of the Kentucky coal yielded by-product water which was less basic, had a more negative redox potential and a significantly higher sulfur content than the by-product water obtained from Illinois coal #6.

The sulfur in each sample was speciated. "Sulfidic sulfur" ($[\text{S}^=] + [\text{S}_2^=] + \dots + [\text{S}_x^=]$) was determined by titration with thallous nitrate to a thermometric endpoint using a procedure described in an earlier progress report¹². The results were in satisfactory agreement with iodometric

*H-coal is a registered trademark of Hydrocarbon Research, Inc.

titrations¹⁷ performed for verification. Thiosulfate was determined by differential pulse polarography at the dropping mercury electrode⁷ (results agreed with iodometric verification experiments). Polysulfidic sulfur* and total sulfur were quantitated by classical gravimetric procedures¹⁷. The results are shown in Table IV.2. The following salient features are apparent,

- a) The sulfur content of the sample obtained from processing Illinois coal (LO 2097) is accounted for by sulfide, polysulfide and thiosulfate which are present in appreciable amounts.
- b) The sample obtained from Kentucky coal (LO 2098) contained only sulfide, and no sulfur in any other form. This accounts for its more negative redox potential.

Generally sulfite and higher oxidation states of sulfur were absent.

*As defined in Table IV.2, footnote (a).

Table IV.1

Acidity, Oxidation Potential and Sulfur Content of By-Product Water Samples^(a)

(1) <u>Specimen Number</u>	(2) <u>Run-Period No. and Date</u>	(3) <u>Type of Coal Processed</u>	(4) <u>pH at 25°C</u>	(5) <u>Redox Potential, E Volt Versus NHE</u>	(6) <u>Total Sulfur Grams/Liter</u>
L0 2097	130-82-15 September 1977	Illinois #6	9.73	-0.35	49
L0 2098	130-89-12 September 1979	Kentucky #11	9.46	-0.38	60

(a) H-Coal[®] 0-14 "sour water" specimens supplied by P. Stepanoff, Hydrocarbon Research, Inc., Research and Development Center, Lawrenceville, NJ 08648.

Table IV.2

Speciation of Sulfur in H-Coal® By-Product Water Samples^(a)

<u>Moiety</u>	<u>Amount of Sulfur (Moles Sulfur/Liter) Found in Form Listed in Column 1</u>	
	<u>LO 2097^(b) Illinois Coal</u>	<u>LO 2098^(b) Kentucky Coal</u>
(1) Sulfidic sulfur ^(c)	0.80	1.91
(2) Thiosulfate	0.194	$< 3 \times 10^{-4}$
(3) Sulfite	$< 2 \times 10^{-4}$	$< 2 \times 10^{-4}$
(4) Polysulfidic sulfur ^(d)	0.44	Negligible
(5) Total sulfur by summation of lines 1-4	1.43	1.91
(6) Total sulfur by analysis	1.5	1.9

(a) Specimens identified in Table IV.1, Column 1.

(b) See Table IV.1.

(c) $([S^{2-}] + [S_2^{2-}] + \dots) = \sum_x [S_x^{2-}]; \quad x = 1-5$ (d) $([S_2^{2-}] + 2[S_3^{2-}] + \dots) = \sum_x (x-1)[S_x^{2-}]$

CONCLUSIONS

TASK 1. EXTENSION AND REFINEMENT OF THERMODYNAMIC SURVEY AND CONSTRUCTION OF POURBAIX DIAGRAMS. The development of computer software for estimating sulfur speciation from a thermodynamic data base has been completed. Requisite inputs include the experimentally measured pH, redox potentials (and temperatures) of the relevant process streams.

TASK 2. VOLTAMMETRIC METHODS DEVELOPMENT. The differential pulse polarographic "sulfide peak" at -0.6 volt versus SCE appears actually to provide a measure of the sum of "sulfidic" plus "polysulfidic sulfur," i.e., $[S^{2-}] + 2[S_2^{2-}] + 3[S_3^{2-}] + \dots$

TASK 3. ENTHALPIMETRIC METHODS DEVELOPMENT. Thallous nitrate is found to yield precipitates with polysulfides as well as monosulfide. Applications of this reaction to selective quantitative speciation warrant further investigation.

TASK 4. APPLICATION AND TECHNOLOGY TRANSFER TO COAL CONVERSION PLANTS. H-Coal® (Hydrocarbon Research, Inc.) "sour water" had a pH ranging from 9.4 to 9.7, and redox potentials (E) between -0.35 and -0.38 versus the normal hydrogen electrode. A specimen obtained from processing Kentucky #11 coal (E = -0.38 volt) contained 60 gram per liter of total sulfur, all of it in the form of sulfide. On the other hand, in a specimen obtained from Illinois #6 coal (E = -0.35) the inorganic sulfur was distributed between sulfide, polysulfide and thiosulfate.

LITERATURE CITED

1. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-1, U.S. Department of Energy, January 1978.
2. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-2, U.S. Department of Energy, April 1978.
3. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-3, U.S. Department of Energy, July 1978.
4. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-4, U.S. Department of Energy, October 1978.
5. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-5, U.S. Department of Energy, January 1979.
6. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-6, U.S. Department of Energy, April 1979.
7. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-7, U.S. Department of Energy, July 1979.
8. J. Jordan, "Instrumental Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-8, U.S. Department of Energy, October 1979.
9. J. Jordan, "Development of Instrumental Methods of Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-9, U.S. Department of Energy, January 1980.
10. J. Jordan, "Development of Instrumental Methods of Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-10, U.S. Department of Energy, April 1980.
11. J. Jordan, "Development of Instrumental Methods of Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-11, U.S. Department of Energy, July 1980.
12. J. Jordan, "Development of Instrumental Methods of Analysis of Sulfur Compounds in Coal Process Streams," FE-2710-12, U.S. Department of Energy, October 1980.
13. J.J. Renard, G. Kubes, and H.I. Bolker, *Anal. Chem.*, 47, 1317 (1975).
14. D.L. Noel, *Tappi*, 61(5), 73 (1978).
15. L. Julien and M.L. Bernard, *Electrochim. Acta*, 13, 149 (1968).
16. F. Feigl, Spot Tests in Inorganic Analysis, 5th Ed., Elsevier, New York, 1958, pp. 372, 491.
17. J.H. Karchmer, The Analytical Chemistry of Sulfur and its Compounds, Wiley-Interscience, New York, 1970.

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