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

Quarterly Technical Progress Report for the Period July—September 1980

By
Joseph Jordan

October 1980

Work Performed Under Contract No. AC22-77ET10482

The Pennsylvania State University
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University Park, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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ABSTRACT

A synopsis of progress during July-September, 1980, is presented. This is the fourth 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. Appropriate user-oriented computer program listings have been consolidated and will be incorporated in a subsequent report. Meanwhile, prepublication copies are available upon request.

TASK 2. VOLTAMMETRIC METHODS DEVELOPMENT. The electroreduction of tetrathionate to thiosulfate was investigated at the dropping mercury electrode. Well-defined differential pulse voltammograms were obtained.

TASK 3. ENTHALPIMETRIC METHODS DEVELOPMENT. A solution containing OH^- , CO_3^{2-} , S^{2-} , SO_3^{2-} was analyzed by titrating first with TlNO_3 to precipitate Tl_2S and then with HCl . Progress of the titration was simultaneously monitored thermometrically and potentiometrically. All components were successfully determined by sequentially titrating a single aliquot.

TASK 4. APPLICATION AND TECHNOLOGY TRANSFER TO COAL CONVERSION PLANTS. Cartesian displays of pH-redox potential correlations were constructed, revealing distinct patterns which clearly differentiate between liquefaction and gasification by-product water samples.

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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 developments, 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 non-aqueous 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)

- 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 method 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.D. Stutts, and J. 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 in 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

Scheduled

Scheduled Extension

Progress

Early Start

SUMMARY OF PROGRESS TO DATE

This is the twelfth 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 thirty-six months period, October 1977-September 1980, is given below, complementing and recapitulating the corresponding summary page of FE-2710-11.

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. Software (in BASIC and FORTRAN) can be supplied upon request. Simple procedures have been developed for taking into account the "blocking" of specified reactions by slow kinetics.

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. The current status of the work is as follows.

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: $\text{Hg} + 2\text{SO}_3^{2-} = \text{Hg}(\text{SO}_3)_2^{2-} + 2\text{e}^-$ (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: $2S_2O_3^{2-} = S_4O_6^{2-} + 2e^-$ (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: $Hg + 2S_2O_3^{2-} = Hg(S_2O_3)_2^{2-} + 2e^-$ (anodic depolarization)

Status: Tested in actual process streams.

D. Determination of Sulfide

Conditions: DM in aqueous solution

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

Status: Dynamic range up to 1.2×10^{-2} M; tested in actual process streams.

E. Determination of Tetrathionate

Alternative Method I:

Conditions: RGCD in aqueous solution

Electrode Reaction Employed: $S_4O_6^{2-} + 2H_2O = 2SO_4^{2-} + 2S + 4H^+ + 2e^-$ (electrooxidation)

Status: Phenol interferes in process stream samples.

Alternative Method II:

Conditions: DM in aqueous solution

Electrode Reaction Employed: $S_4O_6^{2-} + 2e^- = 2S_2O_3^{2-}$ (electroreduction)

Status: Dynamic range studies in progress.

F. Determination of Dibenzothiophene (DBT)

Conditions: RGCD in acetonitrile

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

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

G. Determination of Benzothiophene (BT)

Conditions: RGCD in acetonitrile

Electrode Reaction Employed: $2BT = \text{benzothiophenyl-benzothiophenium}^+ + 2e^- + H^+$ (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 $\text{S}^{=}$ 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 $\text{S}_x^{=}$ 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 ($\text{S}^{=}$) or sulfite ($\text{SO}_3^{=}$) in the presence of hydroxide (OH^-) and carbonate ($\text{CO}_3^{=}$). By pretitrating with TlNO_3 to precipitate Tl_2S , a solution containing both sulfide and sulfite can be determined in a single aliquot.

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^- , $\text{S}^{=}$) and sulfite (SO_2 , HSO_3^- , $\text{SO}_3^{=}$) 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" procedure, 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.

DESCRIPTION OF TECHNICAL PROGRESS

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

Computer program listings have been consolidated for predicting concentrations of thirty significant inorganic sulfur moieties as function of three measured variables, viz., pH, redox potential and temperature. Requisite inputs include one additional measurement, viz., the total sulfur concentration and the following thermodynamic assignments (available in tabulations):

- (a) standard free energies of formation
- (b) heat capacities.

When warranted by experimental conditions, specified moieties can be appropriately eliminated from consideration, while assuming attainment of equilibrium between all other species. This procedure provides the option to take into account the effective blocking of certain reactions by slow kinetics. A comprehensive user-oriented program, written in BASIC, will be incorporated in a subsequent Quarterly Technical Progress Report.

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

The method for the determination of tetrathionate using a rotated glassy carbon electrode (RGCE) by differential pulse voltammetry (DPV) is described in a previous progress report¹⁰. However, phenol, a known contaminant in coal conversion by-product water samples¹², interferes as it does for the determination of thiosulfate by DPV using a RGCE⁸. The dropping mercury electrode (DME) can be used to circumvent this problem.

Tetrathionate is known to irreversibly reduce at the DME with a half-wave potential of -0.258 volt versus SCE¹³. Zezula¹⁴ attributes the electrode reaction to the reduction of tetrathionate to thiosulfate

A "family" of current-voltage curves obtained for tetrathionate using DPV is shown in Figure 2.1 along with the experimental conditions. The peak signals were proportional to tetrathionate concentration.

Task 3. Enthalpimetric Methods Development. (John Stahl)

Acidimetric titrations, simultaneously monitored thermometrically and potentiometrically have been shown useful for analyzing mixtures of OH^- , CO_3^{2-} , SO_3^{2-} or of OH^- , CO_3^{2-} , S^{2-} ¹¹. However, when a mixture containing both S^{2-} and SO_3^{2-} was titrated with HCl, the pH reading became erratic and a continuous temperature rise was observed. No endpoints were apparent on the thermometric titration curve after the solution became acidic. This may have been due to the heat of the so-called "Wackenroder" reaction¹⁵, viz.,

Figure 2.1

Differential Pulse Voltammograms of Sodium Tetrathionate, $\text{Na}_2\text{S}_4\text{O}_6$. Supporting electrolyte: aqueous 0.1 M Na_2HPO_4 + 0.1 M KH_2PO_4 , pH 6.5. Indicator electrode: dropping mercury electrode, drop time of 0.5 sec; reference electrode: saturated calomel half-cell (SCE). Pulse amplitude: $\Delta E = 0.005$ volt; pulse duration: 57 msec. Current sampling time: 17 msec.

Reaction 3.1 is known to proceed slowly. The reaction mechanism is not well understood, and the products are a complex variable mixture of polythionic acids. If acidimetric titration is to be useful for the analysis of mixtures containing both sulfite and sulfide, this side reaction must be blocked.

The approach taken to solve the problem was to precipitate the sulfide before the acidimetric titration. Many metal ions precipitate sulfide, but most also form insoluble hydroxides and carbonates in solutions of high pH. Thallium(I), however, has been recognized as a rather sulfide specific precipitant¹⁶. Solubility product constants (K_{sp}) for relevant compounds of thallium(I) are given in Table 3.1. These data suggest that sulfide can readily be separated from hydroxide by precipitation with a soluble thallous salt. Preliminary thermometric titrations revealed that a saturated (≈ 0.3 M) TlNO_3 solution titrated into a dilute (≈ 0.01 M) hydroxide, carbonate, sulfite, or chloride yielded (as expected) no measurable reaction heats.

Table 3.1

Solubility Products¹⁷ of Selected Thallium(I) Salts at 25°C

<u>Compound</u>	<u>pK_{sp}</u>
Tl_2S	20.3
TlI	7.19
TlBr	5.47
TlCl	3.76
TlSCN	3.77
$\text{Tl}_2\text{C}_2\text{O}_4$	3.7
TlOH	<1

In the pH range of 7-12, the overall precipitation reaction of interest is:

The heat of Reaction 3.2 was calculated from heats of formation¹⁷ which yielded

$$\Delta H^\circ_{3.2} = -34.9 \text{ kcal/mole} \quad (3.3)$$

Experimentally, using thermometric titration, Reaction 3.2 was found to proceed quickly to a sharp stoichiometric endpoint, yielding an average ΔH of $-34.8 \text{ kcal/mole} \pm 2\%$ which is in excellent agreement with assignment 3.3. Tl_2S began to redissolve at about pH 3. In order to analyze a mixture containing OH^- , CO_3^{2-} , S^{2-} , and SO_3^{2-} , it was possible therefore to titrate first with TlNO_3 solution until the sulfide endpoint was indicated on the thermometric titration curve (plot of change of temperature, ΔT , versus volume of thallous nitrate), and then to titrate with HCl to determine OH^- , CO_3^{2-} , SO_3^{2-} by simultaneously monitoring pH and ΔT as described in a preceding report¹¹.

A "model test solution" was made up by dissolving NaOH (8.9 millimoles per liter), Na_2CO_3 (5.1 millimoles per liter), Na_2S and Na_2SO_3 (approximately 5 millimoles per liter each). A positive pressure of nitrogen was maintained over the aqueous solution at all times while allowing for samples to be withdrawn via a syringe. After allowing a day for the solution to equilibrate with the traces of CO_2 , and the O_2 initially present in the water (which might slowly oxidize some of the sulfide and sulfite), aliquots were withdrawn and analyzed by a classical iodometric procedure. Other aliquots were titrated sequentially with thallous nitrate and HCl using the procedure outlined above. A typical titration curve is shown in Figure 3.1 and analytical results in Table 3.2.

Two things are noteworthy in the titration curve, Figure 3.1. During precipitation of Tl_2S , via Reaction 3.2, the pH did indeed drop slightly as expected due to hydroxide consumption. The acidimetric portion of the curve is identical to that of an OH^- , CO_3^{2-} , SO_3^{2-} mixture alone. Only when the pH dropped below 3 did Tl_2S begin to redissolve and the Wackenroder Reaction 3.1 to occur.

There was good agreement between the iodometric and thermometric methods for the determination of sulfide. The potentiometric-thermometric determination of sulfite was precise, but not accurate when compared to the classical iodometric determination, which, however, was poorly reproducible. These difficulties were probably due to air oxidation occurring during manipulations. Refinement of air exclusion techniques should improve the agreement.

Thallous nitrate appears to be a promising reagent for sulfide in this context. Further investigations will include the reactions of Tl^+ with polysulfides, thiocyanate, thiols, thiourea, and other organic compounds of interest. The acidimetric portion of the titration will be extended to include other Bronsted-bases of interest in coal conversion process streams (NH_3 , phenols, etc.), eventually utilizing an iterative curve-fitting procedure to extract analytical information.

Task 4. Application and Technology Transfer to Coal Conversion Plants. (S.J. Ankabrandt, J.D. Stutts, J. Yakupkovic)

Several coal conversion by-product water samples were referred to in the preceding Quarterly Technical Progress Reports^{8,9,11}. Additional information on the nature of some of these samples has since become available and is presented in Table 4.1 (where data previously reported are also recapitulated, in order to provide a comprehensive synopsis). The values listed in columns 3

Figure 3.1 Simultaneous potentiometric and thermometric titration of a mixture containing approximately 5 mM each of OH^- , CO_3^{2-} , SO_3^{2-} , S^{2-} with first 0.20 M TlNO_3 and then with 1.0 M HCl .

Table 3.2
Analytical Results

	$[\text{OH}^-]$	$[\text{CO}_3^{=}]$	$[\text{SO}_3^{=}]$	$[\text{S}^{=}]$	$[\text{S}_2\text{O}_3^{=}]^b$
Approximate concentrations taken ^a	8.9 mM	5.1 mM	≈5 mM	≈5 mM	0
Determined by classical iodo-metric methods (2 replicates)	NA	NA	4.9 mM ±10%	3.83 mM ±2%	0.75 mM ±1%
Determined from Figure 3.1 (and 5 similar replicates)	6.84 mM ±1%	5.69 mM ±2%	4.24 mM ±2%	3.88 mM ±1%	NA

a) Altered prior to analysis by equilibration with traces of CO_2 and O_2 initially present in solvent water. This accounts for the fact that actual $\text{CO}_3^{=}$ concentrations found were higher, and that sulfide, sulfite and hydroxide concentrations found were lower than those initially taken.

b) Presumably generated by air oxidation of sulfide, see note (a) above.

Table 4.1

Characterization^(a) of Coal Conversion By-Product Water Samples^(b)

(1) Identification No.	(2) <u>Description</u>	(3) pH ^{8,11}	(4) Redox Potential ^{c,8,11}	(5) Total _d Sulfur
PS-1-515	Waste water, SRC I liquefaction plant	9.3	-0.31	13.0
PS-2-515	Waste water, fixed-bed coal gasifier, METC	9.1	-0.19	0.4
PS-3-515	Waste water, disposable catalyst, coal liquefaction development unit, PETC, Run #DCD 12	9.6	-0.32	16.1
PS-4-515	Same as PS-3-515, Run 13B	9.7	-0.32	11.7
PS-5-515	Waste water, fluidized bed coal gasifier, Rosebud coal, PETC	8.7	+0.02	
40-CHPM He 378/379	Gasifier condensate; 40 atm. He; Montana Rosebud coal, 40 lbs/hr	7.6	+0.12	
40-CHPBATI- 356/357	Gasifier condensate; 40 atm. N ; catalyst impregnated Illinois #6 coal, 40 lbs/hr	8.6	+0.10	
DCD-11	Liquefaction scrubber water, light oil, Blacksville #2 coal.	9.0	-0.28	

^(a)Including information previously reported^{8,9,11}^(b)Supplied by Dr. H. Schultz (PETC)^(c)Volt versus normal hydrogen electrode^(d)Gram per liter.

and 4 have been combined in a Cartesian display in Figure 4.1 where each sample is represented by a point whose abscissa is the redox potential and whose ordinate is the pH. Remarkably, the liquefaction waste waters are clearly separated from their gasification counterparts by a well-defined boundary line in the Cartesian plane. The liquefaction waste waters:

- (a) have redox potentials clustered in a narrow range, viz., (-0.31 ± 0.01) volt versus the normal hydrogen electrode;
- (b) tend to be more alkaline than gasification waste waters.

In future studies, it is planned to explore the significance of such classifications. Obviously, more negative redox potentials favor relatively greater abundances of the lower oxidation states of sulfur. That such is indeed the case is documented by the analytical results shown in Table 4.2.

Table 4.2

Analysis of Coal Conversion By-Product Water Samples

<u>Identification No. (a)</u>	<u>Nature of Sample (a)</u>	<u>Percentage of Total Sulfur Present as</u>	
		<u>Sulfide (b)</u>	<u>Thiosulfate (c)</u>
PS-2-515	Gasification	0.03	70.1
PS-1-515	Liquefaction	76.9	0.4
PS-3-515	Liquefaction	82.0	13.9
PS-4-515	Liquefaction	93.4 ^(d)	9.3 ^(d)

(a) See Table 4.1 for further details.

(b) Determined by thermometric enthalpy titrations¹⁰.

(c) Determined by differential pulse voltammetry⁷.

(d) Summation exceeding 100% ascribed to experimental error.

Figure 4.1

Cartesian Display of pH-Redox Potential Correlations in Coal Conversion By-Product Water Samples. Data from columns 3 and 4 of Table 4.1. Points correspond to the following samples identified in column 1 of Table 4.1: 1, PS-4-515; 2, PS-3-515; 3, PS-1-515; 4, DCD-11; 5, PS-2-515; 6, PS-5-515; 7, 40-CHPBATI-356/357; 8, 40-CHPM He 378/379.

CONCLUSIONS

TASK 1. EXTENSION AND REFINEMENT OF THERMODYNAMIC SURVEY AND CONSTRUCTION OF POURBAIX DIAGRAMS. When warranted by slow kinetics, specified moieties can appropriately be eliminated from consideration while assuming attainment of equilibrium between all other species.

TASK 2. VOLTAMMETRIC METHODS DEVELOPMENT. Tetrathionate can be quantitated by differential pulse polarography at the dropping mercury electrode.

TASK 3. ENTHALPIMETRIC METHODS DEVELOPMENT. Sulfide can be determined by titration with standard thallous nitrate to a thermometric endpoint. The Tl_2S precipitated does not interfere in the subsequent acidimetric titration of Bronsted-base moieties, such as sulfite, carbonate and hydroxide.

TASK 4. APPLICATION AND TECHNOLOGY TRANSFER TO COAL CONVERSION PLANTS. Generally, liquefaction by-product water samples are characterized by more negative redox potentials than their gasification counterparts. This reflects a preponderance of sulfidic sulfur versus thiosulfate. In gasification by-product waters, the situation is reversed.

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