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IDENTIFICATION AND REACTIONS OF CYANIDE AND THIOCYANATE IN COAL GASIFICATION WASTEWATERS

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PROLOGUE

In July of 1976, the Department of Energy initiated a comprehensive program for environmental assessment of its high-BTU coal gasification pilot plant installations. The overall objective of the program is to develop the methodology and data base necessary for meaningful assessment of the environmental impact of the coal gasification processes. The environmental characterization efforts at each pilot plant are focused on scalable process units, with the goal of establishing rules and strategy for scaleup to commercial-size installations.

Carnegie-Mellon University, in its role as assistance, coordination and evaluation contractor for the DOE environmental assessment program, has prepared a series of technical documents in support of program objectives and activities within and across the coal gasification facilities. This report represents one in that series. Reports are also available describing the unique C-MU role and summarizing program activities.

Abstract

The paper discusses: (i) procedures for preservation and identification of cyanide and thiocyanate in coal gasification wastewaters, (ii) possible pathways for aqueous phase formation of thiocyanate in these wastewaters, and (iii) reaction of cyanide and polysulfide-sulfur to produce thiocyanate. Cyanide preservation procedures require the removal of sulfide and high levels of carbonate. An analytical procedure for thiocyanate determination based on a copper-pyridine colorimetric method with pre-extraction has been tested successfully on most samples. Kinetic studies on the reaction of cyanide with polysulfide-sulfur showed that the reaction was of order 1.54 ± 0.25 with a rate constant of about 0.24 $(M/\ell)^{-0.54}$/min. Results of this work may help predict interrelationships among cyanide, sulfur and thiocyanate during oxidation of coal gasification wastewaters. Control of cyanide-polysulfide reaction requires selective control of sulfide oxidation kinetics.

IDENTIFICATION AND REACTIONS OF CYANIDE AND THIOCYANATE IN COAL GASIFICATION WASTEWATERS

Introduction

The Department of Energy (DOE) is evaluating the technical feasibility of a number of coal gasification processes for the production of synthetic natural gas from coal. The Environmental Studies Institute of Carnegie-Mellon University (C-MU) has been engaged by DOE to provide a range of assistance, coordination, and evaluation services concerning the environmental aspects of this program. This paper discusses on-going work related to the development of suitable analytical methods for preservation and identification of cyanide and thiocyanate in gasification wastewaters, and to the investigation of aqueous reaction pathways leading to the formation of thiocyanate from cyanide.

Preservation and Identification of Cyanide and Thiocyanate in Coal Gasification Wastewaters

The following discussion presents developments related to the evolution of an effective methodology for coal gasification aqueous effluent sample preservation and analysis for cyanide and thiocyanate.

Cyanide Preservation and Analysis

Studies on cyanide degradation and interaction with sulfide presented later show that sulfide must be removed as part of sample preservation procedures in order to prevent a reaction of cyanide and sulfur. As explained below, carbonate must also be removed in situations where alkalinity is exceptionally high.

Many high BTU coal gasification raw product gas quench condensates such as Hygas, Synthane and Slagging Fixed Bed demonstrate exceptionally high concentrations of alkalinity (i.e. 10,000 to 50,000 mg/1 as $CaCO_3$). This is a result of wastewater contact with gasifier product gases under high partial pressures of both NH_3 and CO_2. Serious problems were encountered as a result of extraordinary concentrations of ammonium-bicarbonate in initial efforts to apply the established procedures for total cyanide by the distillation/pyridine-barbituric acid colorimetric method (1). The presence of carbonates complicated both the preservation and analysis of cyanide samples in the following ways: (1) the high buffering capacity provided by the ammonium bicarbonate could only be overcome during sample preservation by large additions of NaOH; (2) release of CO_2 during sample acidification prior to distillation resulted in uncontrollable effervescence and loss of sample; (3) large amounts of CO_2 released during distillation tended to reduce the pH of the alkaline cyanide gas scrubbing solution, which could result in partial loss of cyanide.

The problem with uncontrollable effervescence during acidification could be overcome, given great care and patience, by adding acid to the sample in small increments; however, this is time consuming and it would not solve the problem of reducing the pH of the scrubbing solution unless a proportionally higher strength (more than 0.25N) NaOH scrubbing solution were employed. The difficulty was remedied by replacing NaOH preservative with $Ca(OH)_2$ and then settling, decanting, and filtering the samples at the time of preservation. By this procedure high carbonate concentration is precipitated and removed as a calcium carbonate sludge. Good recoveries and no interference from use of $Ca(OH)_2$ preservative were obtained in controlled known addition and recovery experiments on both a simulated high ammonium bicarbonate wastewater (0.5M NH_4HCO_3) and a coal gasification wastewater sample. These results are shown in Table 1. Sulfide must be removed from wastewater samples either at the time of preservation, or at the time of analysis if the sample is to be analyzed immediately upon collection. Removal of sulfide at the time of preservation prevents potential interaction with cyanide, while removal prior to distillation is always required to prevent sulfide distilling over with the cyanide and adversely affecting the colorimetric procedures. Recommended procedures (1) for sulfide removal suggest addition of either lead or cadmium. It was found in this study that cadmium in excess concentrations greater than about 500 mg/l interfered with the determination of thiocyanate. Since it was desirable to analyze for cyanide and thiocyanate from the same sample, lead was evaluated as a sulfide precipitating agent for coal gasification quench wastewater samples. Spike and recovery studies on CO_2-Acceptor plant wastewater (Table 2) indicate that use of lead nitrate is suitable for sulifide precipitation in these wastewaters.

Figure 1 illustrates in schematic fashion the recommended method for preservation of samples for total soluble cyanide. It is recognized that it is unlikely to find oxidizing agents (viz Cl_2) in coal gasification wastewaters owing to the demand exerted by large concentrations of ammonia and/or organic compounds. However, the test for oxidizing agents should be performed at least initially in order to characterize wastewaters for which no constituent information is available. Sulfide precipitating

Table 1

CYANIDE SPIKE AND RECOVERY STUDIES: EFFECT OF HYDROXIDE PRESERVATIVE

Simulated Gasification Quench Wastewater (0.5 M NH_4HCO_3)

Sample Preservative	No. of Tests	CN^- Conc mg/ℓ	% CN^- Recovery Mean	% CN^- Recovery Coef. of Var.
NaOH	4	0.1	103.6	8.4
NaOH	4	2.0	91.4	10.5
$Ca(OH)_2$	4	0.1	107.4	5.5
$Ca(OH)_2$	4	2.0	96.8	15.8

Actual Hygas Quench Wastewater

Sample Preservative	No. of Tests	% Recovery of a 3 mg/ℓ Spike Mean	% Recovery of a 3 mg/ℓ Spike Coef. of Var.
NaOH	2	92.5	0.8
$Ca(OH)_2$	2	99.0	4.3

Table 2

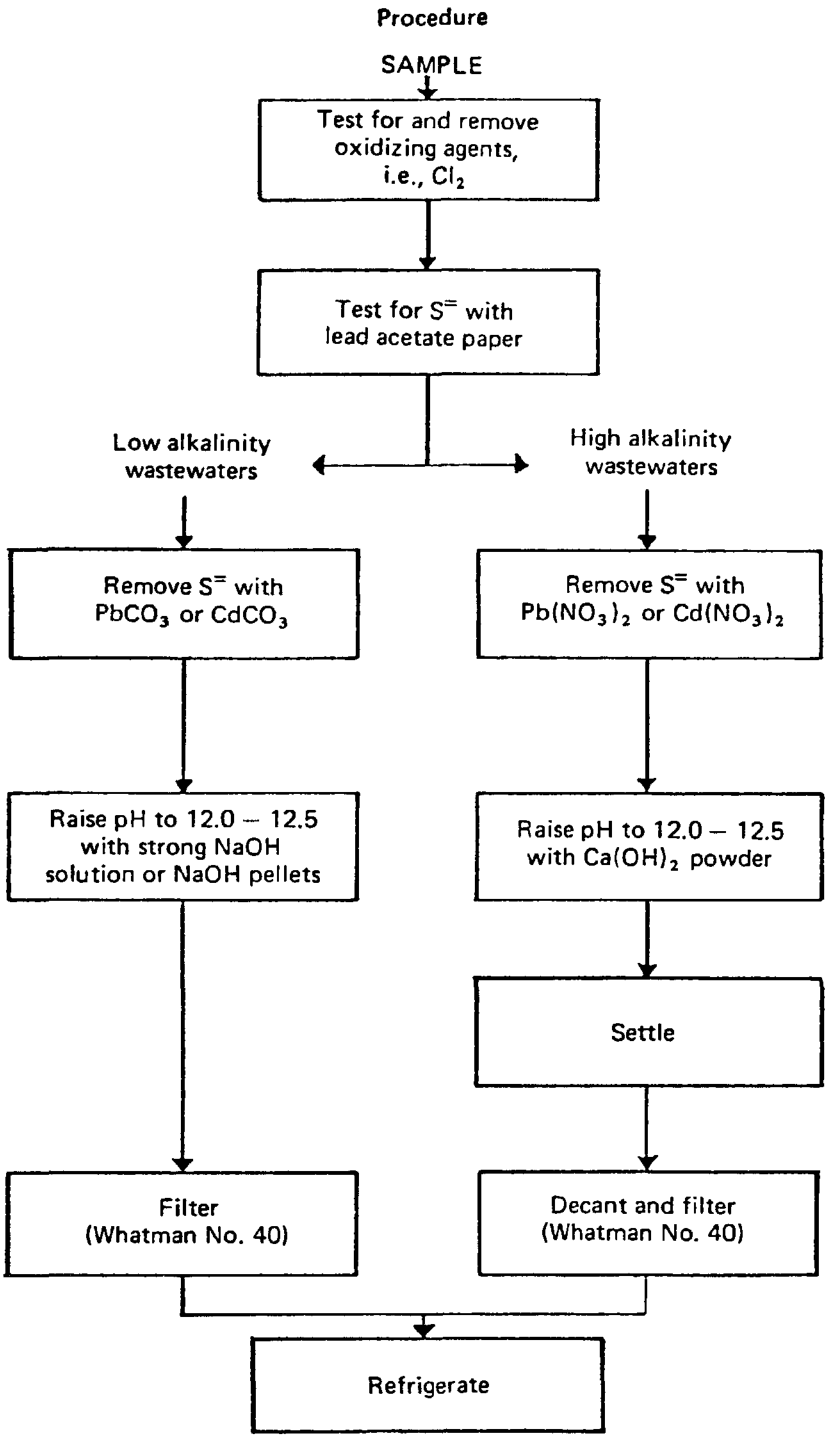
CYANIDE SPIKING AND RECOVERY STUDIES: EFFECT OF $Pb(NO_3)_2$ AS SULFIDE PRECIPITATING AGENT

CO_2-Acceptor Raw Gas Quench Wastewater

No. of Tests	Raw CN^- Conc., mg/ℓ	%Recovery of a 5 mg/ℓ CN^- Spike Mean	%Recovery of a 5 mg/ℓ CN^- Spike Coef. of Var.
2	5.45	100.0	7.1

Figure 1

RECOMMENDED PROCEDURE FOR
PRESERVATION OF COAL GASIFICATION
SAMPLES FOR TOTAL SOLUBLE CYANIDE



Comment

Cl_2 is not likely to be found in samples with appreciable concentrations of NH_3 or organic compounds.

Either path is acceptable for medium alkalinity wastewaters.

High sulfide concentrations preclude reliance on standard additions; add 0.2 g/l excess Pb or Cd; do not add large excess of these compounds. Pb is preferred if sample is to be analyzed for SCN^-.

High buffering capacity requires regular checks on pH response to reagent addition. Use dry reagents on strongly buffered samples to avoid excessive dilution.

Avoid long contact times with precipitates.

agent should be present in about 0.2 g/l excess, with at least 0.2 g/l added even if the sulfide test was negative to assure sulfide removal. The carbonate salt of the sulfide precipitating agent is preferred for samples of low alkalinity because this helps buffer the sample and prevent a loss of cyanide as a result of a drop in pH when sulfide is precipitated. Nitrate salts are preferred in high alkalinity wastewaters because somewhat less lime sludge will be produced when the alkalinity is removed. The sample pH may be raised with either NaOH or $Ca(OH)_2$ depending on sample alkalinity; sample pH should be checked routinely owing to the strong buffer capacity of many coal gasification wastewater samples.

Thiocyanate Preservation and Analysis

A copper-pyridine colorimetric method for measuring thiocyanate concentrations in coal gasification wastewaters has been adopted from Kruse and Mellon (2) and Danchik and Boltz(3). The ferric nitrate procedure given in Standard Methods(1) was found to be totally ineffective in coal gasification wastewater owing to severe color interferences.

The principle of the copper-pyridine method relies on the reaction of SCN^- with cupric copper and pyridine to form dithiocyanatopyridine, a light green precipitate soluble in chloroform. The reaction is stoichiometric and the resulting color adheres to Beer's Law to permit determination of SCN^- spectrophotometrically.

$$2SCN^- + Cu^{++} \rightarrow Cu(SCN)_2 \qquad (1)$$

$$Cu(SCN)_2 + 2C_5H_5N \rightarrow Cu(C_5H_5N)_2(SCN)_2 \qquad (2)$$

Details of the procedure are given in Luthy(4). Potential inorganic and organic interferences in the copper-pyridine method were investigated and modifications in procedures were made where necessary. Results of spiking and recovery studies described below indicate a high degree of effectiveness for the method as revised.

(1) Interferences from Inorganic Compounds

Clean water spiking and recovery studies were conducted to determine the levels of interferences from several inorganic compounds:

- Sulfide, ammonia, cyanide. These compounds are typically in the raw waste.
- Cadmium, lead, calcium, sodium, chloride, and nitrate. These species may be added intentionally to the sample during preservation.

Results (Table 3) show excellent recovery of thiocyanate in all cases, except for relatively low values of thiocyanate (11 mg/l) in the presence of high concentrations of cadmium (1000 mg/l).

(2) Interferences from Organic Compounds

A series of experiments were conducted to determine the effect of chloroform extraction on the recovery of thiocyanate spikes in a sample of raw Hygas pilot plant wastewater. Effects of excess lead (lg/l) preservative were also considered. Results (Table 4) indicate that.

(a) Large interferences are introduced by the presence of organics in wastewater, because this material is extracted along with the copper-pyridine thiocyanate complex and influences color development. Chloroform extraction effectively removes this interference. Series 1 of Table 4 shows results of SCN^- spike and recovery studies with raw Hygas wastewater using chloroform pre-extraction; the SCN^- concentration was 32 mg/l and there was excellent recovery of a 50 mg/l SCN^- spike. Series

Table 3

SIGNIFICANCE OF INTERFERENCE FROM VARIOUS INORGANIC COMPOUNDS IN THE DETERMINATION OF THIOCYANATE

Inorganic Species	Average Percent Recovery of SCN^- (two determinations)	
	SCN^- = 11.0 mg/ℓ	SCN^- = 60.0 mg/ℓ
Cadmium ($Cd(NO_3)_2$)		
500 mg/ℓ Cd^{++}	105.6	100.9
1000 mg/ℓ Cd^{++}	78.9	95.3
Sulfide ($Na_2\ S \cdot 9H_2O$)		
20 mg/ℓ $S^=$	101.8	101.2
200 mg/ℓ $S^=$	102.2	101.0
Ammonia (NH_4Cl)		
1000 mg/ℓ NH_3-N	103.7	100.0
5000 mg/ℓ NH_3-N	106.4	100.8
Cyanide (KCN)		
1 mg/ℓ CN^-	100.8	100.8
20 mg/ℓ CN^-	102.3	100.9
Lead ($PbCO_3$)		
200 mg/ℓ Pb^{++}	103.2	101.0
1000 mg/ℓ Pb^{++}	97.8	101.4
Nitrate ($NaNO_3$)		
100 mg/ℓ NO_3^-	103.2	101.0
1000 mg/ℓ NO_3^-	102.3	101.2
Calcium ($Ca(OH)_2$)		
1000 mg/ℓ Ca^{++}	103.7	101.0
5000 mg/ℓ Ca^{++}	102.3	101.2

Table 4

EFFECTS OF CHLOROFORM EXTRACTION AND EXCESS LEAD ON THE DETERMINATION OF SCN^- IN HYGAS WASTEWATER

Series	Pre-Extraction with chloroform	1g/ℓ Pb^{++} Excess	SCN^-, mg/ℓ (Avg of two determinations)	% Recovery of 50mg/ℓ SCN^- Spike (Avg of two determinations)
1	yes	no	32.0	101
2	yes	yes	33.0	101
3	no	no	64.0	153
4	no	yes	61.7	169

Note: All analyses performed on the same wastewater sample.

3 shows that in the absence of pre-extraction the data is biased high (by as much as 100% in this case) and that there is very poor recovery of a SCN^- spike.

(b) The presence of excess lead has no significant effect on the thiocyanate determination. Series 2 of Table 4, which contained 1 g/l excess lead and which was analyzed using the pre-extraction procedure, showed comparable results with series 1. Series 4, which contained 1 g/l excess lead but was not analyzed using the pre-extraction procedure, was biased high and showed poor recovery of the SCN^- spike.

(c) Millipore filtration alone (data not shown) does not effectively remove organic interferences.

Pre-extraction removes intereferences from most wastewaters encountered including coke plant weak ammonia liquor. However, problems have been encountered in analysis of Grand Forks Slagging Fixed Bed gasifier wastewater which contains exceptionally high values of organic material, especially tars and oils (COD = 15,000-25,000 mg/l). Satisfactory solutions to this difficulty are under investigation. Except for this instance, the copper-pyridine method with pre-extraction has proved to be a reliable technique and it is recommended as the method of choice.

Analytical Procedures for Identification of Sulfur Compounds

In the course of several experiments the following sulfur compounds were analyzed in clean water and in coal gasification wastewaters: $S^=$, polysulfide ($S_xS^=$), SCN^-, $SO_4^=$, and total sulfur. The analytical procedure for thiocyanate was described above. Sulfide determination was based on the iodimetric method in which sulfide was separated from solution by precipitation with zinc acetate, dewatered on a membrane filter, and returned to another flask and dissolved in a known acid-iodine solution. The iodine was then back-titrated with thiosulfate solution. Samples containing large amounts of coal fines require preliminary filtration (pH = 12) in order that the titration end point not be obscured. Sulfate was determined by barium precipitation, digestion, and ignition. Samples require ignition to remove traces of wastewater organic residue from the precipitate. Total sulfur was measured by oxidizing reduced forms of sulfur to sulfate with hydrogen peroxide, and then determining sulfate by the barium precipitation procedure. Thiocyanate sulfur is reported by the total sulfur procedure.

Polysulfide measurement was evaluated by a procedure discussed by Krachner(5). Excess cyanide reacts with polysulfide under anaerobic conditions in a boiling boric acid solution to form one thiocyanate-sulfur for each polysulfide-sulfur. In waters containing thiocyanate a preliminary determination is made to differentiate between existing and newly formed thiocyanate. Results of polysulfide recovery studies with coal gasification wastewater showed no dectable polysulfide present in the raw sample, and essentially complete recovery of an 11 mg/l polysulfide-S (20 mg/l SCN^-) spike in Hygas wastewater. Occasionally a white precipitate would form within the chloroform phase during polysulfide analysis. This was believed to be due to the boric acid salt precipitating out of solution while cooling the sample. The precipitate was removed by filtering the choloform extract through Whatman No. 1 filter paper.

It should be noted that there is no known totally effective technique for preservation of polysulfide samples. Prevention of oxygenation;

elimination of contact with cyanide, maintaining pH = 12., and refrigeration retards sample degradation. Stock polysulfide solution must always be standardized immediately prior to use.

Formation of Cyanide and Thiocyanate in Coal Conversion Processes

The following is a synopsis of available knowledge on mechanisms believed to be responsible for the formation of cyanide and thiocyanate during coal gasification. It is emphasized that much of the information presented below is based on experiences in the coal coking industry and presumably this information is applicable to coal gasification. Further, a literature search has revealed that most of the available information is qualitative and that little progress has been made since the 1940's. Chemistry of Coal Utilization, H.H. Lowry Ed. (6), is the best general reference source, albeit over thirty years since publication. The information presented below will be used to help explain the occurrence of cyanide and thiocyanate in gasification quench waters and to interpret findings of field and laboratory experiments on interrelationships between cyanide, ammonia, sulfur and thiocyanate.

Cyanide Formation

It is believed that cyanide forms as a result of a reaction of ammonia with other compounds in the gasifier. The formation of ammonia is dependent to a certain extent on the nitrogen content of coal which usually ranges from 1 to 2 percent for American varieities. During carbonization (coking) or gasification of coal a fraction of the nitrogen i.e. $\simeq$ 70 to

80 percent based on the solid phase N balance, appears in the gas as molecular nitrogen, ammonia, cyanogen and various organic base materials. Mechanisms for ammonia formation are still somewhat questionable, but it is believed that ammonia results from the release of ammonia-type side chains, e.g. amino or substituted amino groups from the coal structure. This probably occurs rapidly during coal heat-up since most side chains are relatively unstable as coal temperature is raised. The nitrogen which remains in coke or char is believed to be contained within multi-ring compounds and to be much more refactory than amino-nitrogen. Under hydrogeneration conditions during gasification much more ammonia is formed than under normal coal carbonization conditions, probably resulting from hydrogen attack of the ring bound nitrogen. Consequently the yield of ammonia from gasification is on the order of 15-20 lb/ton coal (moisture and ash free, MAF) compared to about 6-8 lb/ton coal (MAF) from coking. Possible pathways for formation of hydrogen cyanide in coking entail reaction of NH_3 with C, CH_4, C_2H_4, C_2H_2, and/or CO (7).

There is no question that cyanide production is enhanced by high temperatures, and is the result of secondary reactions. It is certainly not derived from the coal substance itself by primary breakdown because it has never been observed in any low temperature ($\simeq 400^{\circ}F$) treatment of coal, whether by extraction or distillation. It has also been derived in small quantities by pyrolysis of nitrogenous compounds obtained as primary products of coal decomposition in particular, pyridine(8). However, data to refute or support suggested formation mechanisms await the collection of adequate gas phase data from the coal gasification pilot plants.

Thiocyanate Formation

Much less is understood about the formation of thiocyanate during gasification. It is unknown if it may form as a result of gas phase reactions. For example, one possible gas phase mechanism for the formation of SCN^- is the reaction of carbon disulfide and ammonia (8); however Hill (9) could find no documentation showing the presence of gas phase thiocyanate during coal conversion. Progress will likely be made on this problem as a result of gas probe sampling efforts now underway at several coal gasification pilot plants (10) .

Regardless of whether or not thiocyanate may be present in gasifier product gas, there is no question that thiocyanate is found in significant quantities in coal gasification quench waters, in coke plant waste ammonical liquors, and in coke oven gas distribution line condensates and deposits (10,11). These observations are explained in the case of the coking industry on the basis of oxidation of coke oven gas constituents through various complex reactions to form thiocyanate and thiocyanate complexes. These reactions occur largely in the aqueous phase, and presumably some of these pathways are applicable to the situation existing during the formation and subsequent handling of coal gasification process wastewaters. Table 5 presents a summary of possible oxidation reaction pathways for the formation of thiocyanate during gasification. All of these pathways, except possibly number 3, have been observed to occur at coke plants. Certainly not all of the reactions on Table 5 are of equal importance, nor would all necessarily be competing simultaneously.

An essential feature of all the pathways on Table 5 is that an oxidizing agent (O_2) is required to initiate the reactions. Pathways 3,

Table 5

SUMMARY OF POSSIBLE REACTION PATHWAYS FOR AQUEOUS PHASE PRODUCTION OF THIOCYANATE DURING COAL GASIFICATION

Description	Reaction Paths	Comments	Feasibility
1. Reaction of cyanide and polysulfide.[1,2]	$4(NH_4)_2S + O_2 + H_2O \xrightarrow{k_1} (NH_4)_2S_2 + NaOH$ $(NH_4)_2S_2 + NH_4CN \xrightarrow{k_2} (NH_4)_2S + NH_4SCN$	Sulfide is oxidized to sulfur forming polysulfides. Polysulfide reacts with CN^- to yield SCN^- and $S^=$.	This reaction may occur to the extent that O_2 or other oxidizing agents are introduced in process units. May also occur upon oxidation of process wastewaters.
2. Reaction of cyanide with thiosulfate.[2,3,4]	$2(NH_4)_2S + 3O_2 \xrightarrow{k_1} 2(NH_4)_2SO_3$ $(NH_4)_2S_2 + (NH_4)_2SO_3 \xrightarrow{k_2} (NH_4)_2S_2O_3 + (NH_4)_2S$ $NH_4CN + (NH_4)_2S_2O_3 \xrightarrow{k_3} NH_4SCN + (NH_4)_2SO_3$	Sulfide is oxidized to $SO_3^=$ which reacts with polysulfide to produce $S_2O_3^=$. $S_2O_3^=$ reacts with cyanide to give SCN^- and $SO_3^=$.	This study found higher reaction rates for CN^- with polysulfide than reported rates with $S_2O_3^=$. Thus the significance of this pathway is dependent on the sequence of reactions entailing k_1 and k_2.
3. Reaction of cyanide and sulfur.[4]	$8NH_4CN + S_8 \rightarrow 8NH_4SCN$	Rate determining step is the opening of the S_8 ring; subsequent displacement reactions yield SCN^-.	Not an important pathway because most S^o-sulfur probably exists as polysulfide rather than as S_8 (e.g. pathways 1,2, and 4).
4. Reaction of cyanide with polysulfide formed from sulfiding of iron.[5]	$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$ $Fe_2S_3 + 3/2\ O_2 \rightarrow Fe_2O_3 + 3S$ $(NH_4)_2S + S \rightarrow (NH_4)_2S_2$ $(NH_4)_2S_2 + NH_4CN \rightarrow (NH_4)_2S + NH_4SCN$	Coke oven gas iron-oxide box reactions; favored by moisture, low temperatures, and alkaline conditions. Greater than 0.4% by volume O_2 required in gas to initiate reaction.	Relative importance is unknown, significance depends on O_2 concentration and reactivity of steel lines and vessels.
5. Reaction of ferrocyanide with polysulfide	$(NH_4)_4Fe(CN)_6 + 2(NH_4)_2S_4 \rightarrow$ $6NH_4SCN + FeS + (NH_4)_2S$	Requires elevated temperature and pressure.	Relative importance unknown; the reaction is dependent upon presence of ferrous iron and polysulfide.
6. Reaction of ferrocyanide with thiosulfate.[1]	$(NH_4)_4Fe(CN)_6 + 8(NH_4)_2S_2O_3 \rightarrow$ $6NH_4SCN + (NH_4)_2S + 6(NH_4)_2SO_4$ $+ FeS + S_2$	Requires elevated temperature and pressure.	Relative importance unknown; the reaction is dependent upon the presence of ferrous iron and $S_2O_3^=$.

References:

(1) Williams, (9)
(2) Hill, (8)
(3) Nickles, (12)
(4) Bartlett and Davis, (13)
(5) Massey, et. al., (14)

5, and 6 presuppose the presence of O_2 in that sulfide-sulfur produced during gasification has been oxidized to a higher state. Hill (8) reports that air oxidation is responsible for the formation of polysulfides, thiocyanates and thiosulfates in ammonical liquors (i.e., reaction paths 1 and 2). Thus thiocyanate formation may occur either by reaction with polysulfide (8,9), or by reaction with thiosulfate (8,12,13). Polysulfide formation is reported to be favored in cooler parts of coke oven gas condensing systems (8); note that the reaction of polysulfide and cyanide was in fact the basis for measurement of polysulfide as described previously.

Cyanide is also reactive with elemental sulfur (reaction 3 on Table 5); the rate determining step in the reaction sequence consists of cyanide attack to open the S_8 ring; subsequent displacement reactions to yield thiocyanate were reported as being relatively fast though no kinetic data was given for these reactions (13). Reaction pathway 4 occurs in iron-oxide box reactions for removal of H_2S from coke oven gas; and reaction pathways 5 and 6 require ferrous iron and either polysulfide or thiosulfate respectively.

Table 5 also presents a qualitative interpretation as to the feasibility of the reaction pathways occuring in coal gasification process wastewaters. Reaction pathways 4, 5, and 6 are dependent upon reactivity of steel distribution lines and reaction vessels. No coal gasification process information was found on this subject, and we chose not to explore these pathways later in our experimental studies in light of more tractable reaction mechanisms. Though not investigated in this study, these pathways may play potentially significant roles in fouling and corrosion of coal gasification gas processing and distribution systems, such as observed in the handling of coke oven gas. Reaction pathway 3 does not appear to be significant because any elemental sulfur formed as a result of oxidation will likely be found as polysulfide rather than as S_8. Thus reaction pathways 1 and 2 are probably the most significant routes for aqueous phase formation of SCN^-; the relative importance of these two pathways is difficult to assess because of the complex chemistry of sulfide oxidation.

Recent kinetic studies on the oxygenation of sulfide in aqueous solution have been reported by Chen and Morris (15,16) and O'Brien and Birkner (17). Reaction rates and products depend on solution pH, the $(S^{=}_{Total})/(O_2)$ ratio, catalytic effects of metal ions and organic compounds, and inhibitory effects of other species. O'Brien and Birkner conclude that the formation of sulfur (S^o) requires a $(S^{=}_{Total})$ concentration greater than 10^{-3} M/l. Coal gasification quench waters typically are mildly alkaline with $(S^{=}_{Total})$ ranging from about $5 \cdot 10^{-3}$ to 10^{-2} M/l(11); these conditions should favor the formation of polysulfide. Figure 2 summarizes a model for the oxygenation of sulfide in coal gasification wastewaters to yield SCN^-. The model incorporates the essential features of reaction pathways 1 and 2 of Table 5, and features of the sulfide reaction scheme following polysulfide formation as presented by Chen and Morris (16). Thiocyanate is formed from reaction of cyanide with either polysulfide or thiosulfate. Observations on the rate of reaction of cyanide with polysulfide are presented later.

Time Stability of Cyanide and Thiocyanate in Gasifier Quench Waters

An experiment was designed to investigate cyanide degradation in unpreserved gasifier quench waters from the CO_2-Acceptor pilot plant

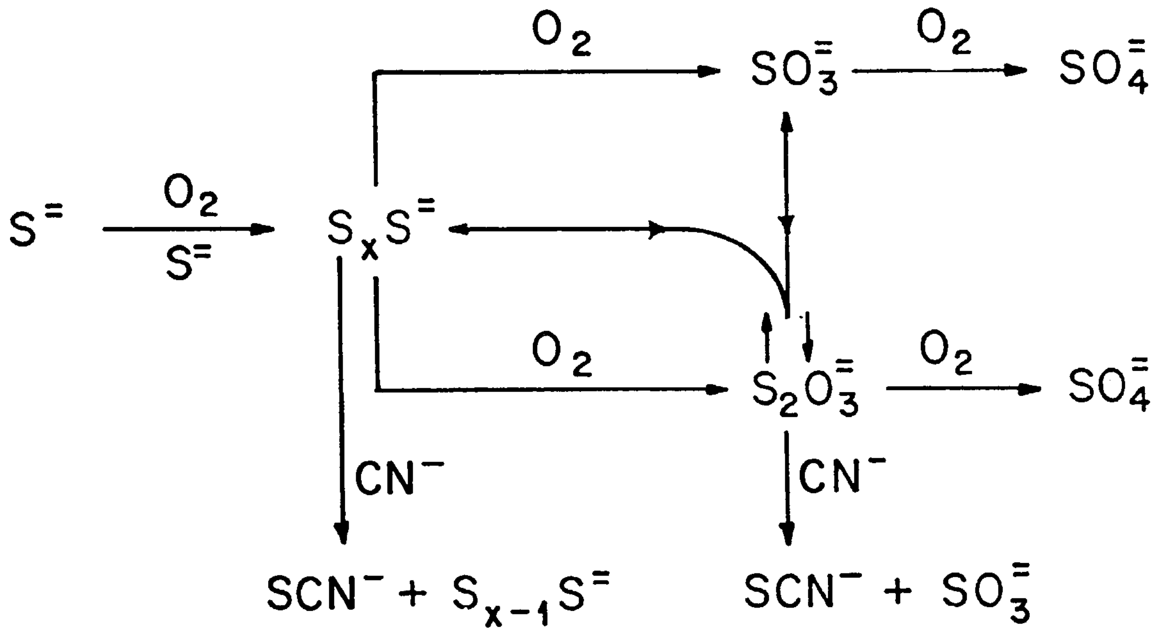


Figure 2. Reaction pathways of oxygenation of sulfide to yield thiocyanate.

in Rapid City, South Dakota. The experiment also served to document the necessity of the recommended preservation procedures. The sample handling procedure consisted of withdrawing $\simeq$ 10 gallons of gasifier quench water, decanting and filtering to remove coarse solids, and dividing into two aliquots. One aliquot was preserved according to the procedures outlined in Figure 1; sulfide was precipitated with lead; calcium hydroxide was used for pH adjustment, and the mixture was then filtered. The other aliquot consisted simply of raw quench water as sampled. Samples from both the preserved and unpreserved aliquots were analyzed simultaneously covering a total period of 72 hours. Thiocyanate determinations were completed at the specified times, whereas cyanide in each sample was fixed by distillation with the color being developed at a later date. Duplicate determinations were performed on each sample. This data is presented in Figure 3. Cyanide and thiocyanate values for the preserved samples were fit with a least squares regression line, and in both cases the slopes were found not to be significantly different from zero at the 95% confidence interval. Hence this data is represented by a straight line at the mean concentration level. Unpreserved samples show a different trend, cyanide concentration dropped significantly within 3-4 hours, and then remained relatively constant with time. Thiocyanate showed essentially no change until after 17 hours when it began to increase until the final time at seventy-two hours.

The data of Figure 3 suggest that a relation between decreasing cyanide and increasing thiocyanate does exist. However, for unknown reasons, the loss of CN^- in the unpreserved sample could account for only about one half the observed increase of SCN^-. The data of Figure 3 also

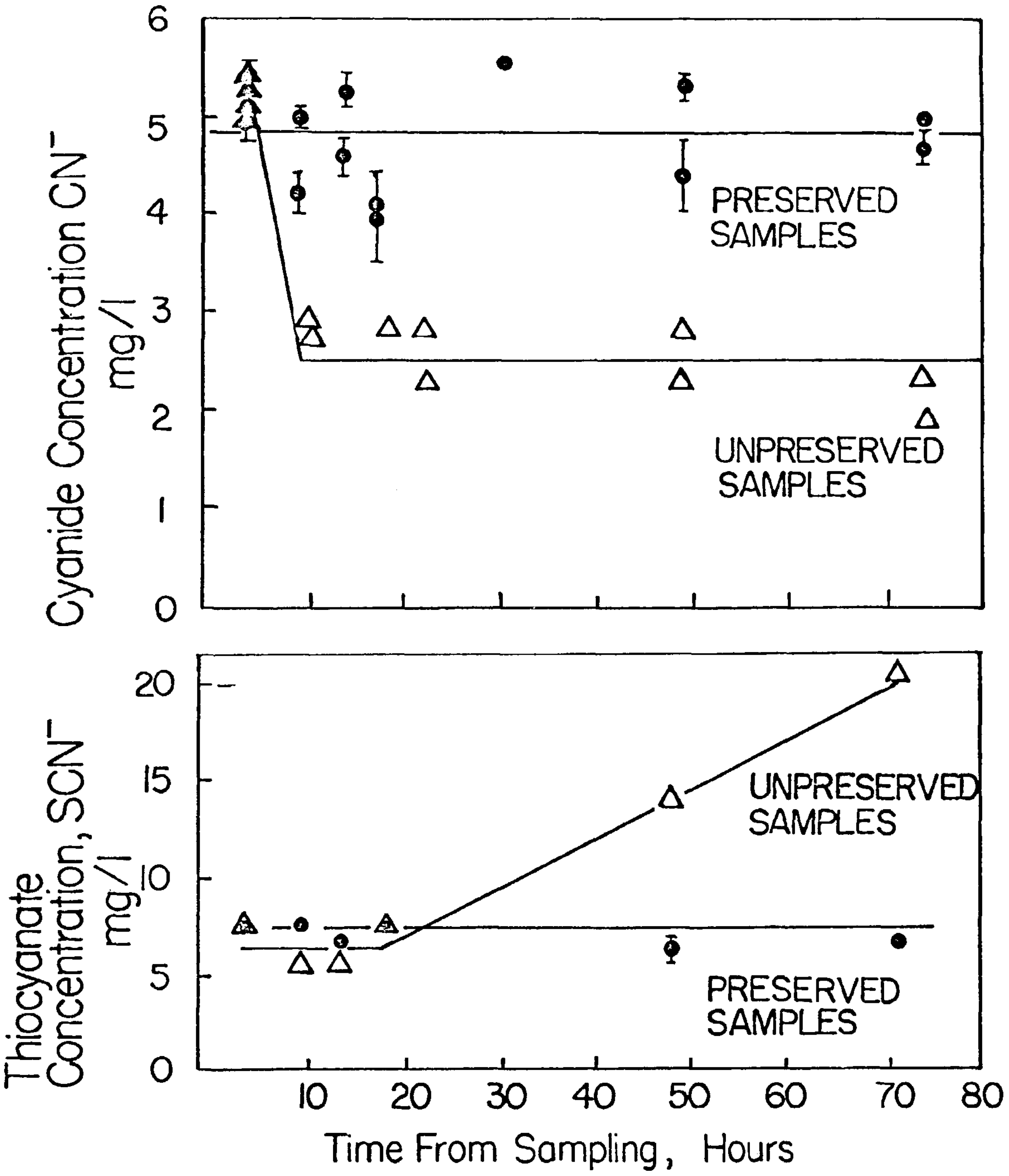


FIGURE 3. TIME STABILITY OF CYANIDE AND THIOCYANATE IN CO_2-ACCEPTOR GASIFIER QUENCH WATERS. INITIAL VALUE OF pH=8.5, NH_3-N=2000mg/l, $S^=$ = 160 mg/l, TEMP= 20-25°C.

suggests that the presence of sulfide plays an instrumental role in the observed trends, because preserved samples with sulfide removed were unaffected.

To test the hypothesis that polysulfide sulfur is reactive with cyanide in coal gasification wastewaters another time series experiment was configured with cyanide-spiked Hygas process quench wastewater from the Hygas pilot plant in Chicago, Illinois. The sample was divided in two aliquots and in both cases the cyanide levels were raised to about 95 mg/l from an initial value of 0.01 mg/l. One sample was spiked with 123 mg/l polysulfide-S (3.84 mM/l Na_2S_4) and maintained under a N_2 purge to inhibit sulfur oxidation. The other aliquot contained no polysulfide spike; but it was aerated to promote sulfide-sulfur oxidation. The results of these tests are shown in Figure 4; the curves are drawn to follow thiocyanate production, also shown are initial and final cyanide concentrations.

The upper curve of Figure 4 illustrates that there is a reaction between cyanide and polysulfide to produce thiocyanate in coal gasification wastewaters. The reaction proceeded rapidly and within ten hours SCN^- increased from about 35 to 183 mg/l, and cyanide decreased from 95 to 17 mg/l. The increase of SCN^- (148 mg/l) can account for approximately 85% of the loss of cyanide. The remainder may have been lost either by volatilization or by the result of other reactions. The rate of formation of SCN^- was much lower (100 mg/l after 10 hours) in the aliquot which was aerated but not spiked with polysulfide. In this case 64% of the loss of cyanide can be accounted for by gain in SCN^-, the remainder may have been lost largely as a result of volatilization from aeration.

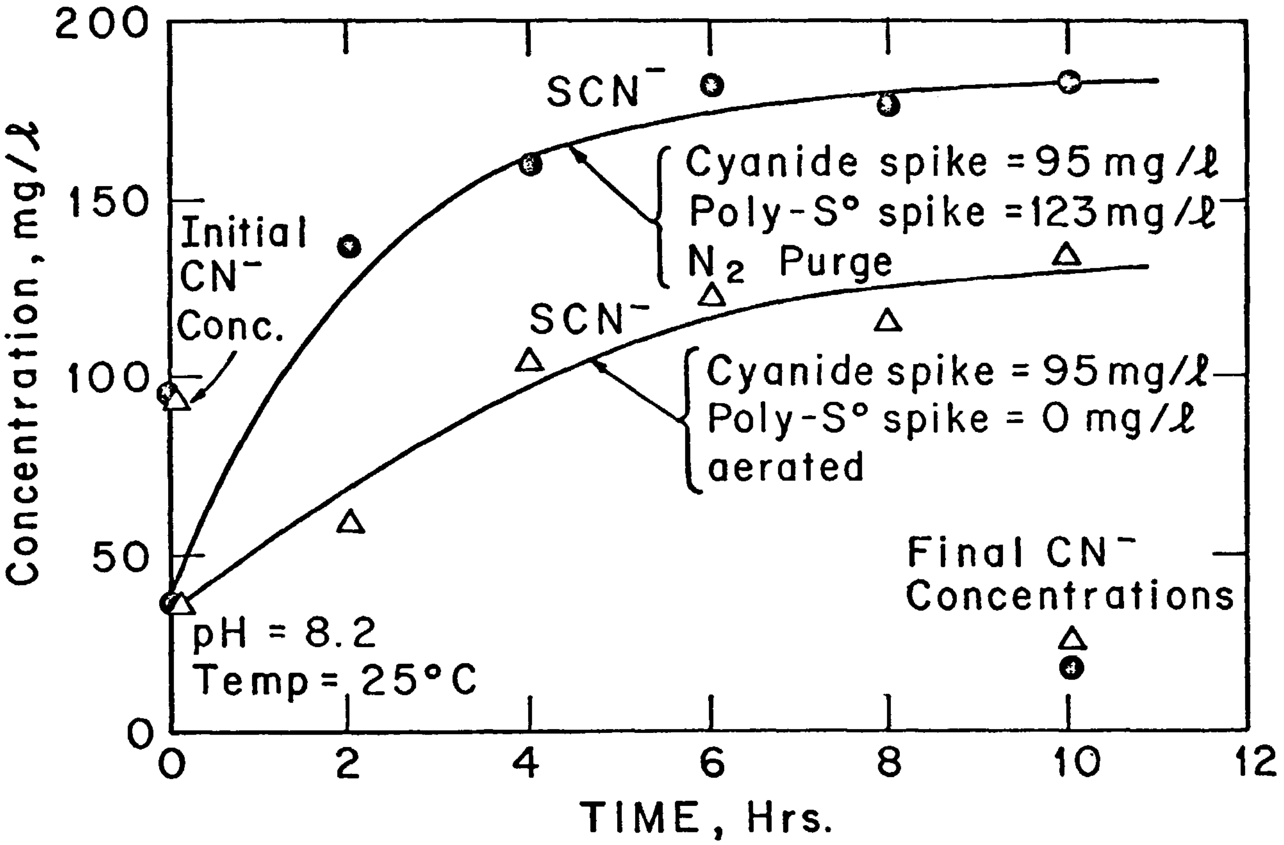


Figure 4. Time series analysis of SCN^- production in Hygas quench wastewater. Raw wastewater chacteristics (mg/ℓ): $CN^- = 0.01$, $SCN^- = 35$, $NH_3-N = 8600$, $S^{=} = 241$, poly-S° < 5, alkalinity(as $CaCO_3$)=53,000.

Polysulfide analysis of this sample showed that there was no accumulation of this compound; hence it appears that reactions to oxidize sulfide to polysulfide or to other forms of sulfur reactive with cyanide must necessarily be slower or not as favorable as the reaction of polysulfide with cyanide.

In order to better interpret Figures 3 and 4, thiocyanate production was observed in clean water samples using KCN, Na_2S, and Na_2S_4. Figure 5 presents data on effect of aeration, pH, and sulfide form on SCN^- production. In each case the stoichiometry indicates direct conversion of cyanide to thiocyanate. The presence of polysulfide-sulfur enhanced the formation of thiocyanate. Sulfide-sulfur was not reactive; oxidation of the sulfide system tended to promote the production of SCN^- at pH = 12, but not to a very great extent. Figures 4 and 5 show conclusively that polysulfide-sulfur is reactive with cyanide, while sulfide-sulfur is not. Further studies were initiated to investigate the kinetics of the reaction of polysulfide-sulfur and cyanide.

Kinetic Studies

Experimental Design

Five systems were investigated to study the kinetics of the reaction of cyanide and polysulfide. The experimental format is outlined in Table 6. Four of the systems consisted of distilled water solutions, the fifth was a sample of Hygas wastewater.

Three values of pH were chosen for study: 12, 10, and 8.2. The choice of these pH's was somewhat arbitrary although it should be observed that pH 10 and pH 12 are both above the pK_A of hydrogen cyanide (pK_A = 9.2) and that pH 12 is the value specified for cyanide-thiocyanate

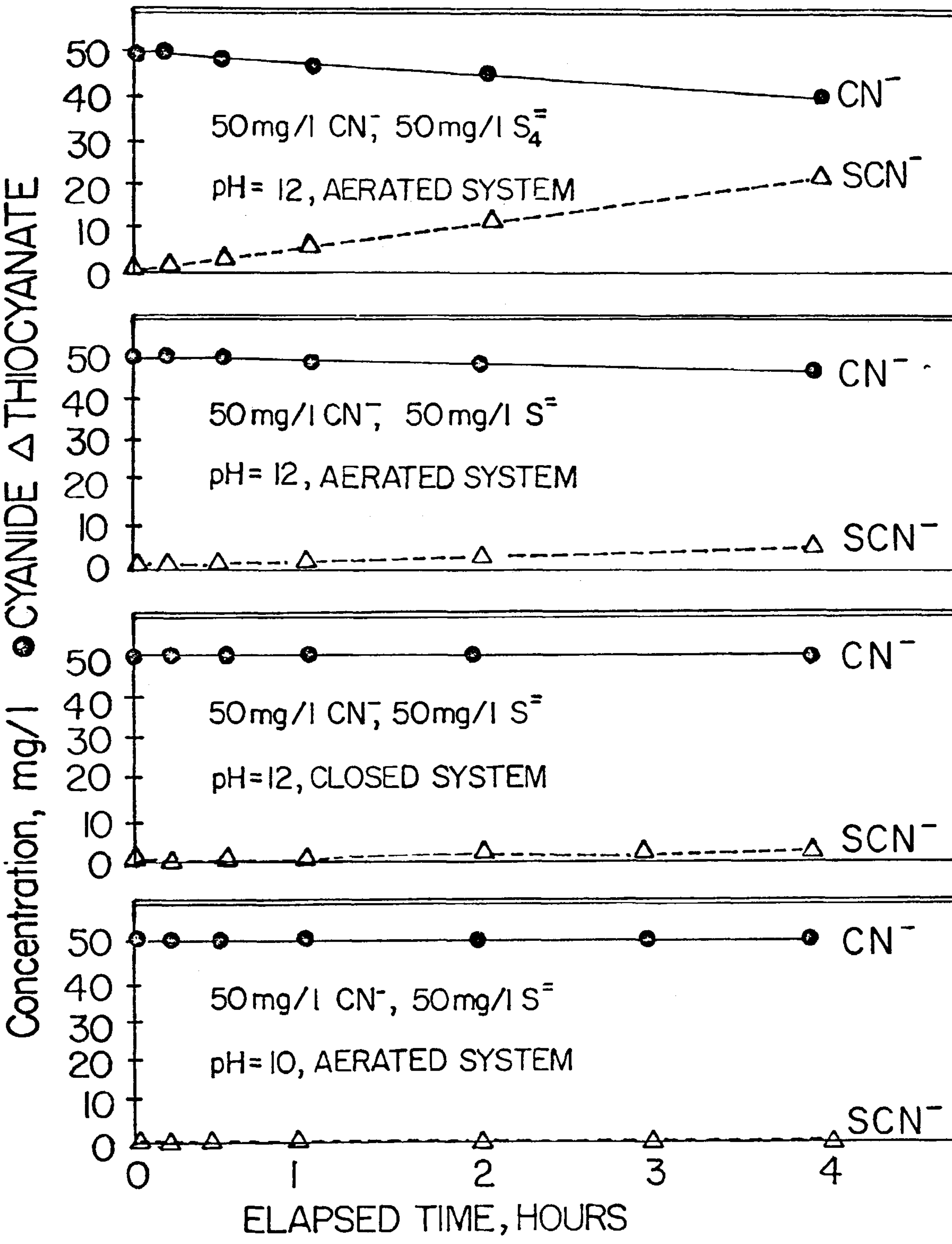


Figure 5. Thiocyanate Production In Clean Water Solutions

Table 6

EXPERIMENTAL FORMAT FOR SCN^- KINETIC STUDIES

	SYSTEM				
Configuration	1	2	3	4	5
Medium	Distilled water	Distilled water	Distilled water	Distilled water	Hygas Quench Water*
Purging Gas	N_2	N_2	N_2	N_2	N_2
pH	12	10	8.2	8.2	8.2
Poly-S^o, mg/ℓ	123	123	123	123	123
CN_{Total}, mg/ℓ	100/50	100/50	100/50	100/50	100
Buffer	--	--	0.1 M/ℓ $NaHCO_3$	0.25 M/ℓ NH_4HCO_3	--
Number of Studies at each CN^- conc.	7/2	4/2	2/2	2/2	2

*Raw wastewater characteristics, mg/ℓ: phenol 1010; COD 5600, $S^=$ 315, NH_3-N 6180, CN^- 0.20, alkalinity as $CaCO_3$ 22,500.

sample preservation. It should also be noted that pH 8.2 is somewhat representative of the wastewater systems under investigation, and that it is midway between pK_1, the first disassociation constant for hydrogen sulfide (7.2), and pK_A for hydrogen cyanide. The distilled water systems at pH = 8.2 were buffered owing to the acid producing tendency of the reaction. Two buffers were evaluated, 0.1 M/1 $NaHCO_3$ and 0.25 M/1 NH_4HCO_3; it being supposed that the ammonia present in wastewater may affect the reaction in some fashion. No buffer was required for the Hygas wastewater sample because of the high ammonia and alkalinity values.

Cyanide was added to the sample as potassium cyanide (KCN); cyanide concentrations were expressed as total cyanide (CN_{Total}) which equals to the sum of HCN plus CN^-. Polysulfide was added to the sample as tetrapolysulfide (Na_2S_4); measured polysulfide concentrations were expressed as polysulfide-sulfur (poly-S^o). The molar ratio of poly-S^o to total sulfur in Na_2S_4 is 3 to 4; however because solid Na_2S_4 decomposes upon exposure to air, polysulfide solutions were standardized regularly prior to use.

The experimental procedure for the kinetic studies is discussed below.

1. Sample preparation involved preliminary analysis and make-up solution to be used in the study.

2. Reaction vessels and contents were prepared as outlined in Table 6. Replicate reactor studies were performed for each system at each cyanide concentration.

3. Samples were taken from the reactor and acidified with nitric acid (1:1) to a pH of 3.0-3.5. At this pH polyside was precipitated from the system and removed by

millipore filtration; the acidification and filtration stopped the reaction of polysulfide and cyanide. A 20 ml aliquot, or dilution of filtered sample, was then added to a Nessler tube containing the thiocyanate color development reagents (5 ml 1g/ℓ copper reagent plus one ml pyridine), extracted with 20 ml chloroform and the absorbance read at 407 nm with a Baush and Lomb Spectronic 88 spectrophotometer.

4. Cyanide analyses were also performed on samples to document loss as a function of time. For the pH = 12 and pH = 10 experiment, cyanide loss by volatilization was negligible. However at pH = 8.2 cyanide mass balances showed that cyanide was lost by volatilization and this necessitated regular cyanide measurements to follow the course of the reaction. Samples taken for cyanide analysis were prepared according to the scheme outlined in Figure 1. Polysulfide mass balances showed that the decreases in poly-S^o was directly proportional to gain in SCN^- for all systems.

Data Reduction

In order to establish a rate constant and the order of the reaction the differential method for kinetic data reduction was used on both the clean water and wastewater systems. The general form of the rate equation

$$r = k_{a+b} C_A^a C_B^b \tag{3}$$

was used where the two components of interest were cyanide and polysulfide.

r = rate of production of SCN^-, M/ℓ/min
k_{a+b} = rate constant
C_A = concentration of cyanide, CN_{Total}
C_B = concentration of polysulfide, Poly-S^o

$a+b$ = order of the reaction

A plot of thiocyanate concentration vs. time of reaction was constructed; the slope of the curve at various points is equal to r.

$$r = \frac{d\ SCN^-}{dt} = \frac{-d\ CN_{Total}}{dt} = \frac{-d\ Poly\text{-}S^o}{dt} \tag{4}$$

By assuming this general form, log r is plotted against log $[(CN_{Total})(poly\text{-}S^{o})]$ remaining. For pH = 12 and pH = 10, the decrease in CN_{Total} and poly-S^{o} is proportional to the increase in SCN^{-}, thus the rate may be computed directly from SCN^{-} production:

$$\log r = \log k_{a+b} + \log ((CN_{Total})_{t=0} - SCN^{-})^{a}((Poly\text{-}S^{o})_{t=0} - SCN^{-})^{b} \qquad (5)$$

Because of cyanide loss by volatilization at pH = 8.2, the rate was correlated with measured values of cyanide remaining:

$$\log r = \log k_{a+b} + \log ((CN_{Total})_{t}^{a} (Poly\text{-}S^{o} - SCN^{-})^{b}) \qquad (6)$$

Figure 6 and 7 show SCN^{-} production data at pH = 10 and pH = 12 respectively; Figure 8 shows thiocyanate production and cyanide decrease for the kinetic studies performed at pH = 8.2. The initial value of SCN^{-} in the wastewater sample has been subtracted out for the data presented in Figure 8.

The SCN^{-} production data in Figure 6, 7, and 8 show similar trends for replicate tests run at each objective value of constituent concentration and pH. At pH = 8.2 there is similar SCN^{-} production for given reactant concentration values, though the system evaluated consisted of two different buffers and a wastewater sample. For this reason rate estimates were made using the trend curves shown on Figure 6-8. These data are displayed in Figure 9.

The overall order of reaction of CN_{Total} and poly-S^{o} may be computed from the slope of the rate plot for experiments using equimolar concentrations of CN_{Total} and poly-S^{o}. In this case, if the slope of the rate plot is represented by y, the overall order of the reaction may be computed by

$$\log r = \log k + y \log(CN_{Total})(Poly\text{-}S^{o}) = \log k + 2y \log C \qquad (7)$$

and

$$\log r = \log k + (a+b) \log C \qquad (8)$$

where $C = CN_{Total}$ = poly-S^{o}, and 2y is equal to the overall rate of reaction, a + b. The rate constant is given by the intercept of the rate plot line with the ordinate, CN_{Total} = poly-S^{o} = 1M/ℓ. The application of this method to the pH = 8.2 equimolar system is not strictly correct because some cyanide was lost by volatilization in the course of the experiment. However, in as much as pH 8.2 equimolar rate data coincide with pH = 10 and pH = 12 equimolar rate data, the pH = 8.2 system was used in estimating the slope of the rate plot line. Regression analysis of the equimolar data give an overall mixed order reaction, a + b = 1.54 ± 0.25, with a rate constant of $k = 0.24\ (M/\ell)^{-0.54}/$ min. The half-concentration rate data was not used in determining the overall order of the reaction or rate constant because individual rate constants with respect to CN and poly-S^{o} are not evaluated well by the procedures used in this investigation. Initial rate studies are better suited for determining reaction order with respect to individual components; nonetheless, the half concentration data are plotted on Figure 9 for trend identification purposes.

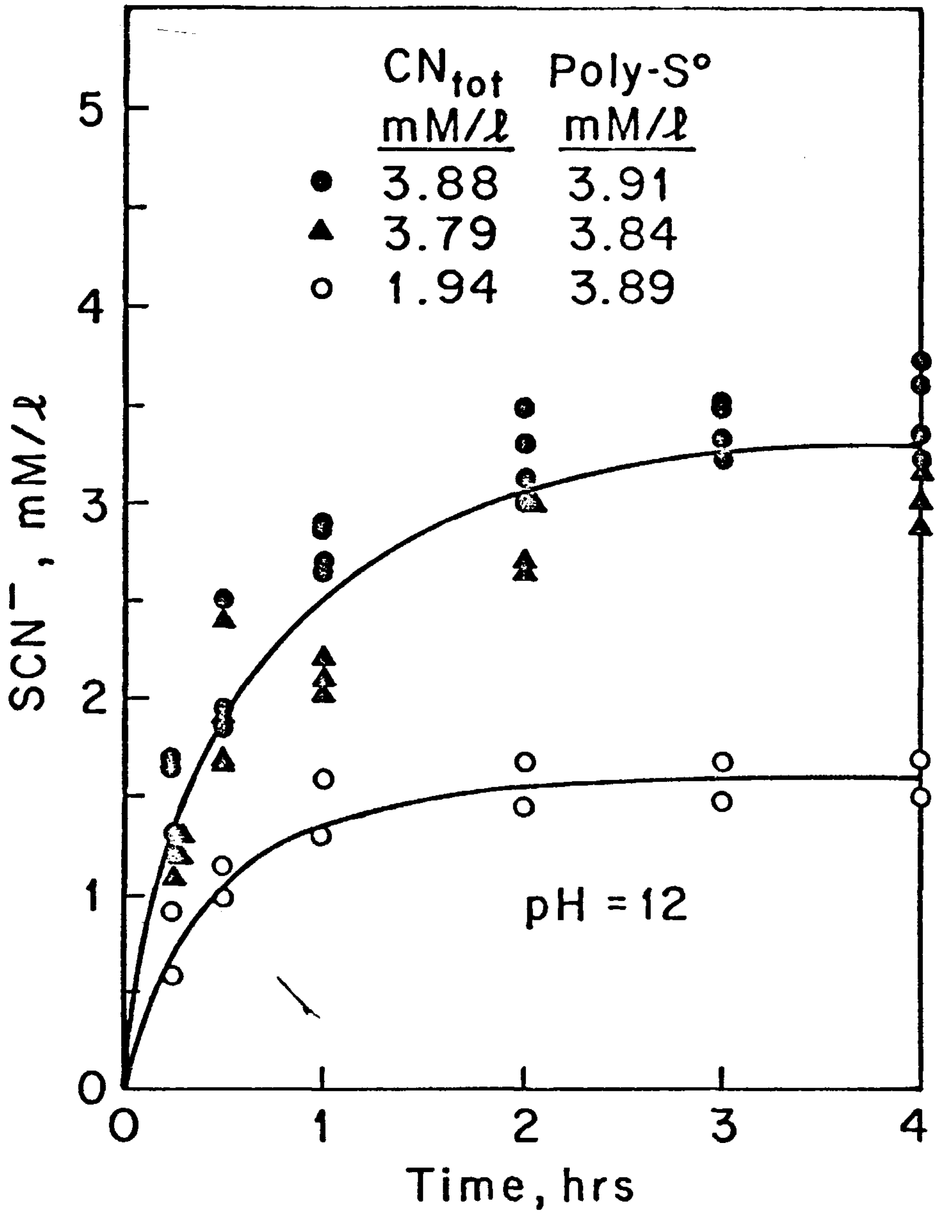


Figure 6. Clean water batch reactor kinetic studies on reaction of cyanide and polysulfide at pH = 12.

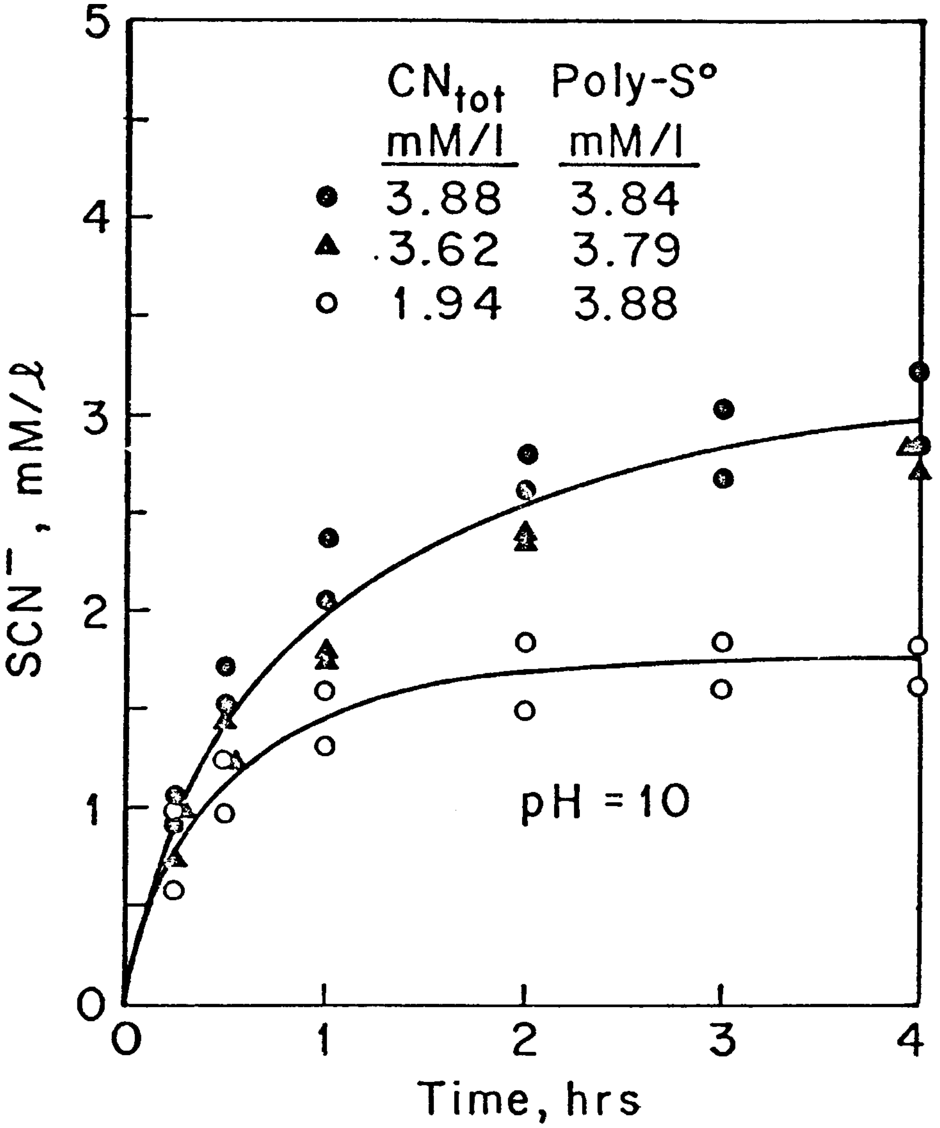


Figure 7. Clean water batch reactor kinetic studies on reaction of cyanide and polysulfide at pH = 10.

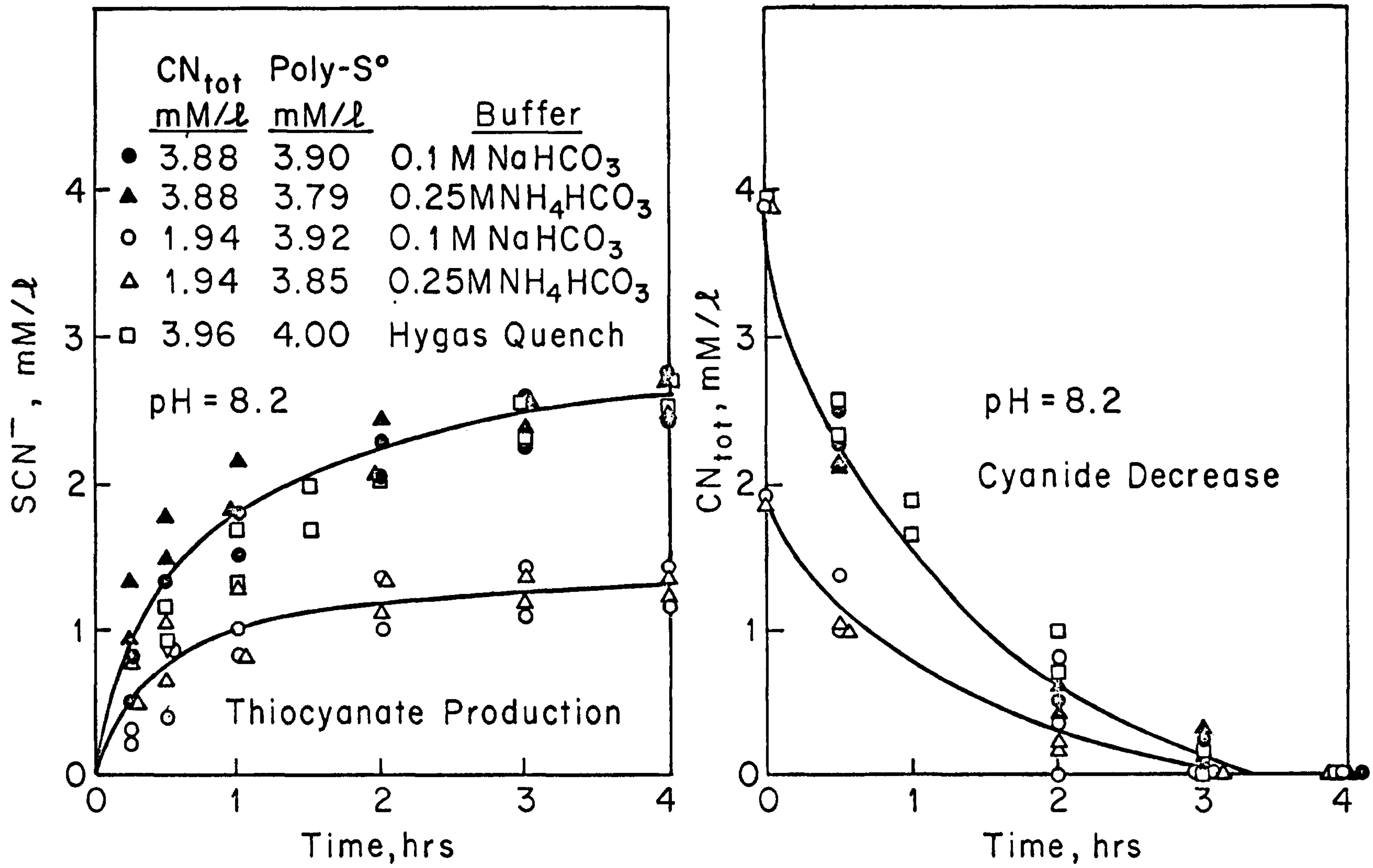


Figure 8 Thiocyanate production and cyanide decrease for batch reactor kinetic studies at pH = 8.2.

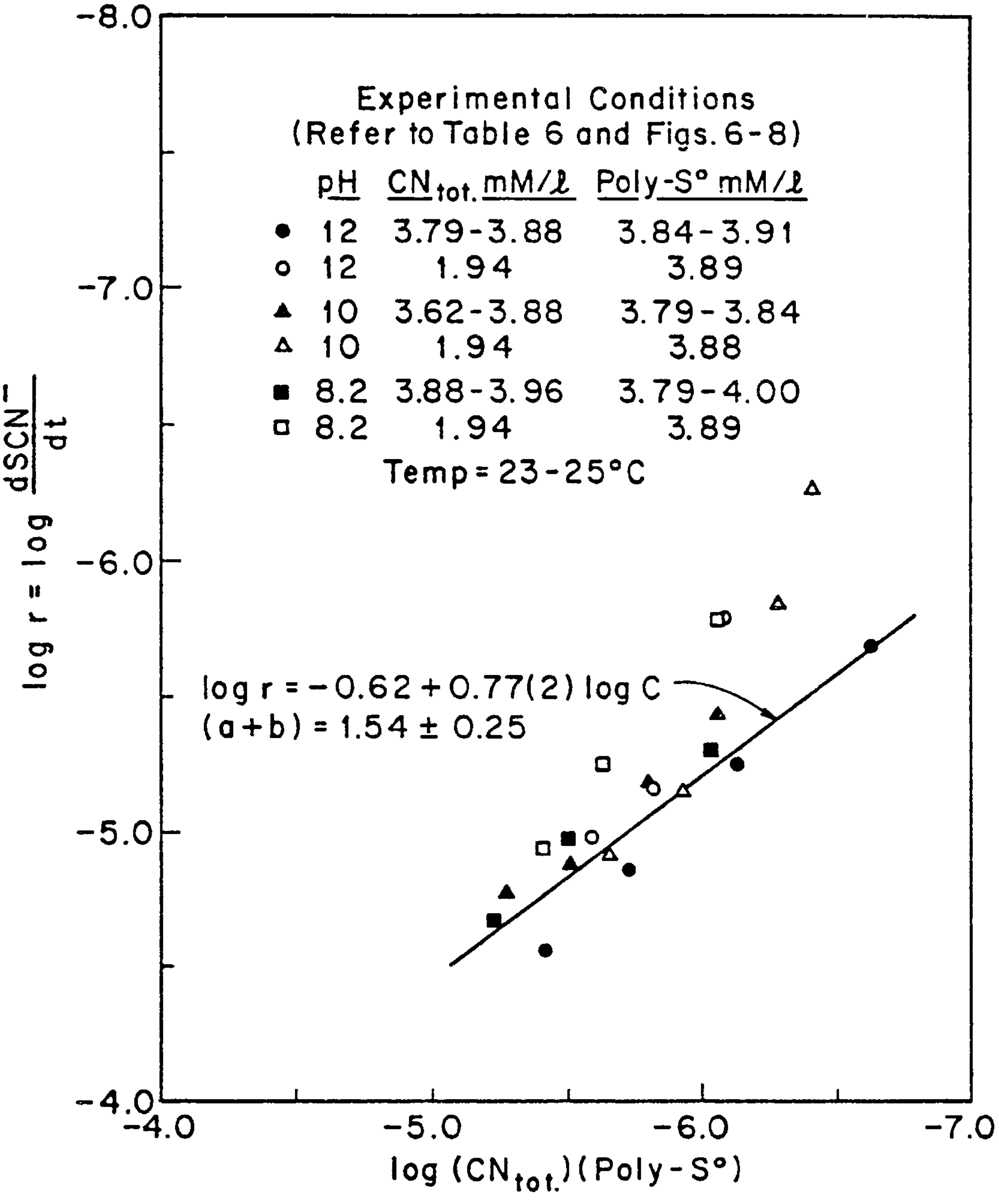


Figure 9 Rate plot for thiocyanate production in waters of varying quality as computed by the differential method from batch kinetic tests. All concentrations computed as M/ℓ, unit of time = min. The line drawn on the figure is used to estimate the overall order and rate constant for the reaction from equimolar test data.

DISCUSSION

Data presented in this paper have pertained to the preservation, identification, and reactions of cyanide and thiocyanate in coal gasification process wastewaters. Significant findings are summarized below.

Development of Procedures for Thiocyanate Determination

A copper-pyridine colorimetric method has been evaluated on a number of samples including wastewaters from the following facilities: Hygas, Bi-Gas, CO_2-Acceptor, Synthane, and Grand Forks Slagging Fixed-Bed coal gasification processes; and coke plant waste ammonia liquor. Clean water spiking and recovery studies were performed to assess levels of interferences from inorganic compounds typically present in the raw waste, and from those compounds which may be intentionally added to the sample during preservation. These tests showed no interferences, excepting higher levels of cadmium which might be added to the sample during preservation. This problem can be eliminated by substitution of lead during preservation. Major problems were encountered with interferences from organic compounds owing to this material being extracted along with the copper-pyridine complex and influencing color development. Pre-extraction removed this interference from all wastewaters analyzed, excepting Grand Forks Slagging gasifier quench water, which contained very high levels of tars, oils, and other organics. Solutions to this problem are under investigation; none-the-less because the copper-pyridine method with pre-extraction has been effective on other wastewaters it is proposed as a method of choice (4). It is noted that the EPA has no recommended procedure for thiocyanate, and that the current procedure recommended by Standard Methods (1) was completely ineffective owing to background color interferences.

Improvement of Procedures for Cyanide Preservation and Analysis

Problems encountered in the use of recommended (1), procedures for cyanide analysis on coal gasification quench wastewaters were traced to extra-ordinary concentrations of ammonium bicarbonate (up to approx. 0.5 M/1). The problem was overcome by use of lime to raise sample pH during preservation, causing excessive alkalinity to be precipitated as a $CaCO_3$ sludge. Sulfide precipitation was also required to prevent a potential interaction between cyanide and polysulfide. Polysulfide may form as a product of oxidation of sulfide. Sample filtration was required to remove the carbonate and sulfide precipitates. Implications of this procedure will be discussed in a following section.

Reaction of Cyanide and Sulfur

Laboratory studies using clean water and samples of coal gasification process quench water showed that no reaction occurred between cyanide and sulfide; however, sulfur in the form of polysulfide ($S_xS^=$) reacts relatively quickly with cyanide (i.e., within a few hours or less) to produce thiocyanate. Preliminary kinetic studies of this reaction indicated no strong effect of pH on rate over the range pH = 8.2-12, and similar response between tests run in clean water or a sample of Hygas quench wastewater. The reaction appears to be of order 1.54 ± 0.25.

Bartlett and Davis (13), reported a second order rate constant of $2.3.10^{-3}$ 1/M/min for reaction of cyanide with $S_2O_3^=$ to produce SCN^-.

This study found reaction rates several orders of magnitudes higher for reaction of cyanide with poly-S^o. Thus, at least initially, it would appear that poly-S^o represents a much more significant pathway for aqueous phase SCN^- production than $S_2O_3^=$; however interpretive analysis requires additional study beyond the observations presented here. Additional work is needed to assess catalysis/inhibition effects on SCN^- production by compounds affecting sulfide oxygenation. These compounds can affect the distribution of sulfide oxidation products (e.g. ratio of poly-S^o to $S_2O_3^=$), and they may also effect the rate constant for reaction of cyanide with poly-S^o or $S_2O_3^=$. Results of experiments to evaluate individual rates of reaction of poly-S^o and $S_2O_3^=$ with CN, and to evaluate the effect of potential catalytic/inhibitory agents are reported elsewhere (19).

Complex cyanides may not be reactive with polysulfide at room temperature, as it was observed in a survey test that $Fe(CN)_6^{-3}$ produced no SCN^- in the presence of polysulfide.

Raw Hygas wastewaters have shown no presence of polysulfide, implying either 1) that no oxidizing agent was present during the formation of the wastewaters to react with sulfide; or 2) that sulfide was preferentially oxidized to higher oxidation states, or 3) that by the time of analysis reaction between cyanide and polysulfide had already gone to completion in the presence of excess cyanide. Until issues such as these are better understood, and until additional gas phase sampling is completed, it is not possible to predict the extent to which reaction of cyanide with polysulfide accounts for the presence thiocyanate in quench waters.

Implications for Analysis and Processing

Data has been presented which illustrates that sulfur in the form of polysulfide and thiosulfate e.g., as may be formed from sulfide oxidation, is reactive with cyanide; hence, the recommended sample preservation procedure (Figure 1) provides for sulfide precipitation. It is noted however that preservation procedures recommended by the EPA (1974) do not include provision for removal of sulfide. Further it is recognized that objectives to the procedure described in Figure 1 may be concerned with the loss of insoluble complex cyanide compounds as a result of filtration prior to distillation. One way to overcome this objection would be to filter the sample before sulfide is precipitated and filtered out, and then reconstitute the sample by returning filtered particles to the sample after sulfide removal, and homogenizing particulates and filter paper before testing (20). Regardless, sulfide precipitation, excessive alkalinity removal, and pH adjustment has been shown to preserve soluble cyanide samples for at least 72 hours, and this is the recommended method(4) for preservation of samples for characterization of aqueous phase constituents of coal gasification process wastewaters. The special nature of coal gasification wastewaters (high levels of sulfide and alkalinity) necessitates careful consideration for cyanide sample preservation and analysis. We have observed that previously reported low levels of cyanide production at some pilot plants was a result of improper sample preservation and analysis rather than a correct characterization of the process (10,21).

Cyanide-sulfur-thiocyanate interactions have important implications for wastewater quality changes which may occur during storage or processing. Wastewater oxidation could produce a certain amount of polysulfide from available sulfide; and to the extent that cyanide is present, thiocyanate should form readily. Thus, cyanide could be transformed to a relatively nontoxic species at the expense of producing a compound which can cause severe corrosion and deposition problems in steel process units and lines. Cyanide, which is more ameenable to physico-chemical treatment for removal (e.g., steam stripping) may be transformed to a compound which is much more difficult to remove from wastewater (e.g., requires chlorination, biological oxidation, or demineralization). The manner in which a coal gasification wastewater changes with respect to cyanide-thiocyanate interaction may largely have to do with the nature of sulfide oxidation. It was observed in this work, as well as by Rosenwald, et. al., (22) that attempts to limit the extent of sulfide oxidation by merely limiting accessibility of oxygen were ineffective, hence the problems associated with cyanide-thiocyanate interaction becomes one of sulfide oxidation kinetic control.

CONCLUSIONS

Procedures for thiocyanate preservation and analysis have been evaluated. A copper-pyridine colorimetric analytical method with pre-extraction has been tested successfully on a number of coal gasification wastewaters, although difficulties have been encountered with some samples containing very high levels of organic compounds. Improved preservation procedures for cyanide analysis require removal of exceptionally high levels of carbonate to eliminate analytical difficulties during sample distillation. Sulfide removal is also necessary to eliminate the possibility of reaction of cyanide with sulfide oxidation products, especially polysulfide.

The extent to which thiocyanate may be observed in coal gasification process quench waters as a result of reactions occurring in the gasifier as compared to aqueous phase reactions is unknown. Aqueous phase thiocyanate formation pathways were reviewed, and a model is proposed whereby the reaction of cyanide with polysulfide-sulfur and thiosulfate are plausible pathways for aqueous phase thiocyanate formation. Preliminary kinetic studies on reaction of cyanide and polysulfide-sulfur in clean water and wastewater over the pH range 8.2-12 showed that the reaction was mixed order (1.54 ± 0.25) with a rate constant of about 0.24 $(M/l)^{0.54}/min$. Thus SCN^- formation via poly-S^o may be much more significant than formation via $S_2O_3^=$; and additional work, which has included an investigation of catalysis/inhibitory effects, suggests that this may be the case (19).

Results of this work may be useful to predict or explain quality changes in coal gasification wastewaters. Attempts to engineer these reactions may largely entail sulfide oxidation kinetic control.

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