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Dissolution of CuS Particles with Fe(III) in Acidic Sulfate Solutions

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ABSTRACT: The dissolution of CuS particles with Fe³⁺ in acidic sulfate solutions was investigated in an oxygen-free environment. CuS particles, used in this study, were obtained from H₂S removal operations from biogas with an acidic CuSO₄ solution in a Vitrisol pilot absorber. The CuS particles were porous with an average diameter of 5.8 × 10^{−6} m. Zero orders of reaction for both Fe³⁺ and H₂SO₄ were determined. Full conversion of CuS could be obtained independent of temperature. The activation energy was determined to be E_A = 22.0 kJ/mol. It seems plausible that the CuS dissolution reaction was affected by diffusion.

1. INTRODUCTION

Hydrogen sulfide (H₂S) is a highly toxic and corrosive gas. Removal of H₂S from acidic gas streams, such as natural gas, industrial gas, or biogas, is important for safety, health, environmental, and economic reasons. Apart from non-regenerative H₂S removal by the use of, for example, adsorbents, all of the regenerative desulfurization processes capture CO₂ to varying extents besides H₂S. Because of the coabsorption of CO₂, capital costs, as well as operational costs, increase.

The novel Vitrisol desulfurization process¹ is based on the removal of H₂S by precipitation with copper sulfate (CuSO₄) in an aqueous, acidic solution. Copper sulfide (CuS), also known as covellite, and sulfuric acid are formed in the gas treating process:^{2,3}

The Vitrisol process is able to remove H₂S from acidic gas streams without the coabsorption of CO₂.^{2,4} Because the precipitation reaction occurs very rapidly, the removal of H₂S is limited by mass transfer in the gas phase.

The current status of the Vitrisol process is scavenger-like. Cu²⁺, the active compound in the absorption liquid, becomes depleted during H₂S removal. It must be noted, however, that nowadays copper is an expensive commodity; increasing amounts of H₂S lead to increasing operational costs. To reduce the operational costs for large amounts of H₂S and/or large-scale applications, a regeneration step has to be developed to replenish Cu²⁺.

CuS can be leached with ferric sulfate (Fe₂(SO₄)₃), an operation encountered in copper ore processing (CuS).^{5,6} Copper sulfate, elemental sulfur (S⁰), and ferrous sulfate (FeSO₄) are produced in the process:

Ferrous sulfate can be reoxidized to ferric sulfate with O₂, according to

This results in the overall net reaction for the removal of H₂S:

Wermink and Versteeg^{4,7} studied the oxidation of ferrous ions in acidic sulfate solutions (reaction 3), and proposed kinetic equations derived by fitting both the initial reaction rates and the experimentally determined Fe²⁺ concentration profiles as a function of time, respectively.

Furthermore, Wermink and Versteeg⁸ studied the behavior of the oxidation of ferrous ions in acidic sulfate solution, in the presence of Cu²⁺. It was concluded that Cu²⁺ enhanced the oxidation rate of Fe²⁺, and that some of the experiments were affected by mass transfer of oxygen.

A Vitrisol pilot absorber was built⁹ to remove H₂S from biogas, to obtain representative samples of CuS, and to verify design rules. Operational boundary conditions were determined with respect to continuous operation in the absorber and batch-wise operation of the absorption liquid.

In this study, the behavior of the dissolution reaction of CuS with Fe³⁺ (reaction 2) was studied. Representative samples of CuS, obtained from Vitrisol pilot absorber operations,⁹ were used in the study.

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2. LITERATURE REVIEW

The dissolution reaction of CuS with ferric sulfate in sulfuric acid solutions has previously been investigated by several authors.

Sullivan¹⁰ investigated the dissolution of natural and artificial covellite in acidic ferric sulfate solutions. Purities of the two sources of natural covellite were 95% and 85–90%, respectively. The covellite particle size ranged between 6.73 and 2.00 mm and below 0.074 mm in size, respectively. Artificial covellite was obtained from leaching chalcocite to a residue with a Cu:S molar ratio of 1:1. The particle size of artificial covellite was not mentioned. Experiments were performed at temperatures of 35, 50, and 98 °C. The experimental solution was not specified. The experimental solution and covellite were placed in bottles that rotated on revolving rolls with a rotation speed of 5.25 rpm. Bottles were in open contact with air. The experiment at 98 °C was performed in a beaker on a hot plate.

Sullivan observed an increase in leaching rate with a decrease in particle size of covellite and an increase in temperature for the natural covellites. The highest leaching rate was observed with artificial covellite.

Thomas and Ingraham¹¹ studied the dissolution of synthetic covellite disks in acidic ferric sulfate solutions. Covellite was synthesized from metallic copper and elemental sulfur and subsequently ground, pelletized, and sintered. Disks were leached by rotating the disk in a cylindrical vessel containing either 3 or 18 L of acidic ferric sulfate solution. Rotational speeds varied between 15 and 500 rpm. Experiments were performed at temperatures ranging from 25 to 80 °C. Initial concentrations of H₂SO₄ and Fe³⁺ were 0.1 and 0.0005–0.25 M, respectively.

Thomas and Ingraham stated that leaching of CuS to sulfate instead of elemental sulfur, according to reaction 5, could have occurred.

They observed that Fe²⁺ to Cu²⁺ ratios did not exceed 2.1:1 and Cu²⁺ to elemental sulfur ratios did not exceed 1.1:1. Additionally, analysis of the turbidity of the solutions showed that 4% of the reacted covellite produced sulfate. Therefore, it was concluded that reaction 2 was the predominant leaching reaction.

The leaching rate increased with rotational speeds up to 500 rpm in 0.005 M Fe³⁺ solutions, indicating that the dissolution of CuS was controlled by mass transfer. The dissolution rate of CuS was directly proportional to the Fe³⁺ concentration in dilute solutions, that is, below 0.005 M Fe³⁺. The dissolution rate appeared to be independent of the Fe³⁺ concentration for Fe³⁺ concentrations above 0.005 M. The dissolution rate of covellite was directly proportional to the outer surface area of the disk. An increase in temperature resulted in an increase in the dissolution rate of CuS. Thomas and Ingraham concluded that the rate of dissolution of covellite at high Fe³⁺ concentrations is controlled by a chemical process at low temperatures, that is, from 25 to 60 °C, and by diffusion at higher temperatures, that is, from 60 to 80 °C. It was observed that during CuS dissolution a uniform sulfur layer was formed on the disk. To the end of an experiment, that is, approximately 18% dissolution of a disk, linear dissolution rates were obtained. Thomas and Ingraham concluded that the

sulfur layer did not provide an additional resistance toward mass transfer. The temperature dependence of the dissolution of covellite with ferric ions was determined from the maximum linear rate, that is, not the initial rate. Activation energies were determined to be 92.1 and 33.5 kJ/mol for temperature ranges of 25–60 and 60–80 °C, respectively.

Mulak¹² investigated the dissolution of synthesized, fine particles of covellite in acidic ferric solutions. Experiments were performed at temperatures ranging from 30 to 90 °C. Covellite was synthesized in a steam bath from copper powder, obtained by hydrogen-induced reduction of cupric oxalate, and sulfur solution in carbon disulfide. Covellite was grinded to produce fine particles with a diameter of 60 μm and below. The covellite consisted of 65.40 wt % copper and 34.60 wt % sulfur, that is, covellite with a molecular formula of Cu_{0.954}S. Initial concentrations of Fe³⁺ varied between 3.58 × 10^{−5} and 8.95 × 10^{−4} M. The pH varied between 0 and 1.5. The type of acid was not mentioned. The stirrer speed varied between 100 and 1000 rpm. A protective atmosphere was used to prevent oxidation by air.

Mulak observed no change in the rate of dissolution of covellite with a variation in stirrer speed. No effect of pH on the dissolution rate of CuS was measured. A first-order dependency in Fe³⁺ was observed below a Fe³⁺ concentration of 8.95 × 10^{−5} M. The CuS dissolution rate appeared to be independent of the Fe³⁺ concentration at Fe³⁺ concentrations above 8.95 × 10^{−5} M. It was determined that the sulfur formed after dissolution was in its elemental form. It was assumed that the elemental sulfur formed did not suppress the dissolution of covellite because the derivative of the grain age with time was observed to be constant for all temperatures investigated. Mulak determined the rate-controlling step to be the chemical reaction on the surface. The activation energy was determined to be 82.0 kJ/mol.

Dutrizac and MacDonald⁶ studied the dissolution of synthetic covellite disks and natural covellite in acidic ferric sulfate solutions. Synthetic covellite was prepared from copper foil with elemental sulfur in a vacuum sealed tube at an elevated temperature. The reaction product was crushed, pelletized, and sintered. The apparent density was determined to be 4210 kg/m³ (theoretical density of covellite is 4670 kg/m³). Disks were leached by rotating the disk at a given speed in an acidified ferric sulfate solution. Rotational speeds varied between 0 and 200 rpm. Experiments were performed at temperatures ranging from 25 to 95 °C. A protective atmosphere was used to prevent oxidation by air. Initial concentrations of Fe³⁺, Fe²⁺, and H₂SO₄ were 0.00025–0.3, 0–3.29, and 0.03–0.3 M, respectively. Experiments performed at low Fe³⁺ concentrations were performed with larger volumes of solution to prevent Fe³⁺ depletion during CuS dissolution.

Dutrizac and MacDonald observed no change in rate of dissolution of synthetic covellite with a variation in stirrer speed. The dissolution rate of synthetic covellite was determined to be independent of the H₂SO₄ concentration. A first-order dependency in Fe³⁺ was observed below a Fe³⁺ concentration of 0.005 M, and a zero-order dependency in Fe³⁺ was observed at Fe³⁺ concentrations above 0.005 M. The rate of dissolution of synthetic covellite decreased with increasing FeSO₄ concentration. Natural covellite dissolved at approximately the same rate and temperature dependence as the synthetic covellite. It was assumed that elemental sulfur formed did not suppress the dissolution of covellite because the dissolution rate increased with time. Dutrizac and

Table 1. Experimental Conditions Reported in Previous Studies

ref	T (K)	$d_{\text{p,CuS}}$ (m)	composition (M)			
			Fe ³⁺	H ₂ SO ₄	pH	FeSO ₄
Sullivan ^a	308.15–371.15	$d_p < 7.4 \times 10^{-5}$ and $2 \times 10^{-3} < d_p < 6.73 \times 10^{-3}$				
Thomas and Ingraham	298.15–353.15	CuS disk	5×10^{-4} to 0.25	0.1		
Mulak ^b	303.15–363.15	$d_p < 6 \times 10^{-5}$ m	3.58×10^{-5} to 8.95×10^{-4}		0–1.5	
Dutrizac and MacDonald	298.15–368.15	CuS disk	2.5×10^{-4} to 0.3	0.03–0.3		0–3.29
Broekhuis et al. ^c	$T_{\text{room}} - 423.15$	$10^{-4} < d_p < 10^{-3}$	excess	0.41 or 0.51		

^aSullivan¹⁰ did not specify the experimental solution. ^bMulak¹² did not specify the type of acid used. ^cBroekhuis et al.¹³ used an excess of ferric sulfate, that is, 10–30% more than required for stoichiometric conversion of CuS.

MacDonald determined by extraction with CS₂ that 0–6% of the sulfur was oxidized to sulfate. The yield of elemental sulfur was observed to be independent of the oxidizing potential of the leaching solution. The temperature dependence of the dissolution of covellite with ferric ions was determined from the initial rate. Dutrizac and MacDonald believed the rate-controlling step to be the chemical reaction on the surface. The activation energies of synthetic covellite and natural covellite were determined to be 74.5 and 82.0 kJ/mol, respectively.

Broekhuis et al.¹³ investigated the dissolution of CuS in acidic ferric sulfate solutions. CuS was produced in a glass autoclave by reacting CuSO₄ in an aqueous acidic sulfate solution, with a gas flow containing 7 vol % H₂S and 93 vol % N₂. The CuS formed was a black solid with small particle sizes and a hydrophobic character. Copper sulfide particles consisted of agglomerates of smaller particles with sizes in the order of 0.2×10^{-6} m, on top of structures of greater size in the order of 10×10^{-6} m. The particles were in the size range of hundreds of micrometers. Experiments were performed in a round-bottom flask and in a glass beaker inside a stainless steel pressure vessel for temperatures up to 130 and up to 150 °C, respectively. A typical experiment consisted of heating an acidic aqueous solution containing CuS, and adding a concentrated solution of ferric sulfate at the desired reaction temperature. Initial concentrations of CuS and H₂SO₄ for experiments up to 130 °C were 0.27 and 0.41 M, respectively. Initial concentrations of CuS and H₂SO₄ for experiments up to 150 °C were 0.27 and 0.51 M, respectively. An excess of ferric sulfate was used, between 10% and 30% more than required for the stoichiometric conversion of CuS.

Broekhuis et al. observed dissolution times ranging from days at room temperature to approximately 40 min at a temperature of 80 °C. A maximum conversion of 99% was obtained for the experiment performed at 80 °C. The solid residue was a green or black solid, consisting mainly of sulfur with a copper species as contaminant. Above 80 °C, but below the melting point of rhombic sulfur, conversions up to 99% were obtained after 40 min at 80 °C and after 5 min at 100 °C, respectively. The solid residue was a green, hydrophobic solid. At temperatures above the melting point of sulfur, a maximum conversion ranging from 80% to 90% was obtained.

Experimental conditions reported in previous studies are summarized in Table 1.

Orders of reaction and activation energies reported in previous studies are summarized in Table 2.

3. EXPERIMENTAL SECTION

3.1. Setup. The CuS dissolution experiments were performed in 0.5 L glass reactors with a diameter of 0.1 m. Two glass reactors were connected in series to a water saturator and immersed in a water bath. Reactors were

Table 2. Orders of Reaction Reported in Previous Studies

ref	order of reaction			
	Fe ³⁺	H ₂ SO ₄	A_{CuS}	E_A (kJ/mol)
Thomas and Ingraham	0 and 1 ^a		1	92.1 and 33.5 ^b
Mulak	0 and 1 ^c	0		82.0
Dutrizac and MacDonald	0 and 1 ^d	0	1	74.5 and 82.0 ^e

^aThomas and Ingraham¹¹ reported a first-order dependency in Fe³⁺ for Fe³⁺ concentrations below 0.005 M, and a zero-order dependency for Fe³⁺ concentrations above 0.005 M. ^bThomas and Ingraham¹¹ reported an activation energy of 92.1 kJ/mol for temperatures ranging from 25 to 60 °C and an activation energy of 33.5 kJ/mol for temperatures ranging from 60 to 80 °C. ^cMulak¹² reported a first-order dependency in Fe³⁺ for Fe³⁺ concentrations below 8.95×10^{-5} M, and a zero-order dependency for Fe³⁺ concentrations above 8.95×10^{-5} M. ^dDutrizac and MacDonald⁶ reported a first-order dependency in Fe³⁺ for Fe³⁺ concentrations below 0.005 M, and a zero-order dependency for Fe³⁺ concentrations above 0.005 M. ^eDutrizac and MacDonald⁶ reported an activation energy of 74.5 kJ/mol for synthetic covellite and an activation energy of 82.0 kJ/mol for natural covellite.

operated batchwise with regard to the liquid phase, and continuous with regard to the gas phase. Nitrogen was fed to provide a protective atmosphere. A water saturator was used to humidify the gas phase and maintain the water balance. The temperature of the water bath was regulated by a Julabo heater. Stirring was performed with a 0.03 m magnetic stirrer to ensure a homogeneously mixed solid–liquid suspension. The glass reactors contained glass baffles to promote mixing. Sampling was performed with syringes. 3.5 mL UV cuvettes were used to collect filtered samples. A Varian Cary 50 UV–vis spectrophotometer (EL98123254) was used to analyze sample compositions. Samples were stored in a refrigerator. Temperature in the reactors was monitored with Teflon-protected PT100 thermometers. A schematic drawing of the experimental setup is shown in Figure 1.

3.2. Materials. ACS reagent grade FeSO₄·7H₂O [7782-63-0], 97% and puriss p.a. grade Fe₂(SO₄)₃·xH₂O [15244-10-7], ACS reagent grade CuSO₄·5H₂O [7758-99-8], and ACS reagent grade H₂SO₄ [7664-93-9] were used as supplied from Sigma-Aldrich. Purified CuS, obtained from Vitrisol pilot absorber operations,⁹ was used in the study. Demineralized water was used.

3.3. Characterization. The particle size distribution, porosity, and density of purified CuS, obtained from a pilot Vitrisol absorber⁹ used for the removal of H₂S from biogas, were measured by Sasol Technology (particle size distribution) and Delft Solids Solutions (porosity and density). The purified CuS contained CuSO₄·5H₂O.

An Analysette 22 MicroTec plus was used to measure the particle size distribution. The particle size ranged from $1.0 \times$

Figure 1. Schematic drawing of the experimental setup.

10^{-7} to 2.2×10^{-5} m, with an average particle size of 5.8×10^{-6} m. Figure 2 shows the duplicate particle size distribution measurements. Figure 3 shows the particle size distribution curve.

The company Delft Solids Solutions was contacted to perform porosity and pore size distribution measurements by mercury porosimetry. A porosity of 92% was determined, and an incorrect skeletal density of 6700 kg/m^3 was determined. The skeletal density of CuS is 4760 kg/m^3 .¹⁴

The Belgian Ceramic Research Centre (BCRC) was contacted for a second opinion. From mercury porosimetry measurements, they determined a porosity of 83% and a skeletal density of 2670 kg/m^3 , respectively. Afterward, BCRC performed a helium pycnometry measurement to verify the skeletal density, which was determined to be 4000 kg/m^3 . Small amounts of salt, that is, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, were present in the CuS sample, which lowered the skeletal density of CuS. The density of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 2286 kg/m^3 .¹⁴

It seems plausible that the following reversible reaction could have occurred during mercury porosimetry measurements:¹⁵

Therefore, incorrect porosities might have been analyzed. Nevertheless, the porosity of the material remains significant

under the assumption that all of the CuS was converted to HgS during mercury porosimetry. The skeletal density of HgS is 7700 kg/m^3 .¹⁴ A minimum porosity of 72.5% is obtained.

$$100\% - (100\% - 83\%) \frac{7700}{4760} = 72.5\%$$

3.4. Procedures. CuS, obtained from Vitrisol pilot absorber operations,⁹ was purified by washing and vacuum filtration to remove most of the salts. Afterward, CuS was dried overnight at a temperature of 80°C and powdered. Powdered CuS was shaken to ensure a homogeneous solid is obtained. The $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ content of the purified CuS was determined via UV-vis spectrophotometry.

An amount of 400 mL of solution was prepared and added to the reactor(s). Nitrogen was supplied to the reactor(s) to prevent oxidation of Fe^{2+} with O_2 . The experimental setup was heated to the required temperature. Prior to initiation of an experiment, a liquid sample was taken. The reaction was initiated by adding CuS to the liquid. Samples were taken periodically. A filter was used to terminate the CuS dissolution reaction. Samples were stored in a refrigerator and analyzed at the end of each experiment at a temperature of 25°C . From each experiment, the overall mass balance was determined.

3.5. Analytical Techniques. Pure ferrous sulfate, ferric sulfate, and cupric sulfate solutions, in the presence of sulfuric acid, absorb light at different wavelengths. A wavelength scan from 200 to 1100 nm was performed with a UV-vis spectrophotometer on a pure acidic ferrous sulfate solution, a pure acidic ferric sulfate solution, and a pure acidic cupric sulfate solution. The scan indicated that at a wavelength of 410–430 nm, $\text{Fe}_2(\text{SO}_4)_3$ had a significant absorbance, whereas FeSO_4 and CuSO_4 had almost no absorbance. A wavelength of 420 nm was chosen to analyze Fe^{3+} concentrations. At this wavelength, the absorbance of $\text{Fe}_2(\text{SO}_4)_3$ was 140 times higher as compared to the absorbance of FeSO_4 and 475 times higher as compared to the absorbance of CuSO_4 . At a wavelength of 640 nm, CuSO_4 absorbed light more significantly as compared to FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, that is, a 35 times higher absorbance. At a wavelength of 900 nm, CuSO_4 absorbed light 7 times higher as compared to the absorbance of FeSO_4 and 76 times higher as compared to the absorbance of $\text{Fe}_2(\text{SO}_4)_3$.

Figure 2. Particle size distribution measurements of purified CuS.

Figure 3. Particle size distribution curve.

Wavelengths of 640 and 900 nm were chosen to measure Cu^{2+} concentrations.

Calibration curves were made for each experiment, depending on the starting composition and resulting time-dependent concentration profile of the experiment.

3.6. Consideration. CuS is hydrophobic in nature. However, CuS produced in the Vitrisol process is hydrophilic in character. Additionally, the density of the CuS formed in the process is lower than that of H_2O due to the porous nature of the solids. However, CuS formed in the absorber forms a (semi-) suspension with the Vitrisol liquid.

A CuS dissolution experiment was performed with CuS containing no salts after purification. The respective CuS did not form a suspension upon initiation of the experiment, but remained at the gas–liquid interface. Therefore, it can be concluded that a minimum amount of salts in the CuS pores is required to obtain a hydrophilic character. The purification procedure of CuS was optimized to ensure a homogeneous solid–liquid suspension during experimentation with CuS containing a minimum content of salts.

All experiments were carried out at a stirrer speed of 550 rpm, except for the experiment investigating the effect of stirrer speed on the dissolution of CuS .

It is assumed that salts, present in purified CuS , dissolve instantaneously and homogeneously after initiation of an experiment. Therefore, CuS conversion and Cu^{2+} concentration profiles, presented in this study, were corrected on the basis of the salt content of purified CuS .

Because of the nature of experimentation, 100% conversion of the initial CuS content cannot be achieved. Samples containing reactor liquid, that is, solution and solids, are removed from the reactor during sampling. The liquid samples are filtered to obtain UV–vis samples. If the solids in solution are homogeneously divided, sampling should not affect the conversion profile.

Sampling could be performed with a minimum time interval of 30 s (two experimenters required).

Experiments were performed at temperatures of 25, 50, and 90 °C, respectively. Initial concentrations of CuS , Fe^{3+} , and H_2SO_4 were 0.046–0.23, 0.25–0.5, and 0.1–0.9 M, respectively.

The accuracies of the PT100 thermometers are temperature dependent. At temperatures of 25, 50, and 90 °C, the accuracies are ± 0.2 , ± 0.25 , and ± 0.33 °C, respectively. The photometric and wavelength accuracies of the UV–vis spectrophotometer are ± 0.01 Abs and ± 0.5 nm, respectively.

The reproducibility of the experiments in this study is estimated to be within 5–10%.

4. MASS TRANSFER MODEL

The dissolution of CuS proceeds via a reaction of Fe^{3+} with the surface of CuS . Fe^{3+} is transferred from the liquid bulk to the external surface of the CuS particles, and, when porous, to the internal surface. Elemental sulfur is formed, and Cu^{2+} is dissolved into the liquid.

Kinetics can be obtained if the resistances to mass transfer from the liquid bulk to the external- and internal surfaces of the particle are negligible. When mass transfer limitations are negligible, the internal and external surfaces are required for an accurate determination of kinetics.

Kinetics can be obtained if both the Carberry number¹⁶ and the Weisz–Prater criterion¹⁷ are satisfied.

The Carberry number is defined as the ratio between the observed reaction rate and the maximum external mass transfer:¹⁶

$$Ca = \frac{r_{\text{obs}}}{a_{\text{p,ext}} k_{\text{LS}} [A]_{\text{b}}} = \frac{[A]_{\text{b}} - [A]_{\text{s}}}{[A]_{\text{b}}} < 0.05 \quad (7)$$

where

$$a_{\text{p,ext}} = \frac{A_{\text{p,ext}}}{V_{\text{p}}} \quad (8)$$

If the Carberry number (eq 7) is below 0.05, kinetics can be obtained.

The liquid to solid mass transfer coefficient can be estimated with the Sherwood number (for $0 < Re < 200$):^{18,19}

$$Sh = \frac{k_{LS}d}{D} = 2 + 0.6Re^{1/2}Sc^{1/3} \quad (9)$$

The Weisz–Prater criterion is defined as the ratio between the observed reaction rate and pore diffusion:¹⁷

$$\Phi_{W-P} = \frac{r_{obs}L^2}{D_{eff,L}[A]_s} \left(\frac{n+1}{2} \right) < 0.1 \quad (10)$$

with

$$D_{eff,L} = D_L \frac{\varepsilon_p}{\tau} \quad (11)$$

$$L = \frac{V_p}{A_{p,ext}} = \frac{1}{a_{p,ext}} \quad (12)$$

The tortuosity of a porous particle is always above 1; common values are $2 < \tau < 4$.

If the Weisz–Prater criterion (eq 10) is below 0.1, kinetics can be obtained.

If the Carberry number and Weisz–Prater criterion are satisfied and the CuS dissolution reaction has zero- and first-order dependencies in Fe^{3+} and CuS surface, respectively, the reaction rate of Fe^{3+} can be described by

$$r_{obs,Fe^{3+}} = -k_1''a_{s,ext} - k_1''a_{s,int}\eta \quad (13)$$

where

$$a_{s,ext} = \varepsilon_s a_{p,ext} \quad (14)$$

$$\varepsilon_s = \frac{V_s}{V_R} \quad (15)$$

and

$$a_{s,int} = \varepsilon_s a_{p,int} \quad (16)$$

$$a_{p,int} = \frac{A_{p,int}}{V_p} \quad (17)$$

The total surface of the particle is defined by

$$a_{p,T} = a_{p,int} + a_{p,ext} \quad (18)$$

The degree of utilization (η) is a measure of the utilization of the internal surface of the solid in the reaction. For a spherical particle, the degree of utilization is given by

$$\eta = \frac{1}{3\phi'^2} \left(\frac{3\phi' - \tanh 3\phi'}{\tanh 3\phi'} \right) \quad (19)$$

The Thiele modulus (ϕ') for an irreversible heterogeneous n -order reaction is defined by

$$\phi' = \delta' \sqrt{\frac{n+1}{2} \frac{k_n}{D_{eff,L}} [A]_s^{n-1}} \quad (20)$$

$$\delta' = L = \frac{V_p}{A_{p,ext}} = \frac{1}{a_{p,ext}} \quad (21)$$

If the CuS dissolution reaction is zero order in Fe^{3+} , the Thiele modulus (ϕ') is defined by

$$\phi' = \delta' \sqrt{\frac{k_1''a_{p,int}}{2D_{eff,L}[Fe^{3+}]_s}} \quad (22)$$

If the conversion of Fe^{3+} is limited by mass transfer, the conversion rate can be described by

$$J_{Fe^{3+}+a_{s,ext}} = k_{LS}a_{s,ext}([Fe^{3+}]_b - [Fe^{3+}]_s) \quad (23)$$

In a stationary situation, the local concentration of Fe^{3+} at the solid interface can be eliminated.

$$[Fe^{3+}]_s = [Fe^{3+}]_b - \frac{k_1''(a_{s,ext} + a_{s,int}\eta)}{k_{LS}a_{s,ext}} \quad (24)$$

5. RESULTS

The effect of varying parameters on the dissolution of CuS was investigated by determining CuS conversion profiles. The degree of CuS conversion was calculated from Cu^{2+} concentrations determined by UV–vis spectrophotometry, and the concentration of Cu^{2+} that could be obtained from fully dissolving the initial amount of CuS.

5.1. Effect of Stirrer Speed. The effect of stirrer speed was investigated at a temperature of 50 °C at two different stirrer speeds, that is, 100 and 550 rpm, respectively (see Figure 4).

Figure 4. CuS conversion profiles at varying stirrer speeds. Initial conditions: $T = 50$ °C, $[Fe^{3+}] = 0.25$ M, $[H_2SO_4] = 0.1$ M, $[CuS] = 0.046$ M.

From Figure 4, it can be concluded that the dissolution of CuS by ferric ions was not affected by mass transfer limitations from the liquid bulk to the external surface of the CuS particle at a temperature of 50 °C. Moreover, Figure 4 indicates that initially the CuS is reacted at a substantially higher rate, and within the experimental accuracy for conditions studied, the observed rate decreases continuously after a CuS conversion of approximately 50% is obtained.

Dutrizac and MacDonald⁶ and Mulak¹² reported that the dissolution rate of CuS was independent of the stirrer speed and disk rotation speed, respectively, as observed in this study. In dilute Fe^{3+} solutions, that is, solutions containing Fe^{3+} at a concentration of 0.005 M, Thomas and Ingraham¹¹ determined the dissolution rate of CuS to be proportional to the square root of the disk rotation speed.

5.2. Effect of Fe^{3+} . The effect of Fe^{3+} on the dissolution of CuS was investigated at two different Fe^{3+} concentrations (see Figure 5). Error bars display standard error.

Figure 5. CuS conversion profiles at varying Fe^{3+} concentrations. Initial conditions: $T = 50\text{ }^{\circ}\text{C}$, $[\text{Fe}^{3+}] = 0.25$ and 0.50 M , $[\text{H}_2\text{SO}_4] = 0.1\text{ M}$, $[\text{CuS}] = 0.053\text{ M}$.

From Figure 5, it can be concluded that the dissolution of CuS is independent of the Fe^{3+} concentration. This indicates that within the experimental accuracy for conditions studied, a zero-order dependency in Fe^{3+} is observed.

Dutrizac and MacDonald⁶ and Thomas and Ingraham¹¹ reported that the dissolution rate of CuS is directly proportional to the Fe^{3+} concentration in dilute solutions, that is, for Fe^{3+} concentrations below 0.005 M . The dissolution rate appeared to be independent of the Fe^{3+} concentration for Fe^{3+} concentrations above 0.005 M . Mulak¹² observed the dissolution rate of CuS to be approximately proportional to the Fe^{3+} concentration for concentrations below $8.95 \times 10^{-5}\text{ M}$, and independent of the Fe^{3+} concentration at concentrations above $8.95 \times 10^{-5}\text{ M}$. This is in good agreement with the present results as the Fe^{3+} concentration of 0.25 M is higher than 0.005 M .

5.3. Effect of H_2SO_4 . The effect of H_2SO_4 on the dissolution of CuS was investigated at four different H_2SO_4 concentrations (see Figure 6).

Figure 6. CuS conversion profiles at varying H_2SO_4 concentrations. Initial conditions: $T = 50\text{ }^{\circ}\text{C}$, $[\text{Fe}^{3+}] = 0.25\text{ M}$, $[\text{H}_2\text{SO}_4] = 0.1, 0.2, 0.4,$ and 0.9 M , $[\text{CuS}] = 0.055\text{ M}$.

From Figure 6, it can be concluded that the dissolution of CuS is independent of the H_2SO_4 concentration. This indicates that within the experimental accuracy for conditions studied, a zero-order dependency in H_2SO_4 is observed.

Dutrizac and MacDonald⁶ and Mulak¹² reported that the dissolution rate of CuS was independent of the H_2SO_4 concentration, as also is observed in this study.

5.4. Effect of CuS. The effect of CuS on the dissolution of CuS was investigated at two different concentrations with two experiments (see Figure 7).

Figure 7. CuS conversion profiles at varying CuS concentrations. Initial conditions: $T = 50\text{ }^{\circ}\text{C}$, $[\text{Fe}^{3+}] = 0.25\text{ M}$, $[\text{H}_2\text{SO}_4] = 0.1\text{ M}$, $[\text{CuS}] = 0.084$ and 0.23 M .

It should be mentioned that two Fe^{3+} ions are required to convert one CuS molecule (reaction 2); therefore, the experiment performed with 0.23 M of CuS could not become fully converted in the respective CuS dissolution experiment, as 0.25 M Fe^{3+} was present initially. Figure 7 shows a secondary axis with the conversion of Fe^{3+} , to demonstrate the extent of conversion of Fe^{3+} in the respective experiment.

From Figure 7, it can be concluded that the dissolution rate of CuS increases with the initial concentration of CuS. This agrees well with the fact that a higher concentration of CuS equals an increased amount of solid particles and therefore in more surface readily available for dissolution. Moreover, in the experiment performed with an excess of CuS, nearly all of the Fe^{3+} available is converted.

It was not possible to obtain more data points in the initial part of the concentration profiles to be able to accurately determine the CuS conversion rates. Therefore, it proved difficult to determine the order in CuS from the concentration profiles.

5.5. Extent of CuS Conversion. CuS dissolution experiments were performed with extended reaction times at varying temperatures to determine the maximal attainable CuS conversion (see Figure 8).

It should be mentioned that initial H_2SO_4 concentrations were not constant in all experiments. An initial H_2SO_4 concentration of 0.1 M was used in the experiments performed at temperatures of 25 and $90\text{ }^{\circ}\text{C}$, and an initial H_2SO_4 concentration of 0.9 M was used in the experiment performed at a temperature of $50\text{ }^{\circ}\text{C}$, respectively. Because a zero-order dependency in H_2SO_4 was observed, the difference in initial H_2SO_4 concentration did not affect the dissolution rate of CuS.

From Figure 8, it could be concluded that, within the experimental accuracy of conditions studied, all experiments obtained full conversion of CuS, independent of temperature. The solids obtained after experimentation were fine particles with a green/gray color, which agrees reasonably with the observation by Broekhuis et al.;¹³ below temperatures of $80\text{ }^{\circ}\text{C}$, green or black solids were obtained, and between temperatures of 80 and $112.8\text{ }^{\circ}\text{C}$, green hydrophobic solids were obtained.

Figure 8. CuS conversion profiles at varying CuS concentrations. Initial conditions: $T = 25, 50$, and $90\text{ }^{\circ}\text{C}$, $[\text{Fe}^{3+}] = 0.25\text{ M}$, $[\text{H}_2\text{SO}_4] = 0.1$ and 0.9 M , $[\text{CuS}] = 0.053$ and 0.055 M .

It must be mentioned that Broekhuis et al.¹³ only reported the CuS conversion profile of one CuS dissolution experiment at $80\text{ }^{\circ}\text{C}$ (their Figure 9). The reaction times of the performed experiments were not clarified. Conversions of CuS of 95–99% were reported for temperatures between 80 and $112.8\text{ }^{\circ}\text{C}$. The solids, consisting mainly of sulfur, were determined to be contaminated with a copper species. Therefore, the possibility exists that full conversion of CuS was not obtained, but that the dissolution of CuS was near-complete.

From Figures 4 to 8, it can be concluded that the nature of sampling is such that data points with low CuS conversions cannot be obtained; CuS conversions are approximately 20% or higher for the first data point in this study.

5.6. Sulfur Recovery. The dissolution of CuS can proceed according to reactions 2 and 5. As explained by Dutrizac and MacDonald,⁶ according to the Gibbs free energies of reactions 2 and 5, it can be concluded that the reaction of CuS to sulfate is favorable, that is, reaction 5. However, Thomas and Ingraham¹¹ and Dutrizac and MacDonald⁶ observed that 4% and 0–6% of the CuS oxidized to sulfate, respectively. The remainder of the CuS oxidized to elemental sulfur. Mulak¹² observed 100% formation of elemental sulfur, and no sulfate was formed.

In this study, the sulfur content was determined gravimetrically via extraction with *o*-xylene. Because solids were removed from the reactor during sampling, not all of the solids were present in the reactor at the end of an experiment. Not accounting for any losses of solids in the samples taken for analytical purposes, 91% of the CuS oxidized to elemental sulfur. On the basis of the assumptions that solids were homogeneously divided in solution, and all of the CuS oxidized to elemental sulfur and not to sulfate, 99% of the sulfur was recovered when losses of CuS and sulfur via the samples were accounted for. It was determined that sulfur was only present in the solids; no sulfur was dissolved in the liquid phase.

The Fe^{2+} to Cu^{2+} molar ratio varied between 2.0:1 and 2.3:1. Thomas and Ingraham¹¹ reported that Fe^{2+} to Cu^{2+} molar ratios did not exceed 2.1:1. Dutrizac and MacDonald⁶ reported that Fe^{2+} to Cu^{2+} molar ratios ranged from 2.07 to 2.53. Mulak¹² reported a Fe^{2+} to Cu^{2+} ratio of 2:1.

It can be concluded that between 91% and 99% of the CuS oxidized to elemental sulfur, and that the oxidation of CuS to sulfate only occurred to a minor extent. It is recommended to investigate the dissolution of CuS with Fe^{3+} continuously to clarify the extent of the oxidation of CuS to sulfate.

5.7. Effect of Purification. The effect of CuS purification on the dissolution of CuS was investigated for purified CuS and untreated CuS slurry (see Figure 9). Error bars display standard error. The CuS was obtained from Vitrisol pilot absorber operations.⁹

Figure 9. CuS conversion profiles for purified CuS and CuS slurry.

The compositions of purified CuS and untreated CuS slurry are given in Table 3.

Table 3. CuS Properties

exp	CuS type	CuS (wt %)	CuSO_4 (wt %)	H_2O (wt %)
12	purified	53.1	30.0	16.9
21	untreated slurry	18.0	16.1	65.9

The experimental settings are provided in Table 4.

Table 4. Experimental Settings of Experiments in Figure 9

exp	T ($^{\circ}\text{C}$)	$[\text{Fe}^{3+}]$	$[\text{H}_2\text{SO}_4]$	$[\text{CuS}]$
12	50	0.25	0.10	0.053
21	50	0.24	0.10	0.055

From Figure 9, it can be concluded that, within the experimental accuracy of conditions studied, the purification of CuS did not significantly influence the dissolution of CuS as compared to untreated CuS.

5.8. Effect of Temperature. The effect of temperature on the dissolution of CuS was investigated at three different temperatures (see Figure 10). The experimental settings are provided in Table 5.

From Figure 10, it can be concluded that the rate of CuS dissolution increases with temperature.

Initially the internal and external CuS surfaces are unaffected by the dissolution reaction. When the degree of utilization of CuS is assumed to be equal at varying temperatures, the kinetic expression (eq 13) can be rewritten as

$$r_{\text{obs,Cu}^{2+}} = -\frac{1}{2}r_{\text{obs,Fe}^{3+}} = 0.5k_1''a_{\text{s,ext}} + 0.5k_1''a_{\text{s,int}}\eta \approx k_1[\text{CuS}] \quad (25)$$

By fitting data points via a polynomial equation, the initial reaction rate can be derived from the slope at $t = 0$ (calculated from the derivative of the smoothed polynomial fit). From the polynomial equations derived from fitting the data points in

Figure 10. Cu^{2+} concentration profiles at varying temperatures.

Table 5. Experimental Settings of Experiments in Figure 10

exp	T (°C)	$[\text{Fe}^{3+}]$	$[\text{H}_2\text{SO}_4]$	$[\text{CuS}]$
19	25	0.25	0.10	0.055
12	50	0.25	0.10	0.053
17	90	0.25	0.10	0.055

Figure 10, the temperature dependence of the CuS dissolution conversion can be determined.

Table 6 summarizes the reaction rate constants determined by curve fitting Cu^{2+} concentration profiles.

Table 6. Reaction Rate Constants at Varying Temperatures

T (°C)	$r_{\text{obs,Cu}^{2+}}$ ($\text{kmol m}^{-3} \text{s}^{-1}$)	$[\text{CuS}]$	k_1 (s^{-1})
25	2.31×10^{-4}	0.055	4.17×10^{-3}
50	6.23×10^{-4}	0.053	11.7×10^{-3}
90	1.16×10^{-3}	0.055	21.1×10^{-3}

By using the Arrhenius equation, the temperature dependence of the reaction rate constant was determined:

$$k_1 = A \exp \left\{ -\frac{E_A}{RT} \right\} \quad (26)$$

A linear curve fit of $\ln(k_1)$ versus T^{-1} resulted in E_A and A (see Figure 11).

This resulted in a value of the activation energy of $E_A = 22.0$ kJ/mol.

Figure 11. $\ln(k_1)$ versus T^{-1} .

$$k_1 = 34.3 \exp \left\{ -\frac{22.0 \times 10^3}{RT} \right\} \quad (27)$$

5.9. Mass Transfer Calculations. From the present study, it was concluded that initially the CuS dissolution rate is the fastest and an increase in temperature results in an increase in dissolution rate. Moreover, the CuS solid surface is unaffected initially from the dissolution reaction. Therefore, the initial CuS dissolution rate for an experiment performed at the highest temperature should be evaluated for diffusion effects.

The geometry of the CuS particle is unknown. In this case, it is assumed that the CuS particles are ideally spherical and uniform in size. A dissolution experiment at a temperature of 90 °C, that is, experiment 17, was analyzed for diffusion effects. Experimental settings are provided in Table 7.

Table 7. Experimental Conditions

	exp 17
T (°C)	90
ω (rpm)	550
$[\text{Fe}^{3+}]$ (M)	0.25
$[\text{H}_2\text{SO}_4]$ (M)	0.10
$[\text{CuS}]$ (M)	0.055
ϵ_p	0.93
$r_{\text{obs,Fe}^{3+}}$ ($\text{kmol m}^{-3} \text{s}^{-1}$)	-2.32×10^{-3}

The assumed geometry and size of the CuS particles are presented in Table 8.

Table 8. Assumed Geometry and Size of CuS Particles

d_p (m)	5.83×10^{-6}
L (m^3/m^2)	9.72×10^{-7}
$a_{p,\text{ext}}$ (m^2/m^3)	1.03×10^6

Table 9 gives the estimated values of the mass transfer parameters. A conservative assumption for the Sherwood number was made on the basis of eq 9.

Table 9. Estimated Mass Transfer Parameters

D_L (m^2/s)	1.00×10^{-9}
Re	5.5
Sh	2
$k_{L,S}$ (m/s)	3.43×10^{-4}
τ	4
$D_{L,\text{eff}}$ (m^2/s)	2.31×10^{-10}

Table 10 shows the values of the Carberry number and Weisz–Prater criterion.

It can be concluded that the dissolution of CuS was not limited by external and internal mass transfer initially. Therefore, it is not required to go into more detail regarding the Sherwood number. Equations 13 and 25 can be used to describe the initial rate of dissolution of CuS. However, the kinetic rate constant k_1 cannot be determined, because the

Table 10. Carberry Number and Weisz–Prater Criterion

Ca	0.0018
$[\text{Fe}^{3+}]_s$ (M)	0.24994
Φ_{W-P}	0.00128

surface of the CuS particle is not known. On the basis of some assumptions, the total surface of the CuS particle can be estimated:

(1) The temperature dependence of the zero-order kinetic rate constant by Dutrizac and MacDonald⁶ can be applied (their eq 2), (2) the CuS particles are uniform in geometry, and (3) the CuS particles are uniform in size.

Table 11 presents the value of the total and internal surfaces of the CuS particle. The internal surface $a_{p,T}$ was iterated between the Thiele modulus (eq 22) and eq 13.

Table 11. Total and Internal Surfaces of the CuS Particle

$k''_{\text{Cu}^{2+}}$ (mol m ⁻² s ⁻¹)	3.33×10^{-5}
$k''_{\text{Fe}^{3+}}$ (mol m ⁻² s ⁻¹)	6.67×10^{-5}
ϕ'	0.0268
η	1
$a_{p,\text{int}}$ (m ² /m ³)	1.31×10^6
$a_{p,T}$ (m ² /m ³)	2.34×10^6

6. DISCUSSION

6.1. Previous Studies. Thomas and Ingraham¹¹ observed an increase in CuS dissolution rate to a maximum linear rate during the leaching of polished CuS disks. They determined kinetics from the maximum linear rate. However, during CuS dissolution pitting occurs, which affects the CuS solid surface. At the start of an experiment, the solid surface is unaffected; therefore, they should have used initial rates instead of the linear maximum rate to determine correct dissolution rates.

Thomas and Ingraham¹¹ stated that the CuS dissolution rate is proportional to the Fe³⁺ concentrations at Fe³⁺ concentrations below 0.005 M. At Fe³⁺ concentrations above 0.005 M, the dissolution rate was determined to be independent of the Fe³⁺ concentration. However, at Fe³⁺ concentrations of 0.005, 0.010, 0.10, and 0.25 M, the dissolution rate was determined to be 5.20×10^{-5} , 5.16×10^{-5} , 6.08×10^{-5} , and 5.94×10^{-5} mol m⁻² s⁻¹, respectively. Because there is a difference in dissolution rate between Fe³⁺ concentrations of 0.005–0.010 and 0.10–0.25 M, it cannot be concluded that there is a zero-order dependency in Fe³⁺ above a Fe³⁺ concentration of 0.005 M. Moreover, the dissolution rates were incorrectly determined.

Mulak¹² investigated the temperature effect of the dissolution of CuS in solutions containing a concentration of Fe³⁺ ions of 0.02 g/L. The results were presented in their Figure 2. However, the description of their Figure 2 states that the dissolution of CuS was studied for solutions containing a Fe₂(SO₄)₃ concentration of 0.01 M, that is, a Fe³⁺ concentration of 0.02 M. This description does not agree with the Fe³⁺ concentration reported to be 0.02 g/L, which is equal to a molarity of 3.58×10^{-4} M.

Mulak reported the mass of CuS used in the experiments to be 1 g; however, the volume of the experimental solution was not provided. If it is assumed that the concentration of CuS was 1 g/L, a CuS molarity of 0.0105 M would be obtained. To be able to reach a CuS conversion of 70% as given in their Figure 2, a Fe³⁺ concentration of at least 0.0147 M is required (according to reaction 2). On the contrary, to reach a conversion of 70% with a solution containing Fe³⁺ with a concentration of 3.58×10^{-4} M, at least 40.2 L of solution is required.

Therefore, it seems likely that a Fe³⁺ concentration of 0.02 M was used in the experiments to determine the effect of temperature. Moreover, if Mulak reported the concentration in this incorrect manner, it could be concluded that the CuS dissolution rate is not proportional with the Fe³⁺ concentration below 0.005 g/L, but with a Fe³⁺ concentration below 0.005 M (and independent of the Fe³⁺ concentration above 0.005 M). This would agree well with the observation by Thomas and Ingraham¹¹ and Dutrizac and MacDonald,⁶ that the CuS dissolution rate is proportional with the Fe³⁺ concentration below 0.005 M and independent of Fe³⁺ at concentrations above 0.005 M.

Broekhuis et al.¹³ determined that CuS, formed during the absorption of H₂S in an aqueous, acidic CuSO₄ solution, consisted of black solids with a small particle size and a hydrophobic character. In this study, it was observed that CuS, formed during the absorption of H₂S in an aqueous, acidic CuSO₄ solution, was hydrophilic of character, because it formed a homogeneous suspension in the aqueous, acidic Fe³⁺ solution used for dissolution experiments. This characteristic could be attributed to salts like CuSO₄·5H₂O present in the CuS after purification. Dry CuS, purified to such an extent that no salts were present in the CuS anymore, became hydrophobic of character and did not form a suspension with the Fe³⁺ solution. Instead, the particles remained floating on the gas–liquid interface.

Broekhuis et al. did not explain whether the CuS was purified and/or dried before experimentation. If metal sulfate slurries were obtained, as stated by them, the CuS should have been hydrophilic of character, and therefore Cu²⁺ from salts present in CuS would have been introduced into the solution. It does not seem likely that Broekhuis et al. accounted for this effect. Therefore, the true degree of CuS conversion determined via atomic absorption spectroscopy (AAS) remains debatable.

6.2. This Study. In the present study, it was determined that, for experimental conditions studied, the CuS dissolution was independent of both the Fe³⁺ and the H₂SO₄ concentrations. These observations agree well with the zero-order dependency in H₂SO₄ reported by Dutrizac and MacDonald⁶ and Mulak¹² and the zero-order dependency in Fe³⁺ reported by Thomas and Ingraham,¹¹ Mulak,¹² and Dutrizac and MacDonald⁶ for Fe³⁺ concentrations above 0.005 M.

From CuS dissolution experiments performed with extended reaction times, it could be concluded that full conversion of CuS could be attained for temperatures ranging from 25 to 90 °C; therefore, sulfur, formed on the CuS during dissolution, was porous and did not form a protective layer. This was also observed by Thomas and Ingraham,¹¹ Mulak,¹² Dutrizac and MacDonald,⁶ and Broekhuis et al.¹³ Thomas and Ingraham¹¹ and Dutrizac and MacDonald⁶ noticed time-accelerating kinetics, and Mulak¹² found that the derivative of the grain age with time was constant for all temperatures investigated. They concluded that the accumulating layer of elemental sulfur on the CuS disk during dissolution did not affect the rate of dissolution of CuS. Broekhuis et al.¹³ reported conversions of CuS of 95–99% for temperatures between 80 and 112.8 °C.

The porous nature of the sulfur layer formed during dissolution of CuS could be related to changes in geometry of the particle surface. Copper atoms are larger in size than sulfur atoms; as copper dissolves from CuS, the remaining

particle layer will become more porous (below the melting point of sulfur).

The remaining solids obtained from experiments with maximum CuS conversion were fine particles with a green/gray color, which is in agreement with Broekhuis et al.¹³ From sulfur recovery experiments, it was concluded that between 91% and 99% of the sulfur formed could be recovered. From $\text{Fe}^{2+}:\text{Cu}^{2+}$ ratios ranging between 2.0 and 2.3, it was concluded that in some experiments part of the CuS oxidized to sulfate instead of sulfur. This observation is in agreement with Thomas and Ingraham¹¹ and Dutrizac and MacDonald.⁶ Thomas and Ingraham¹¹ reported that Fe^{2+} to Cu^{2+} molar ratios did not exceed 2.1:1. Dutrizac and MacDonald⁶ reported that Fe^{2+} to Cu^{2+} molar ratios ranged from 2.07 to 2.53. Mulak¹² reported a Fe^{2+} to Cu^{2+} ratio of 2:1. The true extent of CuS oxidation to sulfate needs to be determined in a continuous process.

Moreover, the description of the solids by Broekhuis et al.¹³ that remained after CuS dissolution experiments agrees reasonably with the present observations. They reported that below temperatures of 80 °C, green or black solids remained in solution. Between temperatures of 80 and 112.8 °C, green hydrophobic solids were obtained. In the present study, only green/gray solids were obtained in experiments with a high degree of CuS conversion.

It should be noted that the use of the Carberry number and the Weisz–Prater criterion may lead to erroneous interpretations. The Carberry number and Weisz–Prater criterion (eqs 7 and 10, respectively) state that below a specific number, the extraparticle and intraparticle mass transfer resistances, respectively, are considered to be negligible. Although both of the equations are valid, the observed conversion rate in an experiment is not necessarily a kinetically determined rate. For instance, if the observed reaction rate is diffusion-controlled, the Carberry number and the Weisz–Prater criterion will result in lower values as compared to those calculated with the true kinetic rate and could therefore indicate that the observed reaction rate was not controlled by diffusion.

Therefore, it cannot be concluded that the initial dissolution rate of experiment 17, evaluated in *Mass Transfer Calculations*, was not affected by mass transfer limitations.

In the present study, it was not possible to obtain data points at conversions lower than 20%, which generally is required for a kinetic study. Besides, the degree of utilization of the internal CuS surfaces was assumed to be equal at varying temperatures (see eq 25). Moreover, it could not be concluded that the dissolution rate of CuS was not affected by mass transfer limitations from the use of the Carberry number and the Weisz–Prater criterion. Additionally, experiments were carried out at a temperature of 50 °C to check the presence of external mass transfer limitations. It was observed that a variation of the stirrer speed from 100 to 550 rpm did not affect the concentration profile as a function of time (see Figure 4). This, however, was not checked at a temperature of 90 °C. Therefore, the temperature dependence derived in this study over the temperature range of 25–90 °C must be regarded as an approximation of the temperature dependence of the CuS dissolution rate.

The activation energy of $E_A = 22.0$ kJ/mol derived in this study is lower than activation energies reported in previous studies.^{6,11,12} It seems plausible that the dissolution reaction in this study was controlled by diffusion.

Because it seems plausible that the dissolution reaction was diffusion-controlled, the derived specific internal and external surfaces in *Mass Transfer Calculations* are minimum values (the degree of utilization is likely to be below 1).

7. CONCLUSION

The dissolution of CuS particles with Fe^{3+} in acidic sulfate solutions was investigated in an oxygen-free environment. CuS particles, used in this study, were obtained from H_2S removal operations from biogas with an acidic CuSO_4 solution in a Vitrisol pilot absorber. The CuS particles formed in the Vitrisol process were porous with an average diameter of 5.8×10^{-6} m.

The effects of Fe^{3+} , H_2SO_4 , and temperature on the conversion rate of CuS were determined. Zero orders of reaction for both Fe^{3+} and H_2SO_4 were determined. Solid sulfur was formed on the CuS particles during dissolution. It seems plausible that full conversion of CuS could be obtained independent of temperature. Therefore, it can be concluded that the sulfur layer, formed on the CuS surface during dissolution, was porous. Accounting for losses in sulfur because of sampling, up to approximately 99% of the sulfur could be recovered after experimentation. The Fe^{2+} to Cu^{2+} molar ratio varied between 2.0:1 and 2.3:1; therefore, the oxidation of CuS to sulfate proceeded to a minor extent. It is recommended to investigate the dissolution of CuS with Fe^{3+} continuously to clarify the extent of the oxidation of CuS to sulfate.

The activation energy was determined to be $E_A = 22.0$ kJ/mol. It seems plausible that the CuS dissolution reaction was affected by diffusion.

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Notes

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NOMENCLATURE

- A = surface [m^2]
- A = pre-exponential factor
- a = specific surface [m^2/m^3]
- Ca = Carberry number [–]
- D = diffusion coefficient [m^2/s]
- d = diameter [m]
- ε = porosity [–]
- E_A = activation energy [kJ/mol]
- η = effectiveness factor [–]
- k_1 = reaction rate constant [1/s]
- k_1'' = reaction rate constant [$\text{mol m}^{-2} \text{s}^{-1}$]
- k = mass transfer coefficient [m/s]
- L, δ' = characteristic particle size [m]
- n = order of reaction [–]

R = universal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]

r = reaction rate [$\text{kmol m}^{-3} \text{s}^{-1}$]

Re = Reynolds number $[-]$

Sc = Schmidt number $[-]$

Sh = Sherwood number $[-]$

T = temperature [$^{\circ}\text{C}$, K]

ϕ' = Thiele modulus $[-]$

t = time [s]

τ = tortuosity $[-]$

V = volume [m^3]

Φ_{W-P} = Weisz–Prater criterion $[-]$

ω = stirrer speed [rpm]

Subscripts and Superscripts

b bulk

eff effective

ext external

int internal

L liquid

LS liquid to solid

obs observed

P particle

s solid

T total

Cu^{2+} cupric ion

CuS covellite

Fe^{3+} ferric ion

(12) Mulak, W. Kinetics of dissolving polydispersed covellite in acidic solutions of ferric sulphate. *Roczniki Chemii Ann. Soc. Chim. Polonorum* **1971**, *45*, 1417–1424.

(13) Broekhuis, R. R.; Koch, D. J.; Lynn, S. A medium-temperature process for removal of hydrogen sulfide from sour gas streams with aqueous metal sulfate solutions. *Ind. Eng. Chem. Res.* **1992**, *31* (12), 2635–2642.

(14) *CRC Handbook of Chemistry and Physics*, 87th ed.; Lide, D. R., Ed.; Taylor and Francis Group: Boca Raton, FL, 2007.

(15) Yan, T. Y. Mercury removal from oil by reactive adsorption. *Ind. Eng. Chem. Res.* **1996**, *35* (10), 3697–3701.

(16) Carberry, J. J. Physical-chemical aspects of mass and heat transfer in heterogeneous catalysis. In *Catalysis, Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer Verlag: Berlin, 1987; Vol. 8, pp 131–171.

(17) Weisz, P. B.; Prater, C. D. Interpretation of measurements in experimental catalysis. *Adv. Catal.* **1954**, *6*, 143–196.

(18) Ranz, W. E.; Marshall, W. R., Jr. Evaporation from drops. Part I. *Chem. Eng. Prog.* **1952**, *48*, 141–146.

(19) Ranz, W. E.; Marshall, W. R., Jr. Evaporation from drops. Part II. *Chem. Eng. Prog.* **1952**, *48*, 173–180.

REFERENCES

(1) Versteeg, G. F.; Ter Maat, H. Method and system for selective removal of contamination from gas flows. WO patent 1998055209 A1, June 2, 1997.

(2) Ter Maat, H.; Hogendoorn, J. A.; Versteeg, G. F. The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent. Part I. The absorption of hydrogen sulfide in metal sulfate solutions. *Sep. Purif. Technol.* **2005**, *43*, 183–197.

(3) Ter Maat, H.; Al-Tarazi, M.; Hogendoorn, J. A.; Niederer, J. P. M.; Versteeg, G. F. Theoretical and experimental study of the absorption rate of H_2S in CuSO_4 solutions. The effect of enhancement of mass transfer by a precipitation reaction. *Chem. Eng. Res. Des.* **2007**, *85* (1), 100–108.

(4) Wermink, W. N.; Versteeg, G. F. The oxidation of Fe(II) in acidic sulphate solutions with air at elevated pressures. Part 1. Kinetics above 1 M H_2SO_4 . *Ind. Eng. Chem. Res.* **2017**, *56* (14), 3775–3788.

(5) Peacey, J.; Guo, X.-J.; Robles, E. Copper hydrometallurgy – current status, preliminary economics, future direction and positioning versus smelting. *Trans. Nonferrous Met. Soc. China* **2004**, *14*, 560–568.

(6) Dutrizac, J. E.; MacDonald, R. J. C. The kinetics of dissolution of covellite in acidified ferric sulphate solutions. *Can. Metall. Q.* **1974**, *13* (3), 423–433.

(7) Wermink, W. N.; Versteeg, G. F. The oxidation of Fe(II) in acidic sulphate solutions with air at elevated pressures. Part 2. Influence of H_2SO_4 and Fe(III) . *Ind. Eng. Chem. Res.* **2017**, *56* (14), 3789–3796.

(8) Wermink, W. N.; Spinu, D.; Versteeg, G. F. The oxidation of Fe(II) with Cu(II) in acidic sulphate solutions at elevated pressures. *Chem. Eng. Commun.*, in press.

(9) Ter Maat, H.; Versteeg, G. F.; Vergunst, F. Sour Oil & Gas Advanced Technology 2012. *Proceedings of the 8th International Conference*; Abu Dhabi, UAE, March 27–28, 2012.

(10) Sullivan, J. D. Chemical and physical features of copper leaching. *Trans. Am. Inst. Min. Metall. Eng.* **1933**, *106*, 515–546.

(11) Thomas, G.; Ingraham, T. R. Kinetics of dissolution of synthetic covellite in aqueous acidic ferric sulphate solutions. *Can. Metall. Q.* **1967**, *6* (2), 153–165.