

## THEORETICAL AND EXPERIMENTAL STUDY OF THE ABSORPTION RATE OF H<sub>2</sub>S IN CuSO<sub>4</sub> SOLUTIONS: THE EFFECT OF ENHANCEMENT OF MASS TRANSFER BY A PRECIPITATION REACTION

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In this paper the desulfurization of gas streams using aqueous copper sulfate (CuSO<sub>4</sub>) solutions as washing liquor is studied theoretically and experimentally. The desulfurization is accomplished by a precipitation reaction that occurs when sulfide ions and metal ions are brought into contact with each other. The absorption experiments of H<sub>2</sub>S in aqueous CuSO<sub>4</sub> solutions were carried out in a Mechanically Agitated Gas Liquid Reactor. The experiments were conducted at a temperature of 293 K and CuSO<sub>4</sub> concentrations between 0.01 and 0.1 M. These experiments showed that the process efficiently removes H<sub>2</sub>S. Furthermore the experiments indicate that the absorption of H<sub>2</sub>S in a CuSO<sub>4</sub> solution may be considered a mass transfer limited process at, for this type of industrial process, relevant conditions. The extended model developed by Al-Tarazi *et al.* (2004) has been used to predict the rate of H<sub>2</sub>S absorption. This model describes the absorption and accompanying precipitation process in terms of among others elementary reaction steps, particle nucleation and growth. The results from this extended model were compared to results obtained with a much simpler model, regarding the absorption of H<sub>2</sub>S in CuSO<sub>4</sub> containing aqueous solutions as absorption of a gas accompanied by an instantaneous irreversible reaction. From this comparison it appeared that the absorption rate of H<sub>2</sub>S in a CuSO<sub>4</sub> solution can, under certain conditions, be considered as a mass transfer rate controlled process. Under a much wider range of conditions the error that is made by assuming that the absorption process is a mass transfer controlled process, is still within engineering accuracy. This simplification allows for a considerable reduction of the theoretical effort needed for the design of a G/L contacting device. Furthermore, the simulations also indicated that the absorbent composition can be further optimized by the addition of a buffering solution (i.e., if the pH of the absorbent is controlled). A comparison of the experimental results and the simulated results showed that the extended model gives an under prediction of the H<sub>2</sub>S absorption rate for the experimental conditions applied.

### INTRODUCTION

Gas-liquid processes are commonly employed in the chemical industry. In the case of removal of H<sub>2</sub>S from a gas stream, the scrubbing solution may contain dissolved basic reagents (alkanolamines or NaOH), oxidizing chemicals (Fe<sup>3+</sup> ligands) or solids forming components (mostly Me<sup>2+</sup> ions). For a more complete overview of the existing

technologies we would like to refer to the textbook by Kohl and Nielsen (1997). When the absorbed gaseous component reacts in the liquid, it is possible that the rate of absorption of the gaseous component is enhanced by the chemical reaction. Understanding how the reaction rate influences the gas absorption rate is therefore a vital prerequisite for the design of an efficient contactor. For simple irreversible reactions this effect can readily be estimated using analytical or approximate solutions of various mass transfer models (See e.g. Westerterp *et al.* (1984)). For other cases (e.g. complex or equilibrium reactions) the effect of the reaction rate on the gas absorption rate cannot be determined analytically, making a numerical approach necessary. For the case of  $\text{H}_2\text{S}$  absorption in, and reaction with, a metal sulfate containing solution, the rate at which  $\text{H}_2\text{S}$  absorbs in the solution is the result of a number of process steps involving absorption and reaction. The reaction rate at which  $\text{H}_2\text{S}$  and metal ions react to form solid metal sulfide is determined by two processes; first, the formation of new metal sulfide nuclei and second, the growth of existing precipitates. All process steps need to be taken into account to yield an accurate description of the  $\text{H}_2\text{S}$  absorption rate. Unfortunately, the rate of formation of new precipitate particles is a highly non-linear function of the concentration of the reacting components (Nielsen (1964), Söhnel and Garside (1992)). Furthermore, the rate of growth of existing particles is the result of a number of process steps (like diffusion of reacting components to the precipitate surface and the rate at which the ions are incorporated in the crystal), all of which can be rate-limiting. Clearly an accurate model incorporating all absorption and reaction steps is required to describe the rate of absorption of  $\text{H}_2\text{S}$  in a metal salt solution. Such a model has been developed by Al-Tarazi *et al.* (2004). This extensive model was originally developed as a tool for the design of contactors for the removal of heavy metal salts from a liquid stream using  $\text{H}_2\text{S}$ , but can also be used as a tool for the design of contactors for the removal of  $\text{H}_2\text{S}$  from a gas stream using metal salt solutions. However, experimental results (e.g. ter Maat (2005)) seem to indicate that, for many operating conditions, the absorption of  $\text{H}_2\text{S}$  into a  $\text{CuSO}_4$  solution can be described with a very simple model that considers the absorption of  $\text{H}_2\text{S}$  in a  $\text{CuSO}_4$  solution to be a process of mass transfer accompanied by an instantaneous irreversible reaction, or even as gas phase mass transfer limited absorption process. In this contribution the results of this simplified approach will be compared with the results of the rigorous model of Al-Tarazi *et al.* (2004), and the applicability of this simplified approach will be discussed. Furthermore, experimental results are also compared to the model prediction.

## LITERATURE

The use of  $\text{H}_2\text{S}$  for the (selective) precipitation of valuable metal compounds from leaching solutions has been known to the ore refining industry for a long time (for a review see Kroschwitz and Howe-Grant, 1991). Thus far, only limited fundamental research on the phenomenon of absorption of  $\text{H}_2\text{S}$  in a solution, accompanied by a precipitation reaction of a highly insoluble metal sulfide, has been performed. The work of Mishra and Kapoor (1978) can be regarded as a pioneering attempt to couple the concept of absorption of a gas

in a reactive liquid and the theory of precipitation dynamics. They investigated the precipitation of cadmium(II) sulfide from a cadmium(II) chloride solution in a bubble column reactor. The absorption of  $\text{H}_2\text{S}$  in a diluted cadmium chloride solution could, according to their own conclusions, be described by assuming that the absorption of  $\text{H}_2\text{S}$  into the solution was accompanied by an instantaneous irreversible reaction between  $\text{H}_2\text{S}$  and the metal ion. The mass transfer model used in their study was based on the Higbie penetration model (Higbie, 1935). It must be noted however that the cadmium chloride concentration applied was so low, that the influence of the reaction of the absorption rate was rather small, and therefore that the accuracy of their findings might be debatable. The absorption of  $\text{H}_2\text{S}$  into a diluted copper sulfate solution was investigated by Oktaybas *et al.* (1994), who used an experimental setup identical to the one used by Mishra and Kapoor (1978). Oktaybas *et al.* also used the Higbie penetration model and the assumption of an irreversible instantaneous reaction between  $\text{H}_2\text{S}$  and  $\text{Cu}^{2+}$  to explain the results. However, their model description did not explain the observed dependency of the reaction rate on the pH, observed at pH values below 2. It is likely that a change in one of the parameters, which were assumed to be constant (e.g. changes in the diffusion coefficient of  $\text{H}_2\text{S}$  or the bubble rising velocity), or the rate of precipitation, was, at least partially, responsible for the observed change in the absorption rate. Broekhuis *et al.* (1992) investigated the removal of dilute  $\text{H}_2\text{S}$  from a gas stream using copper and zinc sulfate solutions in a stirred cell reactor. Here, the rate of absorption of  $\text{H}_2\text{S}$  in a copper sulfate solution was found to be gas phase mass transfer limited, while the absorption rate of  $\text{H}_2\text{S}$  into a zinc sulfate solution was found to be a function of the amount of unconverted zinc sulfate. They did not attempt to present a fundamental description of the simultaneous absorption and precipitation of  $\text{H}_2\text{S}$  in metal sulfate solutions. Ter Maat *et al.* (2005) investigated the removal of dilute  $\text{H}_2\text{S}$  from a gas stream using copper, zinc and iron sulfate solutions in a bubble column reactor. The  $\text{CuSO}_4$  solution was shown to be the most suitable solution for  $\text{H}_2\text{S}$  removal. The laboratory experiments indicated that the absorption of  $\text{H}_2\text{S}$  in a  $\text{CuSO}_4$  solution, at the experimental conditions tested, is a gas phase mass transfer limited process. In the same study the applicability of a  $\text{CuSO}_4$  solution for the removal of  $\text{H}_2\text{S}$  from a biogas stream was demonstrated on a pilot plant scale. The use of metal salt solutions for desulfurization has further been mentioned in open literature (Manning, 1979, Brown, 1980), and in the patents of Spevack (1980) and Harvey (1980), but no fundamental model description of the absorption of  $\text{H}_2\text{S}$  into a metal salt solution, accompanied by a precipitation reaction, was presented. Such a fundamental model, which will also be used in this study describing the absorption of  $\text{H}_2\text{S}$  into a solution of (a mixture of) metal salts, accompanied by a precipitation reaction, was developed by Al-Tarazi *et al.* (2004).

## THEORY

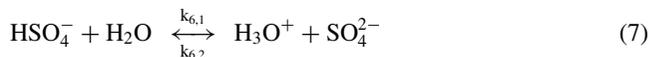
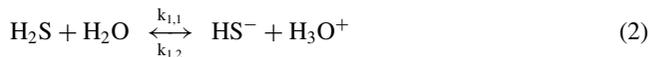
### REACTION SCHEME

Upon the absorption of  $\text{H}_2\text{S}$  into an aqueous bivalent metal sulfate solution a number of reactions will occur. After  $\text{H}_2\text{S}$  is dissolved in water (equation 1) it dissociates in two steps according to equations 2 and 3. When sufficient thermodynamic driving force

**Table 1.** Equilibrium constants

Reaction	Equilibrium constant	Numerical value pK	Source
2	$K_{a1,H_2S} = \frac{[HS^-][H_3O^+]}{[H_2S]}$	6.97	Horvath, 1985
3	$K_{a2,H_2S} = \frac{[S^{2-}][H_3O^+]}{[HS^-]}$	12.9	Horvath, 1985
4	$K_{SP} = [Me^{2+}][S^{2-}]$	23.7 for ZnS 39.2 for CuS	Dean, 1992
6	$K_w = [H_3O^+][OH^-]$	14	Horvath, 1985
7	$K_{a2,H_2SO_4} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$	2.0	Horvath, 1985

(i.e. at a supersaturation ratio larger than 1) is present the subsequent precipitation reaction between the sulfide ion formed during the second dissociation step, and the metal ions can occur (equation 4). The supersaturation ratio is defined as shown in equation 5. Other reactions that can occur are the water equilibrium (equation 6), and the dissociation of the bisulfate ion (equation 7). The equilibrium constants of equations 2 to 7 are presented in Table 1.



#### SIMPLE MODEL DESCRIPTION

It is likely that for a process in which highly insoluble precipitates (as is the case for copper sulfide) are formed, the precipitation (nucleation) may be considered to be fast or even instantaneous with respect to mass transfer (Söhnel, 1992, Nielsen, 1964). In that case,

it is possible to derive a simple set of equations that describe the rate of absorption. For gas absorption accompanied by an instantaneous irreversible reaction the rate of absorption is determined by the mass transfer on both sides of the gas-liquid interface. Two cases can be distinguished: 1) a gas and liquid phase mass transfer limited regime and 2) a gas phase mass transfer limited regime.

Case 1: gas and liquid phase mass transfer limited regime

In case of an instantaneous irreversible reaction, components A ( $H_2S$ ) and B ( $Cu^{2+}$ ) cannot exist simultaneously at the same location in the solution. In this case the overall mass transfer (volumetric transfer rate) can be described by equation 8. For the film model the enhancement factor of the instantaneous irreversible reaction (for the overall mass transfer)  $E_{H_2S,\infty}^*$  is then defined as given in equation 9 (definition of equation 9 according to film model).

Basic equations simple model description.

$$J_{H_2S}a = \frac{C_{H_2S,G}E_{H_2S}^*}{\frac{1}{mk_{L,H_2S}a} + \frac{1}{k_{G,H_2S}a}} \quad (8)$$

$$E_{H_2S,\infty}^* = \left( 1 + \frac{D_{Cu}C_{Cu,L}}{D_{H_2S}mC_{H_2S,G}} \right) \quad (9)$$

$$J_{H_2S}a = k_{G,H_2S}aC_{H_2S} \quad (10)$$

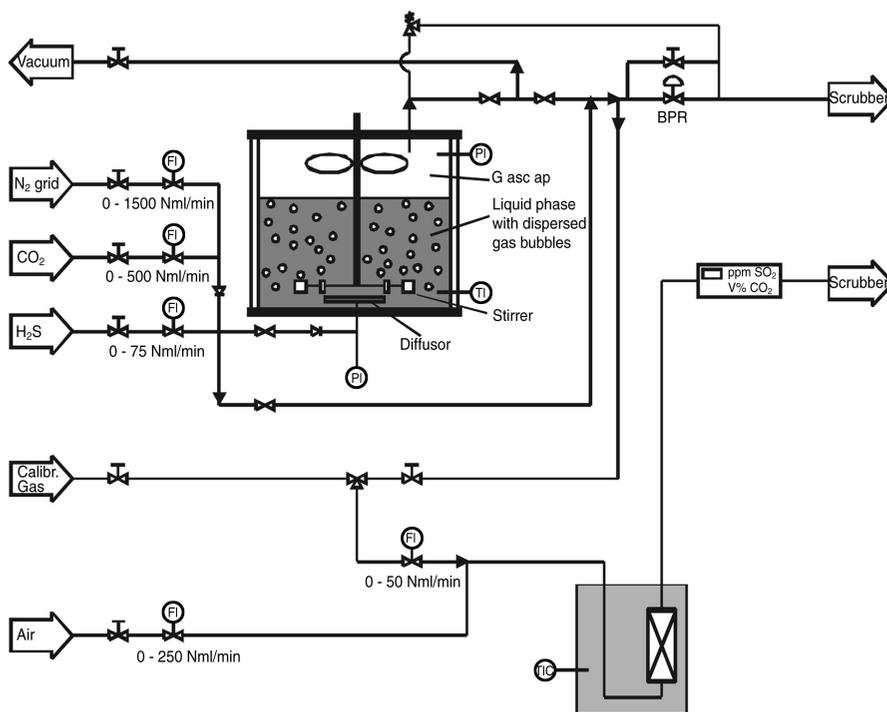
Case 2: gas phase mass transfer limited regime

If the mass transfer rate of  $Cu^{2+}$ -ions from the liquid bulk to the interface is high compared to the mass transfer rate of  $H_2S$  from the gas bulk to the interface, the gas side mass transfer resistance entirely determines the rate of absorption. The gas side limited mass transfer of  $H_2S$  is expressed by equation 10.

In case the simplification is allowed the minimum of these two boundary cases 1 and 2 defines the overall mass transfer rate in the absorption process. In this study, it will be investigated to which degree, and under which conditions, this simplification is allowed. A comparison of the absorption rate as predicted with the model and the extended model of Al-Tarazi will be made (Al-Tarazi *et al.* 2004, a short description is given in the paragraph "Comparison with extended model"). Furthermore,  $H_2S$  absorption experiments will be carried out to verify the validity of both the extended model described by Al-Tarazi and the simplified model that assumes an instantaneous irreversible reaction.

## EXPERIMENTAL SETUP

The experiments were performed in a Mechanically Agitated Gas-Liquid Reactor (MAGLR) (See Figure 1). The experimental setup consisted of a gas mixing section, in which the desired gas flow is composed, a reactor section, and a gas analysis section. The MAGLR was operated batch wise with respect to the liquid phase and continuously



**Figure 1.** Schematic representation of the experimental set-up

with respect to the gas phase. The glass double walled reactor,  $D = 8.25 \text{ cm}$ ,  $V = 1065 \text{ cm}^3$ , was operated batchwise with respect to the liquid phase and continuously with respect to the gas phase. The liquid could be intensely stirred with a six bladed rushton turbine,  $D = 45 \text{ mm}$ ,  $H = 11 \text{ mm}$ , located  $42 \text{ mm}$  from the bottom of the reactor. The gas phase was mixed with a 2-bladed stirrer. Both stirrers were mounted on a single axis with a diameter of  $10 \text{ mm}$ . The speed of the stirrer could be varied between  $0$  and  $2000 \text{ rpm}$ . The reactor was equipped with  $4$  baffles. Gas was sparged into the liquid with a diffuser. The diffuser had  $5$  holes in a rectangular pitch with a diameter of  $1 \text{ mm}$ . The temperature of and the pressure in the reactor were recorded. In the gas mixing section a feed gas mixture with the desired flow rate and composition was prepared from pure gases using Brooks 5150 thermal mass flow controllers. The gas leaving the reactor was led through a caustic scrubber, before discharge to the atmosphere. A Tescom series 1700 back pressure regulator was used to regulate the reactor operating pressure. For H<sub>2</sub>S absorption experiments the gas-liquid reactor was filled with the desired solution (metal sulfate or sodium hydroxide). To avoid interference from gasses which might have absorbed from

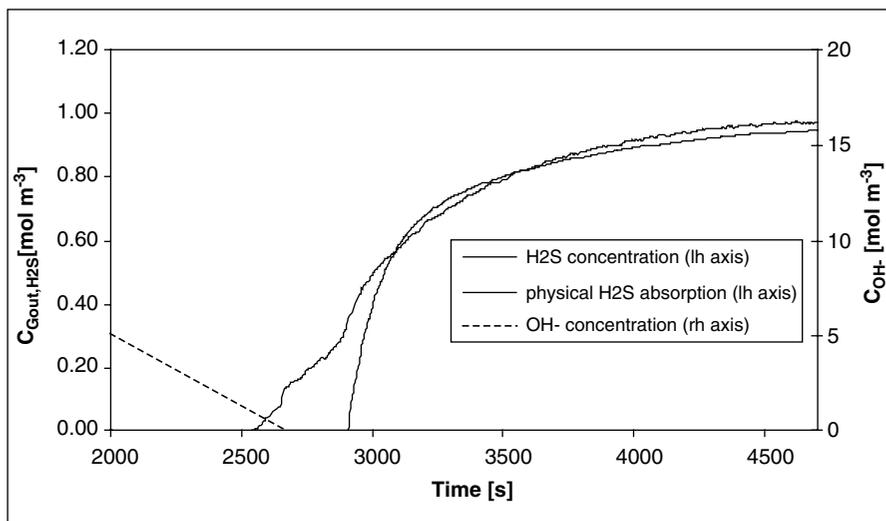
the atmosphere (e.g.  $N_2$  or  $CO_2$ ), the reactor contents were subsequently degassed by evacuation. The temperature of the metal sulfate solution in the reactor was maintained at 293 K, after which, at  $t = 0$ , a gas stream with the desired composition was fed into the reactor at a flowrate of 5.0 Nml/s. The pressure in the reactor was kept at 120 kPa. A small gas sample stream from the reactor effluent was diluted with air, and the  $H_2S$  in that stream was converted to  $SO_2$  at 350 °C over stainless steel wool as catalyst. The resulting  $SO_2$  concentration in the sample stream was determined using a MAIHAK MULTOR 610 multicomponent IR analyser, which simultaneously determined the  $CO_2$  concentration (For details see also Ter Maat, 2005). The volumetric mass transfer coefficient of the MAGLR was determined from  $CO_2$  absorption experiments in pure water or metal sulfate solutions. These experiments were performed either by adding  $CO_2$  to a stream of pure  $N_2$  (to determine the physical characteristics of the setup), or to a mixture of  $N_2$  and  $H_2S$  (to determine the  $k_{OvA}$  during an  $H_2S$  absorption experiment).

## EXPERIMENTAL RESULTS AND DISCUSSION

During introductory (batch) experiments using a stirred cell with an undisturbed, flat G/L interface, the formed copper sulfide particles floated on the liquid surface, probably due to their hydrophobic nature. This hampered the interpretation of the experimental results. Therefore, the mechanically agitated gas-liquid reactor (in which the G/L interface is less static) was chosen as a model reactor. An extra advantage of the MAGLR is that the G/L behavior of an industrial absorber more closely resembles a MAGLR than a flat interface model reactor. A drawback of this reactor type appeared to be that the Residence Time Distribution (RTD) of the gas phase could not be described by plug flow nor by CISTR like behaviour. A review article by Joshi *et al.* (1981) concludes that the gas phase RTD in MAGLR's is equivalent to a single CISTR or two CISTR's in series or in between the two. Hanhart *et al.* (1963) found that the RTD of the gas phase can be described adequately by a single CISTR at stirring speeds above the critical stirring speed (900 rpm for the setup used). At lower stirring speeds, as mostly applied during this study, the RTD of the gas phase can be described by 2 CISTR's in series. Thus, the concentration of the gas leaving the reactor cannot be readily used for the interpretation of the experimental results. This is especially important when the  $H_2S$  conversion is high, and  $H_2S$  concentrations in the gas phase may vary considerably from bubble to bubble.

## ABSORPTION OF $H_2S$ IN NaOH SOLUTIONS

To characterize the experimental setup an  $H_2S$  absorption experiment using an aqueous 0.0198 molar NaOH solution was performed. This experiment was continued up to the point where the NaOH solution was fully depleted. The reaction between  $H_2S$  and NaOH is known to be instantaneous with respect to mass transfer (Danckwerts, 1970). The  $H_2S$  absorption in a NaOH solution is therefore usually gas phase mass transfer limited, provided the gas does not consist of pure  $H_2S$  and the concentration of NaOH is sufficiently high. Therefore this experiment can be used to determine the  $H_2S$



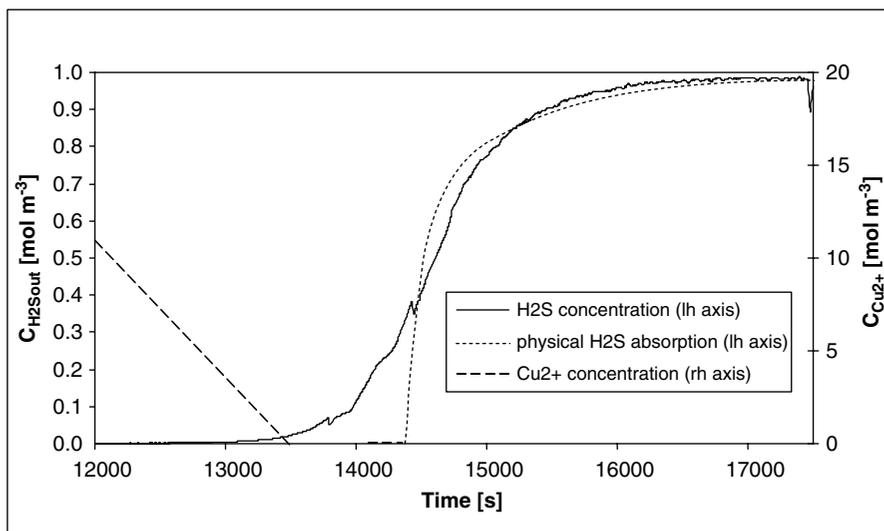
**Figure 2.** The concentration of  $\text{H}_2\text{S}$  in the gas stream leaving the reactor and the concentration of  $\text{NaOH}$  as a function of time.  $N = 200$  rpm

concentration in the gas leaving the reactor in the case of gas phase limited mass transport. At the start of the experiment 600 ml of a  $\text{NaOH}$  solution was added to the reactor. After the desired reaction temperature was reached a gas stream containing 2 V%  $\text{H}_2\text{S}$  was fed to the reactor. In steady state (up to  $t = 2000$  s) the concentration of  $\text{H}_2\text{S}$  in the gas leaving the reactor varied around 30 ppmV. The result of this experiment is shown in Figure 2: The  $\text{NaOH}$  concentration in the reactor was estimated by integrating over the  $\text{H}_2\text{S}$  mass balance in time. It appeared that the  $\text{H}_2\text{S}$  concentration of the gas leaving the reactor was not a function of the  $\text{NaOH}$  concentration of the solution until the  $\text{NaOH}$  solution was nearly depleted. Thus, up to this point  $\text{H}_2\text{S}$  absorption takes place in the gas phase mass transfer limited regime. When the solution is depleted the  $\text{H}_2\text{S}$  concentration in the reactor effluent increases rapidly. As reference the increase in  $\text{H}_2\text{S}$  concentration that would occur in the case of physical absorption only is also shown. The time at which the curve for physical  $\text{H}_2\text{S}$  absorption starts was chosen arbitrarily.

#### ABSORPTION OF $\text{H}_2\text{S}$ IN $\text{CuSO}_4$ SOLUTIONS

With the physical characteristics of the reactor known, the absorption of  $\text{H}_2\text{S}$  in a copper sulfate solution was studied using a 0.5 M  $\text{CuSO}_4$ . For  $\text{H}_2\text{S}$  concentrations of 4% or more foaming occurred (This effect is also mentioned in Ter Maat *et al.*, 2005). Therefore,

the  $\text{H}_2\text{S}$  concentration in the feed gas was kept at 2%. It appeared that very high  $\text{H}_2\text{S}$  conversions could be obtained for a  $\text{H}_2\text{S}$  percentage in the feed gas of 2 V% or lower; concentrations of  $\text{H}_2\text{S}$  in the reactor effluent varied between 20 and 40 ppmV, which was comparable to the  $\text{H}_2\text{S}$  concentration when using a NaOH solution as absorbent. Next, an experiment was carried without an 0.1 M  $\text{CuSO}_4$  solution up to the point where the  $\text{CuSO}_4$  solution was fully depleted. In steady state (up to  $t = 13000$  s) the concentration of  $\text{H}_2\text{S}$  in the gas leaving the reactor again varied around 30 ppmV. The  $\text{CuSO}_4$  concentration had no influence on the  $\text{H}_2\text{S}$  conversion until the  $\text{CuSO}_4$  concentration dropped below  $4\text{--}10 \text{ mol m}^{-3}$  (The copper concentration in the liquid was estimated from the integration of the  $\text{H}_2\text{S}$  mass balance. The accuracy of this mass balance was approximately 5–10%). Only then the  $\text{H}_2\text{S}$  concentration in the reactor effluent started to increase. Taken together with the results from the NaOH experiments this demonstrates that the  $\text{H}_2\text{S}$  absorption in a copper sulfate solution most probably takes place in the gas phase mass transfer limited regime if the copper concentration is sufficiently high. When the solution is depleted the  $\text{H}_2\text{S}$  concentration in the reactor effluent increases rapidly. The experimental result is shown in Figure 3. As reference the increase in  $\text{H}_2\text{S}$  concentration that would occur in the case of physical absorption only is also shown. In a series of experiments the influence of the stirrer speed on the  $\text{H}_2\text{S}$  concentration in the reactor effluent was investigated using a 0.1 M  $\text{CuSO}_4$  solution as absorbent



**Figure 3.** The concentration of  $\text{Cu}^{2+}$  in the liquid and the concentration of  $\text{H}_2\text{S}$  in the gas stream as a function of time.  $N = 200$  rpm

**Table 2.** The concentration of H<sub>2</sub>S in the gas stream leaving the reactor as a function of stirrer speed. T = 293 K, P = 120000 Pa, V = 700 ml, H<sub>2</sub>S = 2 V%, CuSO<sub>4</sub> = 0.1 M

N [rpm]	H <sub>2</sub> S [ppmV]
50	39.0
100	45.3
150	35.1
200	33.2
250	42.2

(See Table 2). The concentration of H<sub>2</sub>S in the reactor effluent hardly changed with increasing stirrer speeds, which can be explained since the relatively small increase in the overall mass transfer coefficient that occurs with increasing stirrer speed may be offset by the increasing fraction of gas bubbles with a relatively short residence time (the gas phase will show a more CISTR-like behavior with increasing stirrer speed).

### COMPARISON WITH EXTENDED MODEL

Al Tarazi *et al.* (2004) have developed a model that describes mass transfer accompanied by reaction for the case of the precipitation of metal sulfides in an aqueous solution containing heavy metal ions (notably Cu<sup>2+</sup> and Zn<sup>2+</sup>) that is continuously contacted with a H<sub>2</sub>S containing gas. This model is thought to be able to predict the effect of operation, process conditions and reactor layout on the rate of H<sub>2</sub>S absorption, precipitation and particle size distribution. The gas phase was modelled using the film model, and at the G-L interface local equilibrium was assumed. The solubility of the gas in the liquid was estimated from literature data (Horvath, 1985). The mass transfer zone was modelled according to Higbie's penetration model (Higbie, 1935), and mass balances for all species were set up incorporating equations 2–7. As a driving force not only the concentration gradient was used, but the electrostatic potential gradient was also taken into account. The concentration profile of the individual species in the liquid, near the gas liquid interface, can be calculated as a function of contact time using equation 11 (penetration model). With the exception of the rate of precipitation, all reaction rate equations are (the summation of) first order reactions. A mass balance for CuS was treated separately since the rate of crystal growth and nucleation are separate functions of the supersaturation ratio and for these, population balances are used (for details see Al Tarazi *et al.* (2004)). The electrostatic potential can be calculated by the use of the Nernst-Einstein equation (Newman, 1973) assuming dynamic electroneutrality (equation 12). The precipitation kinetics are taken into account through equations 13 to 15. The linear growth rate of particles is given by equation 13, the molar growth rate of particles is given by equation 14, and the molar rate of birth of new particles B' is given by equation 15.

Basic equations simple model description.

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - z_i D_i \frac{F}{RT} \frac{\partial(\phi C_i)}{\partial x} - r_i \quad (11)$$

$$\phi(x, t) = \frac{RT}{F} \frac{\sum_{i=1}^{NC} z_i D_i \frac{\partial C_i}{\partial x}}{\sum_{i=1}^{NC} z_i^2 D_i C_i} \quad (12)$$

$$G = k_g \left[ \frac{\sqrt{C_{Cu^{2+}} C_{S^{2-}}}}{\sqrt{K_{SP}}} - 1 \right]^8 \quad (13)$$

$$G' = \sum_{i=1}^{\infty} \{ \beta \rho n(z, L_i^2) G L_i^2 (L_i - L_{i-1}) \} \quad (14)$$

$$B' = \alpha P L_0^3 * k_n \left[ \frac{\sqrt{C_{Cu^{2+}} C_{S^{2-}}}}{\sqrt{K_{SP}}} - 1 \right]^n \quad (15)$$

The particle size distribution of the formed metal sulfide particles was calculated using the population balance as proposed by Randolph (1988). Further details of the model description, the applied boundary conditions and relations used to describe the population balances can be found in Al-Tarazi *et al.* (2004). How the various chemical reactions are related is shown in Figure 4.

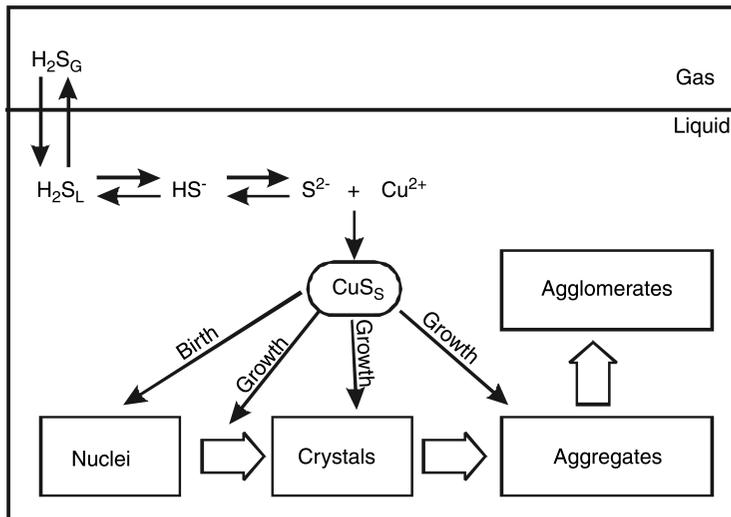
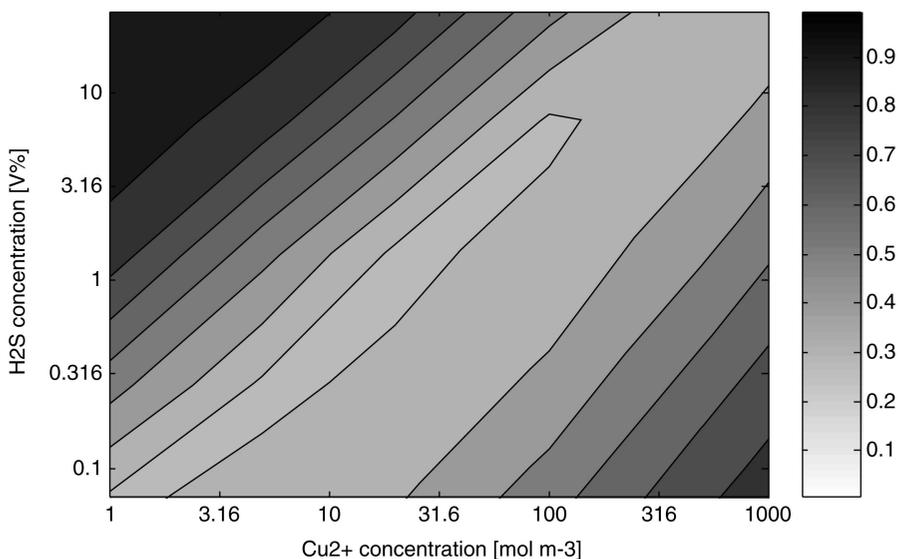


Figure 4. Overview of the model

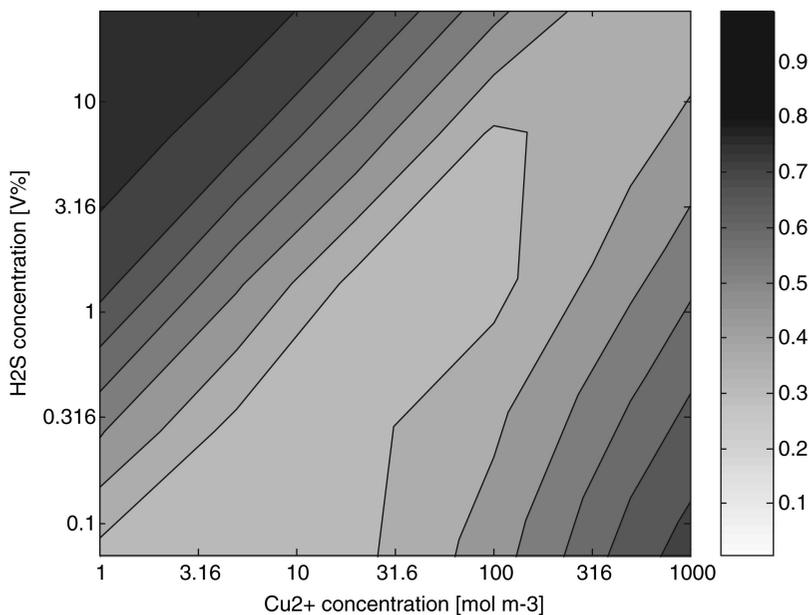
The precipitation growth parameters;  $k_g$ ,  $g$  and nucleation parameters;  $k_n$  and  $n$  were fitted using laminar jet experiments (Al Tarazi *et al.*, 2004). The model can now be used for the prediction of  $H_2S$  absorption rate under various process conditions.

As already pointed out in the introduction, if the precipitation reaction is sufficiently fast, the absorption of  $H_2S$  in the  $Me^{2+}$ -ions containing solution may be regarded as absorption of a gaseous component into a solution, accompanied by a very fast irreversible reaction (the simple model). This can occur when the driving force for the precipitation is sufficiently high (as is usually the case for the formation of highly insoluble metal sulphides). In this case the absorption rate can be described with equation 8 or, in the case of gas phase mass transfer limitation equation 10 which can be regarded as limited cases of the extended model given by Al-Tarazi *et al.* (2005). This simplification allows for a considerable reduction of the computation time needed for the design of a G/L contacting device. Downside of this simplified approach is the loss of data regarding the particle size distribution.

The ratio of the maximal possible absorption rate as obtained with the simplified model (equations 8 and 10) to the flux predicted by the extended model by Al-Tarazi (based on equations 11 to 15) is shown in Figures 5 through 7. Each plot shows the ratio at a different pH.



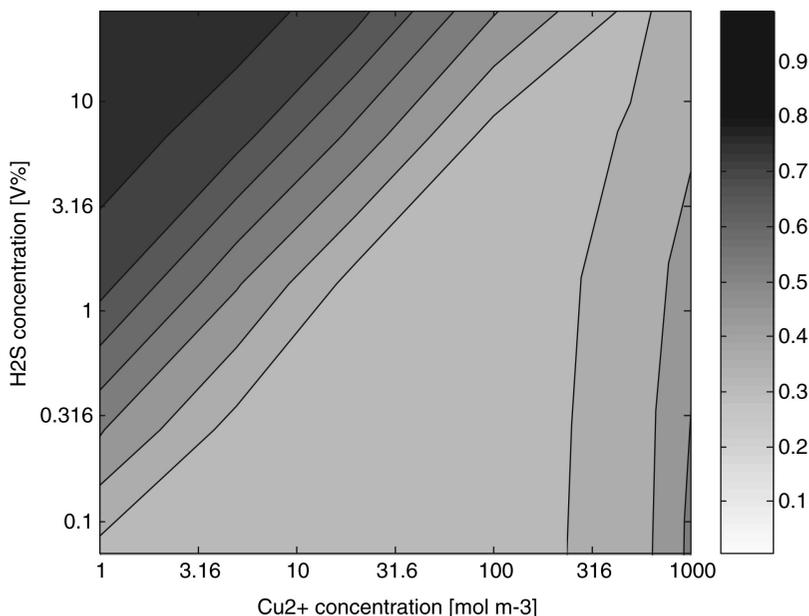
**Figure 5.** Absorption of  $H_2S$  in a  $CuSO_4$  solution: ratio of simulated absorption rate (extended model) and maximum possible absorption rate (simplified model) at  $pH = 5.5$ ,  $k_L = 1.1 \times 10^{-5} \text{ m s}^{-1}$ ,  $k_G = 1.1 \times 10^{-4} \text{ m s}^{-1}$



**Figure 6.** Absorption of  $\text{H}_2\text{S}$  in a  $\text{CuSO}_4$  solution: ratio of simulated absorption rate and maximum possible absorption rate at  $\text{pH} = 3.5$ ,  $k_L = 1.1 \times 10^{-5} \text{ m s}^{-1}$ ,  $k_G = 1.1 \times 10^{-4} \text{ m s}^{-1}$

From these figures it can be seen that the differences between the maximum possible flux as predicted by the simplified model and the predicted flux according to the extended model are small (<30%) for large areas of the investigated combinations of  $\text{Cu}^{2+}$  and  $\text{H}_2\text{S}$  concentrations. At high concentrations of  $\text{H}_2\text{S}$  and low concentrations of  $\text{Cu}^{2+}$  the differences are negligible. Under process conditions that could realistically occur in a biogas desulfurization unit (<2%  $\text{H}_2\text{S}$ , high copper concentration,  $\text{pH}$  3.5 or higher), the simplification can also be applied; however loss of accuracy will occur. At the remaining combinations  $\text{Cu}^{2+}$  and  $\text{H}_2\text{S}$  concentrations the simplified model will give a significantly different result than the extended model (the lighter areas in Figures 5 through 7). However experiments have shown that the applicability of the simplified approach is better than may be expected based on the model results.

$\text{H}_2\text{S}$  absorption experiments were carried out using an  $\text{H}_2\text{S}$  concentration of 2 V% and a copper concentration that varied between 0.01 and 0.1 mole  $\text{dm}^{-3}$ . The experimental results showed that the absorption of  $\text{H}_2\text{S}$  under these conditions may be considered gas phase limited. It may thus be assumed that the extended model (more aimed at giving a correct prediction of the particle size distribution of the produced  $\text{CuS}$ , than



**Figure 7.** Absorption of  $\text{H}_2\text{S}$  in a  $\text{CuSO}_4$  solution: ratio of simulated absorption rate and maximum possible absorption rate at  $\text{pH} = 2.0$ ,  $k_L = 1.1 \times 10^{-5} \text{ m s}^{-1}$ ,  $k_G = 1.1 \times 10^{-4} \text{ m s}^{-1}$

at giving a correct  $\text{H}_2\text{S}$  absorption rate) gives an under prediction of the  $\text{H}_2\text{S}$  absorption rate. Hence it may be concluded that the area in which the absorption may be described by the simplified approach may be more extended than suggested in Figures 5 to 7.

## CONCLUSIONS

In this study the desulfurization of gas streams using aqueous copper sulfate ( $\text{CuSO}_4$ ) solutions as washing liquor has been studied theoretically and experimentally. Absorption experiments were carried out in a Mechanically Agitated Gas Liquid Reactor. This reactor was characterized using the absorption of  $\text{CO}_2$  in water and the absorption of  $\text{H}_2\text{S}$  in  $\text{NaOH}$  solutions.  $\text{H}_2\text{S}$  absorption experiments were conducted at a temperature of 293 K and  $\text{CuSO}_4$  concentrations between 0.01 and 0.1 M. These experiments showed that the copper sulfate solution efficiently removes  $\text{H}_2\text{S}$  even at very low copper concentrations. The experimental results indicate that for industrially relevant process conditions the absorption of  $\text{H}_2\text{S}$  in a  $\text{CuSO}_4$  solution may be considered a gas phase mass transfer limited process. An extended model developed

by Al-Tarazi *et al.* (2004) has been used to predict the rate of H<sub>2</sub>S absorption and was compared to a simplified mass transfer model, assuming an instantaneous irreversible reaction. This comparison showed that the absorption rate of H<sub>2</sub>S in a CuSO<sub>4</sub> solution can be considered a completely mass transfer controlled process under certain conditions. Under a much wider range of conditions the error that is made by assuming that the absorption process is a mass transfer controlled process, is still within engineering accuracy. A comparison of the experimental results and the simulated results of the extended model showed that the extended model gives an under prediction of the H<sub>2</sub>S absorption rate for the experimental conditions applied.

## NOMENCLATURE

### SYMBOLS

a	Specific surface area [m <sup>-1</sup> ]
g	Exponent in growth rate expression [-]
k	Reaction constant [s <sup>-1</sup> ], [m <sup>3</sup> mole <sup>-1</sup> s <sup>-1</sup> ]
k	Mass transfer coefficient [m s <sup>-1</sup> ]
m	Gas distribution coefficient [-]
n	Exponent in nucleation rate expression [-]
r	Reaction rate [mole m <sup>-3</sup> s <sup>-1</sup> ]
t	Time variable [s]
x	Place variable [m]
z	Ion valency [-]
B	Particle nucleation rate [mole m <sup>-3</sup> s <sup>-1</sup> ]
C	Concentration [mole m <sup>-3</sup> ]
D	Diffusion coefficient [m <sup>2</sup> s <sup>-1</sup> ]
E	Chemical enhancement factor [-]
F	Faraday constant [C mole <sup>-1</sup> ]
G	Particle growth rate [m s <sup>-1</sup> ] or [mole m <sup>-3</sup> s <sup>-1</sup> ]
J	Gas absorption rate [mole m <sup>-2</sup> s <sup>-1</sup> ]
K	Equilibrium constant [mole m <sup>-3</sup> ]
L	Particle diameter [m]
N	Stirrer speed [rpm]
R	Universal gas constant [mole J <sup>-1</sup> K <sup>-1</sup> ]
S	Degree of supersaturation [-]
T	Temperature [K]

### GREEK

$\alpha$	Particle shape factor (vol) [-]
$\beta$	Particle shape factor (surf) [-]
$\phi$	Electrostatic potential gradient [V m <sup>-1</sup> ]
$\rho$	Density [kg m <sup>-3</sup> ]
$\Delta$	Denoting a difference [-]

## SUB-SCRIPTS

a	referring to acidity
g	referring to particle growth
i	referring to component i
n	referring to particle nucleation
w	referring to water
G	referring to gas
L	referring to liquid
SP	referring to the solubility product
0	referring to critical nucleus
∞	Infinite

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