

Kinetics of Zinc Hydrosulfite Slurry Reaction

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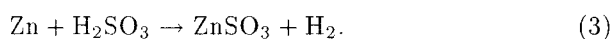
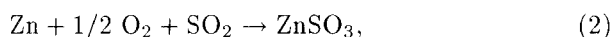
Zinc hydrosulfite is produced by slurry reaction between sulfur dioxide and zinc powder. This reaction is the first step of sodium hydrosulfite production in zinc powder processing. In this paper through performing a series of experiments, zinc hydrosulfite production rate is obtained as a function of SO₂ flow rate, temperature and specific area of zinc powder. In addition, equations for predicting the end-point of the reaction and the decomposition rate of zinc hydrosulfite after that end-point are proposed. Finally, a time dependent flow rate equation is suggested to predict the maximum yield.

INTRODUCTION

Zinc hydrosulfite is a strong reducer used as a bleaching and stabilizing agent in the pulp, paper and dyestuff industries. Due to more strict environmental regulations associated with zinc, the hydrosulfide is substituted with its sodium salt during the bleaching process. The zinc hydrosulfite is produced by the slurry reaction of sulfur dioxide (SO₂) with the zinc powder (Zn):



In addition to the main product, zinc sulfite is also produced as a by-product:



The reaction is carried out at room temperature and atmospheric pressure with a yield of 60% to 80%, defined as the molar ratio of ZnS₂O₄ to original zinc powder.

The slurry color is black during the SO₂ injection, but it changes to a creamy color at the end-point of the reaction. As zinc hydrosulfite suddenly starts to decompose to zinc thiosulfate and bisulfite in an acidic medium and its decomposition chain reaction starts, SO₂ injection must be stopped.

It is suggested in [1] that for yield improvement, SO₂ flow rate would be set to the maximum allowable

value at the beginning of the reaction and then would decrease slowly at the end-point of the reaction.

In the present investigation, the effects of different factors on the reaction yield are presented and three experimental equations for successive stages of the reactions are proposed. Moreover, an equation is presented to give the best time distribution of the SO₂ flow rate for obtaining the maximum yield.

THEORY

The rate of the slurry reaction depends on physical and chemical resistances. All factors that affect the diffusion of SO₂, from the gas bubble surface to the solid particle surface, form the physical resistance. The chemical resistance results from the surface chemical reaction between gas bubbles and the solid.

Basically, different stages of a slurry reaction consist of [2]:

- a) SO₂ diffusion from the gas bubble up to its boundary layer,
- b) SO₂ diffusion from the bubble boundary layer up to the bulk of the liquid,
- c) SO₂ diffusion from the liquid bulk up to the solid boundary layer,
- d) Surface chemical reaction between SO₂ and the solid surface,
- e) Product diffusion from the solid boundary layer up to the liquid bulk.

In this reaction, pure SO₂ gas is used; therefore, Step a) is eliminated. For simplification, the product diffusion resistance might be neglected; therefore, the

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last step is also eliminated. The production rate of zinc hydrosulfite is presented based on the remaining resistances:

$$\begin{aligned} r_1 &= \frac{1}{2} \frac{dC_{SO_2}}{dt} \\ &= \frac{dC_{Z.D}}{dt} = \frac{1}{2} K_l a_g (C_{SO_2}^* - C_{SO_2}) \\ &= \frac{1}{2} K_s a_s (C_{SO_2} - C_{SO_2}^*) = r'' \end{aligned} \quad (4)$$

or:

$$r_1 = \frac{1}{2} \frac{dC_{SO_2}}{dt} = \frac{dC_{Z.D}}{dt} = \frac{1}{2} \frac{(C_{SO_2}^* - C_{SO_2})}{\frac{1}{K_l a_g} + \frac{1}{K_s a_s}} = r'' \quad (5)$$

where $K_l a_g$ is the mass transfer coefficient in the gas boundary layer across the specific surface of gas bubbles. For gas bubble dispersion in a stirred tank this can be calculated as [3]:

$$\begin{aligned} K_l a_g &= 0.06 \frac{D}{d^2} \left(\frac{\rho N d^2}{\mu} \right)^{1.5} \left(\frac{N d}{g} \right)^{0.19} \\ &\times \left(\frac{\mu}{\rho D} \right)^{0.5} \left(\frac{\mu V_{sg}}{\sigma} \right)^{0.6} \left(\frac{N d}{V_{sg}} \right)^{0.32} \end{aligned} \quad (6)$$

The mass transfer coefficient, K_s at the solid boundary layer of a well-stirred solid-liquid system can be calculated from [3]:

$$K_s = \frac{D}{d_p} \left[2 + 0.4 \left(\frac{V_{sg} g d_p^4 \rho^3}{\mu^3} \right)^{0.25} \left(\frac{\mu}{\rho D} \right)^{0.333} \right] \quad (7)$$

Another variable, a_s , is the specific surface of zinc powder, a function of its original concentration and the powder particle size distribution, which can be calculated [4] at a desired time as:

$$\begin{aligned} &\text{for } C_{Zn}^o = 150 \text{ g/l} : \\ a_s &= \exp[6.135725 + 0.61993 \ln(C_{Zn})], \end{aligned} \quad (8)$$

$$\begin{aligned} &\text{for } C_{Zn}^o = 175 \text{ g/l} : \\ a_s &= \exp[6.194609 + 0.619888 \ln(C_{Zn})]. \end{aligned} \quad (9)$$

In the above equations, ρ , μ and σ are density, viscosity and surface tension of solution, respectively, D is the diffusion coefficient of SO_2 in water, d is the paddle diameter, d_p is the average particle size of zinc powder, C_{Zn}^o and C_{Zn} are, respectively, the initial and the actual concentration of zinc powder, and finally V_{sg} is the linear velocity of gas.

$$V_{sg} = \frac{\dot{V}}{A}, \quad (10)$$

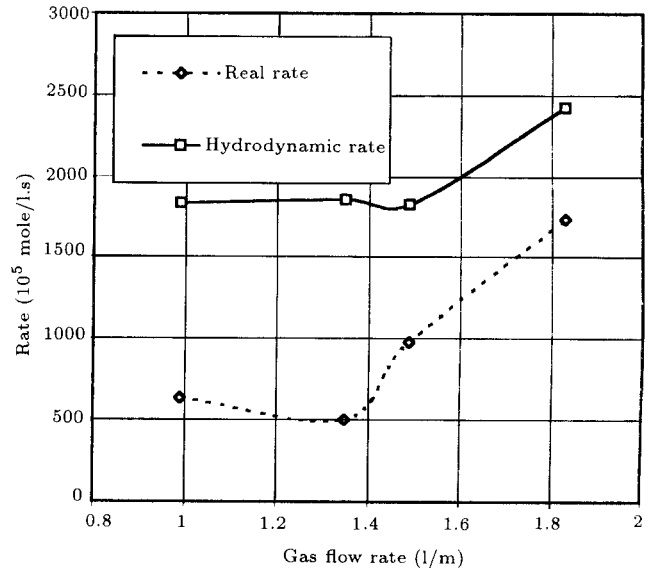


Figure 1. Hydrodynamic and real rate of reaction vs gas flow rate.

where \dot{V} is the volumetric gas flow rate and A is the reactor vessel cross section area. It is emphasized that $C_{SO_2} \cong 0$.

The real rate of reaction and the overall diffusion rate of SO_2 versus the gas flow rate are presented in Figure 1. The "Real Rate" is based on the experimental measurements of second and third columns in Table 1. "Hydrodynamic Rates" are calculated from LHS of Equation 5, for which $K_l a_g$ and K_s are obtained from Equations 6 to 8 and values of Table 2.

Here, Real Rate means the measured reaction rate which includes all resistances: The mass transfer resistance of SO_2 diffusion from the bubble to the solid surface and the surface reaction resistance. However, the hydrodynamic rate represents only the mass transfer resistance of SO_2 diffusion from the bubble to the solid surface.

It is obvious that the overall diffusion rate of SO_2 (hydrodynamic rate of reaction) is more than the real rate of the reaction. Therefore, the variation of hydrodynamic rate versus gas flow rate is different from the real one. Thus, one can conclude that the hydrodynamic rate of reaction either is not controlling or the available equations for $K_l a_g$ and K_s are not suitable. Hence, it is better to look for an empirical equation to represent the behavior.

EXPERIMENT SET UP AND PROCEDURE

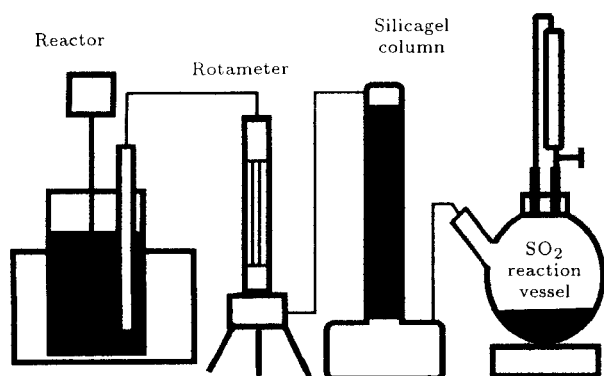
In the bench scale system (Figure 2), SO_2 is produced in a vessel by reacting sulfuric acid with the aqueous solution of sodium metabisulfite. The produced gas passes through a silicagel column, then through a rotameter and finally enters into a 500 ml beaker reactor, submerged in cold water. The required quantity of zinc powder is added to some 350 ml of distilled

Table 1. Set of experimental data for a single run.

Temperature °C	SO ₂ Gas Flow rate, l/min	Exp. Reaction Rate, 10e + 6 mol/l.s	Zn Concentration, g/l
32.8	0.99	636.28	119.6
34.7	1.349	499.59	69.87
36	1.488	973.4	46.47
28.62	1.63	1732.83	39

Table 2. Parameters for calculation of constants in Equation 13.

Parameter	Unit	Value	Parameter	Unit	Value
A	m ²	0.0028	ρ	kg/m ³	997
d	m	0.03	μ	kg/m.s	0.95E-3
d_p	m ² /s	1.014E-9	N	rpm(s ⁻¹)	250 (4.16)
σ	N/m	63.67E-3	C _{Zn} ^o	g/l	150

**Figure 2.** Bench scale setup.

water, in order to obtain 150-180 g/l concentration. Then, the SO₂ gas is introduced inside the slurry. Hydrosulfite ion (S₂O₄²⁻) concentration is measured based on titration by K₃Fe(CN)₆ [3,5]. The reaction time, usually between 25-70 minutes, depends on the temperature, SO₂ flow rate, gas flow rate reduction with time and the initial concentration of zinc powder.

Particle size analysis was carried out and an overall average size of 25 μ m was obtained for the powder whose purity was measured to be 98 wt%. The 2% impurities for the zinc powder might be the zinc oxide present during the zinc powder production. This impurity will not react with SO₂ and may have a stabilizing effect on the hydrosulfite production.

Samples were taken from the reactor every 5 minutes, while the temperature and flow rate were being recorded. The reaction was carried out in the

temperature range of 28°C to 36°C. The SO₂ gas flow rate was maintained between 0.7 to 2 l/min.

ANALYSIS

As the empirical equation should contain the effects of hydrodynamic and chemical factors, experiments were carried out to determine the effects of turbulence, gas flow rate, specific area of zinc powder, temperature and pH.

Turbulence

Generally, the agitation, form of the paddle and reactor shape affect the turbulence. The agitation has two effects: maintaining zinc particles in suspension and distributing gas bubbles in the slurry. The agitation speed affecting the gas distribution and solid suspension varies in a narrow range. Lower agitation speed results in the reduction of reaction yield and a higher one has no effects on the yield of reaction. Therefore, the agitation speed has a fixed range for every system. It was found that, for a good gas bubble distribution, an agitator rpm higher than that for maintaining the solids suspended was needed. Therefore, a turbine mixer was selected.

Gas Flow Rate

The SO₂ flow rate is one of the most effective factors in the reaction rate, which has been discussed while describing the governing equations. The SO₂ needed for the experiments was produced from the reaction of sulfuric acid with sodium metabisulfide, the volume

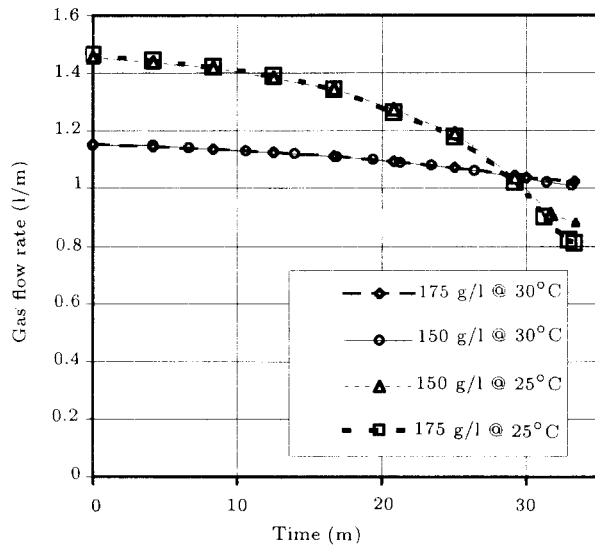


Figure 3. Gas flow rate time distribution.

flow rate of which was not under precise control. The corresponding average flow rates are shown in Figure 3.

Specific Area of Zinc Powder

Because zinc is used in powder form, its specific area is much more than that of gas bubbles, therefore, its effect is almost negligible.

Temperature

Temperature influences the reaction rate in two different and opposite ways:

- Concentration gradient of SO_2 : As temperature increases, the saturation concentration of SO_2 in the gas bubble boundary layer reduces and consequently, the driving force for SO_2 diffusion is also reduced. This is the negative effect of temperature increase on the reaction rate;
- Chemical reaction rate: Increase in temperature causes an increase in the chemical reaction rate according to the Arrhenius law.

The overall reaction rate will be reduced with increase in the temperature.

pH

The slurry pH reduces to 4-5 after the introduction of SO_2 and it reduces further quickly after the end-point of the reaction, after which zinc hydrosulfite decomposition starts. Any external factor, which helps in pH reduction of the slurry during the reaction, causes the decomposition of zinc hydrosulfite prematurely.

EQUATIONS

- The production rate of zinc hydrosulfite (r_1 , mole/l.s) is expressed as a function of SO_2 flow rate (Q_{SO_2} , mole/l.s), the specific area of zinc powder (a_s , m^2/m^3) and the reaction absolute temperature T ($^\circ\text{K}$):

$$r_1 = 40.55E - 3 \exp(974.882/T) Q_{\text{SO}_2}^{1.713} a_s^{0.3693} \quad (11)$$

- For the production rate of zinc sulfite, as a by-product, (r_2 , mole/l.s), the following equation is proposed:

$$r_2 = 339.84 E - 6 Q_{\text{SO}_2}^{0.85} a_s^{0.3693} \quad (12)$$

Data of Stabryn [6] is plotted in Figure 4 and used later on (in Equation 13) to obtain the coefficients. The presented equation is defective, but the effect of its error is negligible because the production rate of zinc sulfite is very low.

- By simulating the reaction, a predictor equation for the end-point of the reaction is suggested. Flow of SO_2 into the reactor causes the production of zinc hydrosulfite and sulfite, while its excess is dissolved in the aqueous solution up to reaching to the saturation concentration of SO_2 . This concentration is called the end-point of the reaction. According to the above theory, whenever the two sides of the following equation will be equal, the end-point of the reaction is reached:

$$\begin{aligned} \sum Q_{\text{SO}_2} t_i - 2 \sum r_1 t_i - \sum r_2 t_i \\ = \exp(-C_{Z.D}/20C_{Zn}) C_{\text{SO}_2}^* \end{aligned} \quad (13)$$

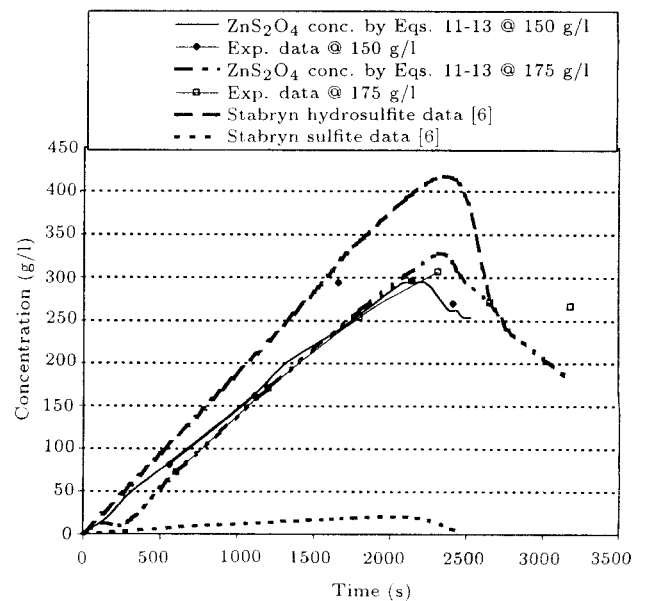


Figure 4. Product concentration variation with time.

All the above quantities are the average values during the time period t_i and $t = \sum t_i$.

$C_{SO_2}^*$ and $\exp(-C_{Z.D}/20C_{Zn})C_{SO_2}^*$ are the saturation concentration of SO_2 in water and aqueous solution, respectively, at the system temperature.

Exponential coefficient is obtained in such a manner that the Equation 13 predicts the end-point of most runs. $C_{Z.D}$ and C_{Zn} are zinc hydrosulfite and zinc concentrations at the time of the reaction.

To derive these equations, first a model is considered, then parameters are calculated from experimental data; for example to derive Equation 11, this model is used: $r_1 = k_0 \exp(-E_a/RT) Q_{SO_2}^\alpha a_g^\beta$. In order to obtain the four unknowns, namely E_a , k_0 , α and β , a set of minimum four experimental data points are needed. By solving this set, four unknown parameters are found after integration.

4. The decomposition rate of zinc hydrosulfite (r_3 , [mole/l.s]). Any excess flow of SO_2 into the reactor after the color change of the slurry, i.e., after the end-point of the reaction, causes the decomposition of zinc hydrosulfite due to the pH reduction:

$$r_3 = 0.283 \exp(-1680.29/T) C_{Z.D}^{0.7} / C_{Zn}^{0.3} \quad (14)$$

The overall rate of the reaction is then equal to r_1 before the end-point of the reaction and is equal to $(r_1 - r_3)$ afterwards.

5. The equation of SO_2 flow rate-time distribution is suggested, based on the balance with the mass transfer of SO_2 for obtaining the maximum yield in the reaction. The following equation presents the best SO_2 flow rate at any instance of the reaction:

$$Q_{SO_2} = 0.5 K_l a_g \exp(C_{Z.D}/20C_{Zn}) C_{SO_2}^*, \quad (15)$$

where K_l and a_g are, respectively, the mass transfer coefficient of SO_2 in the boundary layer of the bubble gas and the specific areas of the gas bubbles.

RESULTS

For predicting the concentration increase of zinc hydrosulfite, the occurrence of the end-point of the reaction and subsequent concentration reduction of zinc hydrosulfite, a computer program [4] was developed. Therefore, in each time increment, the specific area of zinc powder is calculated as a function of the concentration increase of zinc hydrosulfite and it is used in the rate equations.

Plots of predicting equations along with experimental data are presented in Figure 4, from which the capability of the model in predicting different stages of the reaction can be observed.

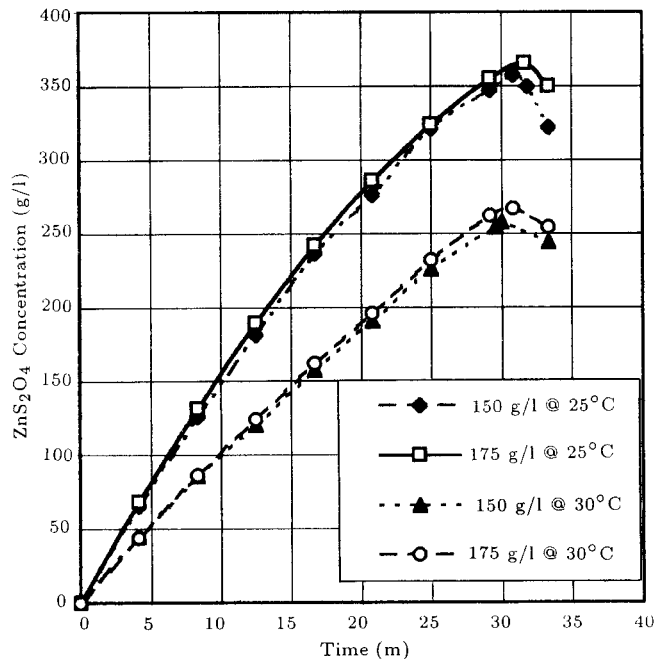


Figure 5. Zinc hydrosulfite concentration vs time.

The best time dependent gas flow rate for initial concentration of zinc powder of 150 and 175 g/l at 25°C and 30°C is presented in Figure 3. Prediction of zinc hydrosulfite concentration versus time for each one of the above four conditions is presented in Figure 5.

CONCLUSION

According to the presented results, an increase in reaction yields depends on the temperature, the initial concentration of zinc powder and time-dependent SO_2 flow rate, with the last one having the most important role.

Based on this prediction, reaction yields for concentration of 150 and 175 g/l at 25°C are 80% and 70% and at 30°C are 57% and 51%.

According to these results, temperature and the initial zinc powder concentration have a negative effect on the reaction yield, but later the temperature gains a very strong positive influence. Naturally an increase in initial concentration of zinc powder would cause the increase of the final concentration of zinc hydrosulfite.

NOMENCLATURE

A	reactor vessel cross section, m^2
a_g	specific area of gas bubble, m^2/m^3
a_s	specific area of zinc powder, m^2/m^3
C_{SO_2}	concentration of SO_2 on solid surface, g/l

$C_{SO_2}^*$	saturation concentration of SO ₂ in water, g/l
C_{lSO_2}	concentration of SO ₂ in bulk of liquid, g/l
C_{Zn}	actual zinc powder concentration, g/l
C_{Zn}^0	initial zinc powder concentration, g/l
$C_{Z.D}$	zinc hydrosulfite concentration, g/l
d	paddle diameter, m
d_p	average zinc particle size diameter, m
D	diffusion coefficient of SO ₂ in water, m ² /s
g	acceleration of gravity, m ² /s
K_s	mass transfer coefficient at the solid particle surface, mole/m ² s (mole/mole)
K_l	mass transfer coefficient at the liquid interface, mole/m ² s (mole/mole)
N	agitator speed, rpm or s ⁻¹
Q_{SO_2}	molar flow rate of SO ₂ into the solution, mole/l.s
r_1	reaction rate of zinc hydrosulfite, mole/l.s
r_2	reaction rate of zinc sulfite, mole/l.s
t_i	time increment, s

T	temperature, °K
V_{sg}	linear gas velocity, m/s
\dot{V}	volumetric gas flow rate, l/min
μ	viscosity of the solution, kg/m.s
ρ	density of the solution, kg/m ³
σ	surface tension of the solution, N/m

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