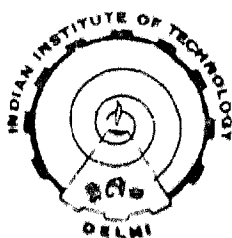


**STUDIES IN GAS-LIQUID REACTIONS
AND
DEVELOPMENT OF REACTOR**

**ABSORPTION OF HYDROGEN SULFIDE IN
AQUEOUS AMMONIACAL ZINC CHLORIDE SOLUTION
AND SIMULATION OF SPRAY REACTION WITH DRYING SYSTEM
FOR PRODUCTION OF DRY POWDERED ZINC SULFIDE**

by
HARISH CHANDER

Thesis submitted to the
Indian Institute of Technology, Delhi
for the award of the degree of
DOCTOR OF PHILOSOPHY



DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
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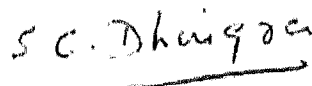
CERTIFICATE

This is to certify that the thesis entitled "STUDIES IN GAS LIQUID REACTIONS AND DEVELOPMENT OF REACTOR: Absorption of Hydrogen Sulfide in Aqueous Ammoniacal Zinc Chloride Solution and Simulation of Spray Reaction with Drying System for Production of Dry Powdered Zinc Sulfide" being submitted by Mr. Harish Chander to Indian Institute of Technology, Delhi, for the award of Degree of Doctor of Philosophy in Chemical Engineering, is a record of bonafide research work carried out by him. Mr. Harish Chander has worked under our guidance and supervision and has fulfilled the requirements for the submission of thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for award of any degree or diploma.



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ABSTRACT

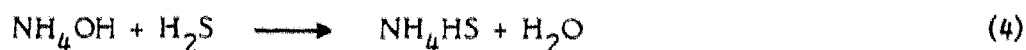
Spraying is one of the versatile operations of Chemical Engineering. It has been extensively used for drying, cooling, humidification, absorption, painting, etc. But it has been employed for absorption with chemical reaction only to a limited extent and scarcely so for drying with reaction for preparation of a chemical in dry powder form. Masters (1979) has highlighted the importance of spray reaction cum drying also known as spray dryer absorber system. Apart from the advantages like ease of operation, various savings and convenient product disposal emphasized in the above reference, the technique can help in preparation of very high purity chemicals such as zinc sulfide powder for phosphor industry without going in for contaminating operations of crushing and grinding.

The ammoniacal solution of zinc chloride is a complex chloride of zinc with ammonia in which four moles of ammonia are attached with every ion of zinc and is a product of reaction between zinc chloride and ammonium hydroxide. In the first phase of present study, the absorption of hydrogen sulfide was carried out in a glass stirred cell of 0.083 m i.d. Both gas and liquid phases were stirred with an independent stirrer. Plane horizontal gas-liquid interface was maintained with the use of a cross baffle made of glass in the liquid. Batch experiments were conducted by taking $2.5 \times 10^{-4} \text{ m}^3$ of the solution. H_2S diluted with nitrogen gas was passed through the cell at constant rate.

A model for absorption of hydrogen sulfide in the solution based on film theory has been proposed. It has been assumed that hydrogen sulfide

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upon absorption reacts instantaneously with ammonium hydroxide to give ammonium hydrogen sulfide which again reacts instantaneously with ammoniacal zinc chloride $[Zn(NH_3)_4Cl_2]$ to form zinc sulfide. The reactions are:



The expression for specific rate of absorption of hydrogen sulfide, R_{H_2S} derived on the basis of above scheme is given by,

$$R_{H_2S} = k_L [H_2S^*] \left\{ \frac{3D_{Zn(NH_3)_4Cl_2} [Zn(NH_3)_4Cl_2]_o}{D_{H_2S} [H_2S^*]} + \frac{D_{NH_4OH}}{D_{H_2S}} \frac{[NH_4OH]_o}{[H_2S^*]} + 1 \right\}$$

A series of experiments were conducted to study the effect of concentrations of hydrogen sulfide, ammonium hydroxide and ammoniacal zinc chloride on the rate of absorption. The experimental results were compared with the model and found to agree within $\pm 30\%$ of model predictions. It was concluded that the assumptions of instantaneous reactions and formation of ammonium sulfide as intermediate made for developing the model are justified. It is found that the specific rate of absorption was significantly affected by the concentration of ammonium hydroxide and ammoniacal zinc chloride. However, the influence of interfacial hydrogen sulfide concentration on specific rate of absorption was found to be marginal.

The absorption model developed in above studies is applied to a single droplet moving in a gas stream. Care has been taken to account for its varying surface area due to drying and to eliminate the term of interfacial gas concentration. A set of expressions for determining the

rate of absorption with reaction of hydrogen sulfide in a droplet is obtained. A mathematical model which incorporates mass transfer with reaction and heat, mass and momentum transfer to cover simultaneous reaction and drying has been proposed. It is assumed that gases and spray droplets move in plug flow mode and spray droplets are monodisperse for sake of keeping the calculations manageable. The relations for variation of different parameters have been written in the form of differential equations. Since the drops and gaseous medium are moving at continuously varying relative velocity, differentiation with respect to length instead of time has been used. The concentrations of species in both phases have been accounted for in dimensionless form as the ratio of amount present at any stage to the amount that was initially there in an enclosed space. Heat, mass and momentum balance equations have been developed using an approach similar to the one given by Parti and Palancz (1974). The differential equations derived have been solved as an initial value problem using Runge-Kutta method. The model has been applied to simulate the spray reactor cum dryer to produce zinc sulfide.

Experimental work was carried out in a glass spray column of 0.14m diameter and 0.65m height. Ammoniacal zinc chloride was sprayed by a pneumatic nozzle made of pyrex glass. It had four concentric glass tubes for separate flow of different species. The innermost one was for feed solution, the ammoniacal zinc chloride. Spray air, hydrogen sulfide and hot air were introduced from the other annuli respectively. The different parameters like temperature, concentration, water content and humidity were measured at inlet and outlet of the column. The model was used to compute the properties at outlet of the spray reactor cum dryer. Experimental results were compared with the model predictions and a reasonable agreement has been obtained.

A numerical example has been worked out. The variations of temperature, humidity, droplet diameter, moisture content and concentration of reactants for two cases with and without drying along the length of reactor are presented. It is observed that there is no basic difference in concentration profile of ammoniacal zinc chloride or hydrogen sulfide due to drying. The additional height of spray column required for combining drying with reaction is marginal. So, this justifies the use of a spray dryer as spray dryer cum absorber. The variation of other parameters like temperature and diameter of drop is also in order.

The model of spray reaction cum drying was then extended to include the effect of range of droplet sizes in the spray. A trend similar to monodisperse spray has been observed. Experimental results have also been compared.

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