固態硼氫化鈉之溶解擴散模式建立與操作分析

（Modeling and Operation Analysis of Concentration Boundary Layer of Solid Sodium Borohydride Dissolution Systems)

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Abstract —In this work, dissolution of solid sodium borohydride tablets in water was investigated in order to analyze the interface concentration profile between $NaBH_4$ and water. The experiment was set-up, and effluent $NaBH_4$ concentration was measured by iodine titration method. A mathematical model was built to describe the mass diffusion through the surface of the solid sodium borohydride tablet to the bulk water solution using material balance equation of $NaBH_4$. The equation of moment method was used to solve and determine the concentration boundary layer thickness which is a function of diffusivity coefficient, velocity of water in the annular space and flow distance. After determining the concentration boundary layer thickness, the profile in the concentration boundary layer can be solved by using Crank Nicolson method. The effluent average $NaBH_4$ concentration from the tube can be evaluated by simulation, and the results fitted with our experiment data. The model accurately predicted the effluent average $NaBH_4$ concentrations by varying the liquid level, the velocity in the annular space and the annular distance.

Keywords: Solid $NaBH_4$, dissolution, Concentration boundary layer thickness

1. Introduction

Much attention has been paid to the concept of using hydrogen used as an energy carrier [1]. In order to overcome the operating problems to satisfy the DOE 2015 target, solid sodium borohydride was used and can achieve 7~9 wt. % of hydrogen storage capacity. Many researchers have focused on: How to improve the catalyst, efficient use of water and testing the hydrolysis performance [2]. Before hydrolysis reaction takes place on the catalyst surface, solid sodium borohydride must dissolve and form a concentration boundary layer. The $NaBH_4$ concentration in the concentration boundary layer is difficult to measure, but it's very important to understand the profile in the concentration boundary layer of the solid sodium borohydride catalyst hydrolysis reaction. In this work, the concentration profiles in the concentration boundary layer (CBL) must be solved in order to accurately measure the reaction concentration on the catalyst surface.

2. Experimental set-up

Fig. 1 shows the dissolution systems for solid sodium borohydride tablets. Recycled water was injected into a tube with a diameter of 1.8 cm and a length of 7.7 cm. The solid sodium borohydride tablet was placed in the center of the tube. The tube was placed in a vertical manner. The size of the seven tablets was 1.5 cm (Diameter) x 1.1 cm (Thickness). The water flow rate was adjusted by a rotary pump with 1.31 ml/min volumetric flowrate. The effluent stream of the tube utilized a manual ball valve which was used to adjust the effluent flowrate and water level in the tube. When the water flow into the tube reached a desired level, the solid sodium borohydride dissolved and diffused into water.

The higher the water level; the higher the exit $NaBH_4$ concentration. Iodine titration method was use to measure the concentration of $NaBH_4$.

2.1 Experimental procedures

2.1.1 Dissolution of solid sodium boroydride

Closure of the effluent manual ball valve was ensured. The round stainless steel mesh was placed in the bottom of the tube in order to prevent: The lower tablet moving, tablets flowing out from the bottom, and obstruction of the flow path. The sodium borohydride tablets were placed in the center of the tube. The 4 wt. % NaOH solution was delivered by a rotary pump into the tube with a 1.31 ml/min flowrate. When the liquid reached a desired level, the effluent manual ball valve was opened to the specific aperture. This maintained the correct level. The effluent solution from the tube was collected by a sampling glass once every 5 mins. The procedure was repeated until complete tablet depletion.

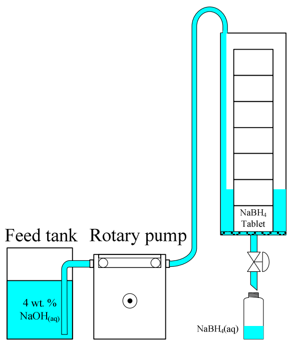

Fig. 1 Process flow diagram of solid sodium borohydride tablets dissolution systems.

2.1.1 Iodine titration method

In order to rapidly and efficiently measure the effluent $NaBH_4$ concentration from the tube, the iodine titration method was used [3]. The equations of Iodine titration are listed as follows:

$3\ BH_4^- + 4\ IO_3^- \rightarrow 4\ I^- + 3\ H_2BO_3^- + 3\ H_2O$ (1)

$4\ IO_3^- + 20\ I^- + 24\ H^+ \rightarrow 12\ I_2 + 12\ H_2O$ (2)

$12\ I_2 + 24\ S_2O_3^{-2} \rightarrow 24\ I^- + 24\ S_4O_6^{-2}$ (3)

The $NaBH_4$ reacted with excess KIO_3 which is shown in Eq. (1). The residue KIO_3 was re-activated by additional KI and H_2SO_4 to form I_2 which is shown in Eq.(2). The $Na_2S_2O_3$ was used to identify the amount of I_2. The stoiochemetric equation is shown in Eq. (3). Back calculation method was used to evaluate the unknown $NaBH_4$ concentration and is shown below:

$$NaBH_4(mg) = \frac{3}{4} M_{NaBH4}\left[KIO_3(ml)\times 0.25M - \frac{Na_2S_2O_3(ml)\times 1M}{6}\right] \quad (4)$$

where the concentration of KIO_3, $Na_2S_2O_3$ and H_2SO_4 solution are 0.25 M, 1M and 2M, respectively.

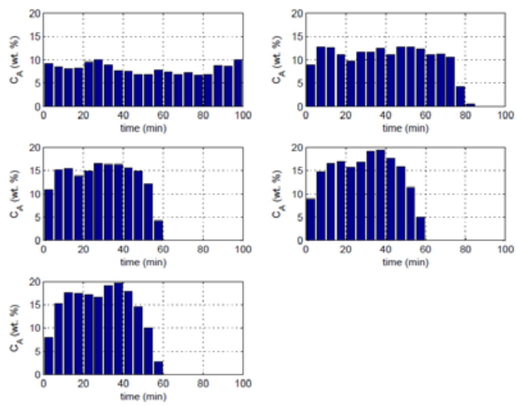

Fig. 2 The effluent $NaBH_4$ concentration effect on liquid level of the tube (a) x_h = 1 cm, (b) x_h = 2 cm, (c) x_h = 3 cm, (d) x_h = 4 cm, (e) x_h = 5 cm

2.2 Experimental result

The diameter of the tablet (D_S) and tube (D_R) are 1.5 cm and 1.8 cm, respectively. The operating temperature was fixed at 22 ± 1 ℃. The inlet volumetric flowrate of 4 wt. % NaOH solution was 1.31 ± 0.005 ml/min. The liquid was injected by a syringe and fed down the inside wall of the tube without coming into contact with the tablets by a pump until the water level rose. The effluent $NaBH_4$ concentrations with respect to time at 1, 2, 3, 4, 5 cm liquid levels are shown in Fig. 2. The effluent $NaBH_4$ concentration was initially lower because of insufficient (solid-liquid) contact time. It was stabilized and maintained at an average of 8.04, 11.90, 15.41, 17.02, and 17.43 wt. % after 10 min.

3. Modeling

In order to describe and predict the effluent $NaBH_4$ concentration, a mathematical model was built to express the $NaBH_4$ diffusion between the solid tablet and bulk water solution. When $NaBH_4$ dissolved and diffused from the surface of tablets, there is a region whose concentration gradient varies with position, called concentration boundary layer (CBL). The $NaBH_4$ concentration of the external CBL is zero.

3.2 Material balance on $NaBH_4$ in the CBL

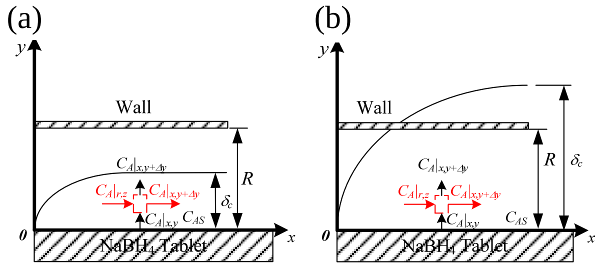

Fig.3 The illustration and notation of the dissolution tablets in the tube (a)$\delta_c < R$,(b)$\delta_c > R$.

Fig. 3 shows the conceptual diagram of the dissolved tablets in the CBL. A very small control volume was chosen to make a material balance on $NaBH_4$ (A) and the governing equation is shown below:

$$v_x \frac{\partial C_A(x,y)}{\partial x} = D_{AB} \frac{\partial^2 C_A(x,y)}{\partial y^2} \quad (5)$$

where C_A and D_{AB} are the concentration of $NaBH_4$ and diffusivity coefficient of $NaBH_4$ and water. v_x is the velocity in x direction.

To solve the Eq. (5) at steady state, we need one boundary condition in x direction and two boundary conditions in y direction.

BC1. x= 0, C_A(x=0, y)=0

BC2. y= 0, C_A (x, y=0)=C_{AS}

BC3. y=δ_C, C_A(x, y=δ_C)=0

where C_{AS} is the saturated $NaBH_4$ concentration at the desired temperature.

For our experiment, some cases may give a different situation and cause BC3. to fail when the thickness CBL is larger than the inner wall of the tube. In that case, the net $NaBH_4$ flux passing the tube wall should be set at zero. Equation should be changed and defined as:

BC3. $D_{AB} \frac{\partial C_A(x,y)}{\partial y}\Big|_{y \geq R} = 0$

In order to determine the concentration profile in the CBL, the boundary layer thickness must be found first. From boundary layer theory, the CBL is a function of velocity, diffusivity coefficient and flow distance. It's a typical moving boundary problem. The first priority is to calculate the thickness of the CBL. Then, the governing equation and boundary conditions are used to evaluate the concentration profiles in the CBL.

3.3 The thickness of the CBL

In order to find the thickness of CBL (δ_C), the equation of moment was used. The linear $NaBH_4$ concentration in y direction is assumed and shown as follows:

$$\frac{C_A(x,y)}{C_{AS}(x,y=0)} = 1 - \sin\left(\frac{\pi}{2}\frac{y}{\delta_c}\right) \quad (6)$$

Substituting BC. 2 and BC. 3 into Eq. (6), we can calculate the unknown constants a, b and the values are 1 and -1, respectively.

At steady-state, the Eq. (5) can be rearranged and integrated both side of the equation. The separation variable method was used to solve the equation and the thickness of the CBL can be represented as:

$$\delta_C(x) = \sqrt{\frac{D_{AB} x \pi}{v_x}\left(\frac{1}{1-2/\pi}\right)} \quad (7)$$

After determining the concentration boundary thickness of CBL, the concentration profile can be solved by using Eq. (5). Crank Nicolson method was used to solve the concentration profile in the CBL. The problem is solved by using MATLAB program.

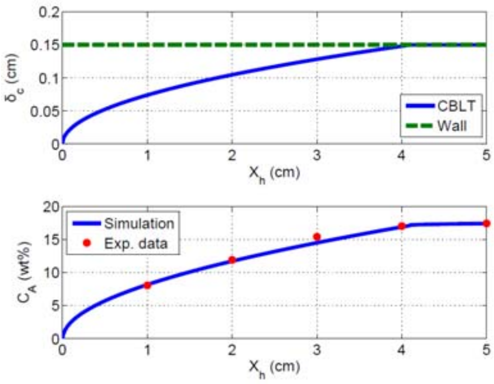

Fig. 4 (a) The concentration boundary layer thickness, (b) the average effluent $NaBH_4$ concentration with respect to liquid level high.

4. Model prediction

In order to verify the accuracy of the model, liquid level (x_h) was investigated. Fig. 4(a) shows the thickness of CBL with respect to flow distance (x). Here, x denotes the internal travel distance in the liquid level (x_h). There are two regions in the CBL with respect to x. One is the thickness of CBL≦annular distance (R). The other is the thickness of CBL＞annular distance. The thickness of CBL is developed from zero at the tube entrance (at x=0) and grows with flow distance, it can be determined by Eq. (7). When the thickness of CBL is greater the annular distance, there is no $NaBH_4$ flux passing through the wall. That means the $NaBH_4$ concentration at y=R is kept constant, this can be seen in Fig. 4(a) at $x_h \geqq$ 4.2 cm. Fig. 4(b) shows the effluent $NaBH_4$ average concentration with respect to liquid level (x_h). The average $NaBH_4$ concentration in the tube exit can be evaluated from:

$$\overline{C}_A(x) = \frac{\int_{R_1}^{R_2} 2\pi r C_A(r)dr}{A_T} \quad (8)$$

where $\overline{C}_A$ is the effluent average $NaBH_4$ concentration. The experimental average $NaBH_4$ concentrations at the tube exit were measured and the data was taken which is shown in Fig. 2. The absolute relative errors of average $NaBH_4$ concentration in the tube exit between simulation result and experimental data of liquid levels from 1 to 5 cm were 2.33, 3.61, 1.09, 2.75, and 2.47 %, respectively. All the experimental data fitted with our simulation result.

5. Conclusion

In this work, dissolution of solid sodium borohydride tablets in water was investigated in order to analyze the interface concentration profile between $NaBH_4$ and water. The result shows that the concentration boundary layer thickness is function of diffusivity coefficient, velocity and flow distant. The governing equation in the CBL was used to describe the concentration profile. The simulation result was confirmed with experiment data.

6. Reference

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