COMPLEX REACTIONS SENSITIVITY TO DIFFERENT FACTORS: 
NUMERICAL INVESTIGATION OF MoS$_2$ REDUCTION BY HYDROGEN IN LIME PRESENCE

M. Mehdi Afsahi$^1$, Bahador Abolpour$^{1,2}$

$^1$Department of Chemical Engineering
Shahid Bahonar University of Kerman
Kerman 76175, Iran
E-mail: mmafsahi@gmail.com
$^2$Department of Chemical Engineering
Sirjan University of Technology
Sirjan, Iran

ABSTRACT

Hydrogen diffusion and the subsequent reduction of porous pellets of solid molybdenum disulfide in presence of lime are treated as a complex reaction in the temperature range from 1173 K to 1373 K. The continuity and energy balance equations referring to the temperature and concentration profiles in the pellet are simultaneously solved. The dusty gas flux model is used to describe the diffusing gas transport. The structural changes in the course of the reaction are accounted for by considering the effect of the particle radius change on porosity. It is found that, in this case, the structural changes and the non-isothermal reaction proceeding do not essentially affect the solid conversions and the sulfur fixation. The effects of the pellet and grain specification, the operating temperature and the reactant gas concentration in the bulk stream are also evaluated on the ground of the simulation results obtained.

Keywords: complex reactions, simulation, molybdenum, molybdenum disulfide, lime.

INTRODUCTION

Many of the industrially important systems follow complex reaction schemes whose modeling is difficult. A complex version of a reaction of two solid components of a pellet occurs in hydrogen reduction of metal sulfide in the presence of lime. Here the gaseous product of the first reaction reacts with another solid component. In these types of reactions the kinetics of both reactions should be studied independently, and then these data should be used to model the overall process.

Sohn and Rajamani [1] propose a model for successive gas-solid reaction of this type. It can be used to determine the optimum structure of the pellet and to provide a useful guideline for the design of experimental investigations of these reactions. Fahim et al. [2] propose a model for metal sulfide reduction in presence of CaO. There the pellet is assumed to consist of CaO and Me$_x$S grains, where Me represents a metallic element. The Me$_x$S grains are treated as nonporous, while CaO grains are accepted being porous. Further each grain of CaO is assumed to consist of spherical non-porous sub-grains. The equations of this model are numerically solved and compared with experimental results in a subsequent paper by Fahim and Ford [3].

Afsahi et al. [4] propose a mathematical model of hydrogen reduction by molybdenum disulphide in presence of lime in accordance with the reactions:

$$\frac{1}{2}MoS_2(s) + H_2(g) \leftrightarrow \frac{1}{2}Mo(s) + H_2S(g)$$ (1)

$$CaO(s) + H_2S(g) \leftrightarrow CaS(s) + H_2O(g)$$ (2)

$$\frac{1}{2}MoS_2(s) + CaO(s) + H_2(g) \leftrightarrow \frac{1}{2}Mo(s) + +CaS(s) + H_2O(g)$$ (3)

They model this reaction following that of Sohn and Won [5], i.e. without investigating the effects of
the structural changes and the non-isothermal reactions proceeding. Abolpour et al. [6] present a fuzzy logic model for lime-enhanced hydrogen reduction by cuprous sulfide. They find a well-defined relationship between the vital variables, i.e. the bulk temperature, the ratio of the molar quantities of the solid reactants, the pellet diameter, the porosity, the sulfide particle size, the weight loss of the pellet, the sulfur fixation in the pellet, and the reaction completion time.

The present paper reports data referring to the effects of the structural changes, the non-isothermal reactions proceeding and other factors like the pellet and grain specification, the system temperature and the reactant gas concentration in the bulk stream on reaction (3) given above in the temperature range from 1173 K to 1373 K.

Mathematical Modeling

The present model considers a porous pellet of a volume \( V_p \) and a superficial surface area \( A_p \) composed of a mixture of molybdenum disulfide (grains B) and lime (subgrains D) particles. This pellet is immersed in a stream of a gas mixture containing hydrogen (reducing agent A). A complex gas-solid reaction of type (3) is occurring in the pellet. Hydrogen diffuses between the solid particles and reacts with molybdenum disulfide to give hydrogen sulfide (gas C) as a product. The latter diffuses back and reacts with lime and water vapor (gas E). Then the water vapor and hydrogen sulfide left unconsumed exit from the pellet. The gas-solid reactions (1-2) can be presented in the general form:

\[
A(g) + bB(s) \leftrightarrow cC(g) + fF(s) \quad (4)
\]

\[
C(g) + dD(s) \leftrightarrow eE(g) + gG(s) \quad (5)
\]

The following assumptions and considerations are taken into consideration to develop of the mathematical model:

1. The reactions are irreversible and take place at constant pressure.
2. The gaseous reactant A is presented as a dilute component in an inert gas (argon in this work).
3. The reduction of molybdenum disulfide by hydrogen follows the nucleation and growth kinetics, while the reaction of hydrogen sulfide with lime is described by the pore-blocking model [7, 8].
4. The gaseous species concentration is pseudo-steady within the pellet [9, 10].
5. Reactions (1) and (3) are endothermic, while reaction (2) is exothermic.
6. The pellet is porous and has a regular geometrical shape of a sphere, a cylinder and a plate, with the pellet shape factor \( F_p \) equal to 1, 2 and 3, respectively.
7. The pellet is made of a uniform mixture of non-porous grains B and porous grains D which are made of nonporous subgrains.
8. Grains B and subgrains D have a regular geometrical shape of a sphere, a cylinder and a plate, with \( F_B \) or \( F_D \) equal to 1, 2 and 3, respectively.
9. Grains B and subgrains D are very small. Therefore the temperature gradients in these grains and subgrains can be neglected.
10. A rapid mass transfer takes place between the external surface of the pellet and the bulk stream. Therefore the diffusional resistance exerted by the bulk of the gas flow to the pellet surface can be neglected. This assumption simplifies the boundary conditions.
11. These reactions can shrink or swell grains B and subgrains D. In other words, the dimensions of grains B or subgrains D are changed due to the difference in the products and reactants molar volume. Therefore the pellet porosity and also the effective diffusion of the reactant gas in the pellet can be changed.

The present model is developed in one-dimensional geometry. The distance from the center of pellet (H) and the time (t) are independent variables. However, dimensionless equations which are functions of the dimensionless position in the pellet \( \eta = \frac{A_p H}{F_p V_p} \) and the dimensionless time \( t^* = b k_1 \left( C_{ab} - C_{cb} \right) t \) can be approached. \( C_{ab} \) and \( C_{cb} \) are the concentrations of gases A and C in the bulk, respectively. The conservation of the gaseous species equations and the energy in the pellet can be presented in dimensionless forms as follows [4]:

\[
\nabla^2 \psi_A - 2F_p \delta^2 B \left( 1 - \omega_b \right) \psi_A + \frac{2F_p \delta^2 B \lambda}{\exp \left( \frac{\omega_b}{2} \right)} \left[ \frac{K_2}{K_1(1 + K_1)} \right] \psi_C = 0 \quad (6)
\]

\[
\nabla^2 \psi_C - \frac{2F_p \delta^2 B \lambda}{\exp \left( \frac{\omega_b}{2} \right)} \psi_C + 2F_p \delta^2 B \left( 1 - \omega_b \right) \left[ \frac{K_1}{1 + K_1} \right] \psi_A = 0 \quad (7)
\]
\[
\frac{\partial \omega_B}{\partial t} = (1 - \omega_B) \psi_A
\]  
\[
\frac{\partial \omega_D}{\partial t} = \frac{\beta \lambda}{\exp(\frac{\omega_D}{\lambda})} \psi_C
\]
\[
\nabla^2 \theta - \xi \nabla^2 \theta + \xi \sigma_B (1 - \omega_B) \psi_A + \xi \beta \lambda \sigma_B \exp\left(\frac{\omega_D}{\lambda}\right) \psi_C = 0
\]  
\[
\frac{\partial \omega}{\partial t} = 0, \quad \theta = 1 \quad \text{at} \quad \eta = 0
\]

where \( \beta \) is the ratio of the reactivities of solids D and B (\( \beta = \frac{dk_B}{bk_D} \)), \( \lambda \) is the inverse of pore-blocking rate constant [7], \( \xi \) is the ratio of the one order rate of reaction (1) to the one dimensional effective heat diffusivity in the pellet

\[
(\xi = \frac{bk_1}{\alpha_e} \left( C_{Ab} - C_{Ch} \right) \left( \frac{A_p}{p_f p_p} \right)^{-2})
\]

\( \theta \) is the dimensionless temperature (\( \theta = \frac{T}{T_B} \)), \( \sigma_B \) and \( \sigma_D \) are the heat modulus for solid B and D (\( \sigma_B = -\frac{a_B \rho_B \Delta H_1}{b \rho_e T_B} \) and \( \sigma_D = \frac{\sigma_B \Delta H_2}{\Delta H_1} \)), \( \delta_b \) and \( \delta_D \) are the generalized gas-solid reaction moduls for solids B and D (\( \delta_B = \frac{V_p}{A_p} \left[ \frac{\sigma_B \rho_B F_p k_1}{2 D_e} \left( 1 + \frac{1}{K_1} \right) \right]^{1/2} \)) and \( \delta_D = \gamma \beta_2 \left[ \frac{k_1}{k_2} \left( 1 + k_2 \right) \left( 1 + \frac{1}{K_1} \right) \right] \), \( K_1 \) and \( K_2 \) are the equilibrium constants for reaction (4) and (5), \( \psi_A \) and \( \psi_C \) are dimensionless concentrations of gases A and C (\( \psi_A = \left( C_A - C_{Ch} \right) \left( \frac{C_{Ab}}{C_{Ch}} \right)^{-1} \) and \( \psi_C = \left( C_C - C_{Ch} \right) \left( \frac{C_A}{C_{Ch}} \right)^{-1} \)), while \( \omega_B \) and \( \omega_D \) are local values of the fractional conversions of solid reactants B and D, respectively. \( C_x, C_y, C_z \) and \( C_C \) are concentrations of gases A, C, and E, \( k_1 \) and \( k_2 \) are the reaction rate constants for reactions (4) and (5), \( a_B \) and \( a_D \) are the fractions of the pellet volume initially occupied by solids B and D, while \( \Delta H_1 \) and \( \Delta H_2 \) are the heats of reactions (1) and (2), respectively.

\( \nabla^2 \) is the Laplacian operator with \( \eta \) as the position coordinate, \( \psi \) is the reaction modulus \( (\psi_B = 1, \psi_C = 0, \theta = 1 \quad \text{at} \quad \eta = 1) \) and \( \omega_B = 0, \theta = 1 \quad \text{at} \quad \eta = 0 \).

It should be noted that, the radius of solid grains B and subgrains D undergo significant changes upon reaction \( (r_B = \rho_B \left( \frac{F_B - F_F D}{\rho_B} \right) + F_D) \) and \( r_D = \rho_B \left( \frac{F_D D}{\rho_B} \right) + F_F \)), because the solid reactants and products have different densities. It is worthy adding that \( \rho_B, \rho_C, \rho_B, \rho_D \) and \( \rho_F \) are the true molar densities of solids B, D, G, F. While \( r_B \) and \( r_D \) refer to the radial position of unreacted cores of solid grain B and subgrains D \( (r_B = r_B (1 - X_B r_B)) \) and \( r_D = r_D (1 - X_D r_D) \), respectively. Assuming a constant porosity of the grains in MoS\(_2\) pellet, the final intragran porosity of solid \( \eta \) can be obtained from final and initial pellet porosity difference equal to 0.267 [8]. The molar density of solid CaO is greater than that of CaS. Therefore, the final intrasubgran porosity of solid \( \eta \) is zero.

If the solid product occupies a larger volume in compression with that of the reactant, the porosity will decrease by the conversion progressing and can bring the reaction to an end prior to its completion. On the other hand, if the solid product occupies a smaller volume in comparison with that of the reactant, the porosity will increase by the conversion progressing leading thus to a faster reaction. The change in the pellet porosity \( (\varphi = 1 - \rho_B) \) is accompanied by a change in the effective diffusivity of the gases in the pellet \( (D_e = \varphi (D_{H_2} - D_{H_2O}) + D_k^{-1}) \), where \( D_{H_2}, D_{H_2O} \) and \( D_k \) are the molecular and Knudsen diffusivities, respectively.

Usually there is no analytical solution for non-isothermal systems. Simple approximate solutions are possible under certain circumstances. When the movement of the gaseous component from the external surface toward the center of the pellet is very slow (i.e. the concentration profile corresponds to the pseudo-steady
state profile), the rate of diffusion of the reactants across a boundary normal to the diffusion path is equal to the rate of reaction within the boundary. Consequently, an analytical solution in respect to the temperature profile in the pellet (\( T = T_p + \frac{D}{\varepsilon C_p} (\Delta H_1 + \Delta H_2) \left( C_A - C_{Ab} \right) \)) is possible [11] by assuming pseudo-steady state conditions for the heat conductions in the pellet and using assumption (10).

A program code is written in MATLAB software and a brief explanation of the different sections of this program code is presented in this section. The data required for the program refers to the state of the governing equation, the initial and boundary conditions, the grain and pellet specifications, the operating conditions, the physical property of the carrier gas, the reaction components and products and the stoichiometric coefficients. This was the input data for the program code developed. Then parameters like the initial porosity (\( \epsilon_0 \)) and tortuosity, the initial effective gas diffusivity in the pellet, the effective heat capacity (\( C_{pe} \)), the thermal conductivity (\( k_e \)) of the pellet and the bulk concentration of reducing gas are calculated. The chemical reactions rate functions and the mass and heat balances equations in the pellet are further numerically solved using the corresponding initial and boundary conditions. Aiming this, coefficients matrices are defined following the finite volume technique. Then the algebraic sets of equations are solved using the matrix operation facilities of MATLAB.

Finally, the solids conversion

\[
X_B = \frac{\int_{0}^{1} \alpha_B \eta^F \rho^{-1} d\eta}{\int_{0}^{1} \alpha_B \eta^F d\eta} \quad \text{and} \quad X_D = \frac{\int_{0}^{1} \alpha_D \eta^F \rho^{-1} d\eta}{\int_{0}^{1} \alpha_D \eta^F d\eta}
\]

and the corresponding structural changes, are calculated in a loop until reaching a conversion.

RESULTS AND DISCUSSION

The validation of this model was previously done by Afsahi et al. [4]. They get an acceptable variation of the model predications from experimental data.

Effects of the structural change and the non-isothermal reaction proceeding

Fig. 1 compares the temperature profiles calculated by the numerical and analytical solutions used in this study. They show a good agreement. The direct hydrogen reduction of MoS\(_2\) in lime presence is endothermic. This is the cause of temperature decrease in the pellet in the initial moments of the reaction duration. After this period of time, the temperature of the pellet increases to the bulk temperature because of reaction rate decrease determined by decrease of the solid reactants content.

Fig. 2 shows the parameters affected by the structural change and the non-isothermal reaction proceeding in a 5 mm thick slab like pellet of 50 % initial porosity and \( \gamma = 3 \). It contains spherical grains B and subgrains D of 1 \( \mu \)m and 0.05 \( \mu \)m initial radiuses (\( r_{B0}, r_{D0} \)), respectively. The effects of these parameters are visualized in Fig. 3. It is seen that the structural change and the non-isothermal reaction proceeding have an inconsiderable effects on the solids conversion and the sulfur fixation (i.e. a fraction of gas C captured by solid D is defined as: \( F = \gamma \frac{X_D}{X_B} \) ) in the pellet.

Effects of different factors

The temperature effect on MoS\(_2\) reduction in presence of lime is shown in Fig. 4. It is evident that the fractions of MoS\(_2\) and CaO participated in the reaction are greatly affected by the temperature. Solids B and D conversion increases with temperature increase, i.e. the reaction rate grows with temperature increase. This results in sulfur fixation increase as well.

Fig. 5 shows the model predictions of solids B and D conversion in pellets of different initial porosities. The latter increase brings about higher molybdenum disulfide
Fig. 2. Profiles of hydrogen, hydrogen sulfide and water vapor gases concentrations, of unreacted core radius of solid grains B and subgrains D, porosity, radius of solid grains B and subgrains D, and effective diffusivity in a slab like pellet undergoing an endothermic reaction and a structural change.

Fig. 3. Evaluated effects of the structural change and the non-isothermal reaction proceeding.

Fig. 4. Temperature effect on the model predictions of solids conversion and sulfur fixation.

Fig. 5. Initial pellet porosity effect on the model predictions of solids conversion and sulfur fixation.

Fig. 6. Effect of the solid mixing ratio on the model predictions of solids conversion and sulfur fixation.
conversion through increase of hydrogen diffusion rate. But, the pellet porosity increase results in sulfur fixation decrease. This is due to the relatively fast diffusion of hydrogen sulfide in pellets of greater porosity.

Fig. 6 shows the effect of solid mixing ratio on the model predictions of solids conversion and sulfur fixation. The increase of the solids mixing ratio ($\gamma = b a D \rho D (da B \rho B)^{-1}$) increases the sulfur fixation in the pellet and the conversion of solid B. It is observed that a large fraction of hydrogen sulfide may escape from the pellet without any reaction in case $\gamma = 1$. An optimum mixing ratio is required. Furthermore, the excess lime acting as essentially inert filler slows down the overall rate of the reaction per unit mass of sulfide.

Fig. 7 shows the effect of hydrogen purity in the bulk stream on the model predictions of solids conversion and sulfur fixation. As shown in this figure, the increase of hydrogen purity results in a higher conversion of molybdenum disulfide, because reaction (1) is a first order reaction with respect to hydrogen concentration. This dependency of reaction (1) on hydrogen concentration leads to decrease of sulfur fixation through increase of the hydrogen concentration in the bulk stream.

Figs. 8 and 9 show the effects of pellet size and shape on the model predictions of solids conversion and sulfur fixation. As the resistance to intrapellet diffusion is increased with pellet size increase, the conversion of solid B is decreased but the conversion of solid D and sulfur fixation are increased. A slab like pellet shows the lowest conversion of solid B, the highest conversion of solid D and the highest sulfur fixation. The effects in case of spherical and cylindrical pellets are relatively small.

Fig. 7. Effect of hydrogen purity in the bulk stream on the model predictions of solids conversion and sulfur fixation.

Fig. 8. Effect of the pellet size on the model predictions of solids conversion and sulfur fixation.

Fig. 9. Effect of the pellet shape on the model predictions of solids conversion and sulfur fixation.

Fig. 10. Effect of the initial radius of grains B on the model predictions of solids conversion and sulfur fixation.
Figs. 10 to 13 show the effects of the shape and initial radiuses of grains B and subgrains D on the model predictions of solids conversion and sulfur fixation. Since solid B has a small volume fraction in the pellet in case $\gamma = 3$, the size and shape of grains B have a low effect on the reactions. The conversion of solid B is decreased, while the conversion of solid D and the sulfur fixation are increased with increasing the initial radius of subgrains D. A slab like subgrains D causes the highest conversion of solid B, the lowest conversion of solid D and the lowest sulfur fixation. The effect are relatively small in case of spherical and cylindrical subgrains D.

**CONCLUSIONS**

The present work advances a mathematical model of description of a complex reaction occurring in a porous pellet. It is applied to molybdenum disulfide reduction by hydrogen in presence of lime. The formulation accounts for the influence of structural changes, a non-isothermal reaction proceeding, pellet and grain specifications, system temperature and reactant gas concentration in the bulk stream.

It is found that the structural changes and the non-isothermal behavior of the reactions proceeding have low effects on the solids conversion and sulfur fixation in the pellet. The size and the geometrical shape of grains B have also no effects on the results. This is not the case with subgrains D. The increase of the temperature, the solids molar mixing ratio, the initial pellet porosity, the hydrogen concentration in the bulk stream, and the decrease of the pellet thickness increase the conversion of solid B, decrease the conversion of solid D and decrease the sulfur fixation in the pellet. It is also found that a slab like pellet provides the lowest conversion of solid B, the highest conversion of solid D and the highest sulfur fixation. The effects observed in case of spherical and cylindrical pellets are relatively small.

The model provides to determine the properties of an optimum pellet and the optimum operating conditions on the ground of a minimum number of experiments. The results obtained can be used for further scale-up applications.

**REFERENCES**

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