

# A NEW APPROXIMATE SOLUTION TECHNIQUE (QUANTIZED METHOD) FOR SIMULTANEOUS GAS-SOLID REACTIONS

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**Abstract** Simultaneous reactions between solids and gases are very important in the chemical and metallurgical processes. In the modeling, the chemical reaction and diffusion of gases must be considered. Therefore, a set of coupled partial differential equations is found. When the kinetic is a function of solid concentration, there is not any analytical solution for these equations. Therefore, numerical or approximate solutions have been used. In this paper a new approximate method has been developed for solution of two gases-one solid reaction equations. This technique offers some new mathematical expressions for rapid calculations. The results of this method are compared with the existing solutions. The quantized solution shows a better accuracy than other approximate method.

**Key Words** New Approximate Solution, Simultaneous, Gas-solid Reactions

**چکیده** واکنشهای چندگانه بین جامدات و گازها در فرآیندهای شیمیایی و متالورژیکی اهمیت زیادی دارند. مدل سازی این واکنشها منجر به یک سری معادلات دیفرانسیل جزئی کوپل شده با هم می شود. وقتی سینتیک تابعی از غلظت جامد باشد، به علت پیچیدگی ریاضی این معادلات حل تحلیلی ندارند. بنابراین روشهای عددی و یا تقریبی برای حل آنها بکار رفته است. در این مقاله یک روش جدید تقریبی برای حل معادلات واکنشهای دو گاز با یک جامد ارائه شده است. این روش روابط ریاضی جدیدی برای محاسبات سریع بدست می دهد. نتایج این روش با روشهای آنالیز عددی و تقریبی موجود مقایسه شده و دقت بهتری نسبت به روش تقریبی نشان می دهد.

## INTRODUCTION

Gas-solid reactions are important in many chemical and metallurgical process industries. However in many industrial operations, more than one reaction can take place simultaneously. Because the gas (or solid) contains multiple reactants, or the products of the reaction are reactive with the solid. For example Spitzer, et al., [1] studied the reduction of hematite with hydrogen which shows a consecutive reaction with respect to solid. Similarly, Tseng, et al., considered the reactions of iron sulfide with  $O_2+SO_2$  which is a consecutive reaction with respect to gases.

Sometime two different gases are used to react with one solid. For example in reduction of hematite, the mixture of  $CO+H_2$  is used. Tsay, et al., [3] present a shrinking core model for this problem, while the effect of the internal diffusion has been studied by Sohn & Braun [4].

Reactions of two solids with a gas have been studied by Ramachandran, et. al., [5] for coke oxidation from catalyst pellets. Szekely & Hastaoglu [6] studied the reduction of  $NiO-Fe_2O_3$  mixture with hydrogen. Karwan & Kotula [7] also studied the reduction of  $ZnO-PbO$  mixture with carbon monoxide.

Reaction of a gaseous product with the second solid, which is important in treatment of sulfide minerals in presence of lime, has been considered by

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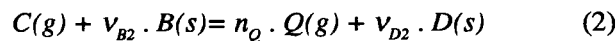
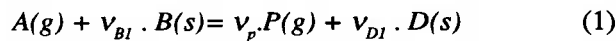
Bartlett & Haung [8], Sohn & Rajamani [9], and Fahim, et al. [10].

Wen & Wei [11], and Rehmat & Saxena [12] studied the problem of simultaneous gas-solid reactions based on nonisothermal shrinking core model. However for pellets of considerable initial porosity Sohn & Braun [4], Sohn & Rajamani [9], and Tone & Wen [13] presented a more general model.

In this work, the reaction of two gases with a porous solid pellet is considered. A new approximate solution technique is proposed for solving related coupled partial differential equations. The results of this technique are compared with the numerical and approximate solutions of Sohn & Braun [4].

### MATHEMATICAL MODEL

The reaction between a porous solid and two gaseous reactants can be represented as:



These reactions are important in direct reduction of iron oxide by reformed natural gas.

For a single porous pellet we have the following assumptions.

- 1- The system is isothermal.
- 2- The pellet size and its porosity do not change during the reaction. Thus, we have a constant effective diffusivity.
- 3- The reaction is reversible and first order with respect to gaseous reactants.
- 4- The pseudo-steady state approximation is valid.
- 5- There is an equimolar counter-diffusion.

The general dimensionless conservation equations of gaseous reactants are given by Sohn & Braun

[4]. These equations are as follows:

$$\frac{\partial^2 \psi_A}{\partial y^2} + \frac{F_P - 1}{y} \frac{\partial \psi_A}{\partial y} = -2F_P \cdot \hat{\sigma}_A^2 \cdot \frac{\psi_A}{f'(b)} \quad (3)$$

$$\frac{\partial^2 \psi_C}{\partial y^2} + \frac{F_P - 1}{y} \frac{\partial \psi_C}{\partial y} = -2F_P \cdot \hat{\sigma}_C^2 \cdot \frac{\psi_C}{f'(b)} \quad (4)$$

With boundary conditions:

$$y=0 \quad \frac{\partial \psi_A}{\partial y} = \frac{\partial \psi_C}{\partial y} = 0 \quad (5)$$

$$y=1 \quad \frac{\partial \psi_A}{\partial y} = Sh^* (\psi_{Ab} - \psi_A) \quad (6)$$

$$y=1 \quad \frac{\partial \psi_C}{\partial y} = Sh^* (\psi_{Cb} - \psi_C) \quad (7)$$

Dimensionless quantities are defined in the nomenclature, and we have:

$$f'(b) = \frac{\partial f(b)}{\partial b} \quad (8)$$

$$f(b) = [-\ln(b)]^{1/h} \quad (9)$$

For the solid reactant, describing equations are:

$$\frac{\partial b}{\partial \theta} = \frac{\psi_A + \psi_C}{f'(b)} \quad (10)$$

$$\frac{\partial b_A}{\partial \theta} = \frac{\psi_A}{f'(b)} \quad (11)$$

With an initial condition:

$$\theta = 0 \quad ; \quad b = b_A = 1 \quad (12)$$

These coupled partial differential equations must

be solved numerically. An approximate solution based on the law of addition of the reaction and diffusion times has also been presented [4].

### QUANTIZED SOLUTION TECHNIQUE

For  $n = 1$  we have:

$$f(b) = -\ln(b) \text{ or } f'(b) = -1/b \quad (13)$$

For spherical pellets ( $Fp = 3$ ), negligible external mass transfer resistance ( $Sh^* = \infty$ ) model equations are simplified to:

$$\frac{\partial^2 \psi_A}{\partial y^2} + \frac{2}{y} \frac{\partial \psi_A}{\partial y} = 6 \hat{\sigma}_A^2 \cdot b \cdot \psi_A \quad (14)$$

$$\frac{\partial^2 \psi_C}{\partial y^2} + \frac{2}{y} \frac{\partial \psi_C}{\partial y} = 6 \hat{\sigma}_C^2 \cdot b \cdot \psi_C \quad (15)$$

$$\frac{\partial b}{\partial \theta} = -(\psi_A + \psi_C) \cdot b \quad (16)$$

$$\frac{\partial b_A}{\partial \theta} = -\psi_A \cdot b \quad (17)$$

The boundary Conditions 6 and 7 are also reduced to:

$$y=1 \quad \psi_A = \psi_{Ab} \quad (18)$$

$$y=1 \quad \psi_C = \psi_{Cb} \quad (19)$$

The quantized or incremental solution technique has been given in [14] and [15]. The outcome of the quantized technique is as follows.

The variable "b" in the right hand side of the Equations 14 and 15 will be treated as a constant, between two small time increments. By this assumption some errors are expected. In the following section it will be shown that these errors are small. By using the quantized assumption we can

define, the new modified and variable Thiele moduli as:

$$M_A = \sqrt{6 \hat{\sigma}_A^2 \cdot b} \quad (20)$$

$$M_C = \sqrt{6 \hat{\sigma}_C^2 \cdot b} \quad (21)$$

Inserting Equations 20 and 21 to Equations 14 and 15 gives:

$$\frac{\partial^2 \psi_A}{\partial y^2} + \frac{2}{y} \frac{\partial \psi_A}{\partial y} = M_A^2 \cdot \psi_A \quad (22)$$

$$\frac{\partial^2 \psi_C}{\partial y^2} + \frac{2}{y} \frac{\partial \psi_C}{\partial y} = M_C^2 \cdot \psi_C \quad (23)$$

Using the above assumption, the Equations 22 and 23 are not any more coupled. Their integration with boundary Conditions 5, 18 and 19 gives:

$$\psi_A = \psi_{Ab} \frac{\sinh(M_A \cdot y)}{y \cdot \sinh(M_A)} \quad (24)$$

$$\psi_C = \psi_{Cb} \frac{\sinh(M_C \cdot y)}{y \cdot \sinh(M_C)} \quad (25)$$

Inserting Equations 24 and 25 to Equation 16 and integration with the initial Condition 12 gives:

$$b = \exp [-(\psi_A + \psi_C) \cdot \theta] \quad (26)$$

Equation 26 seems to be an implicit one. But in this technique it is assumed that the "b" in the  $M_A$  and  $M_C$  is constant for two small time increments. Therefore, we can replace the "b" in the  $M_A$  and  $M_C$  with "b" which has been calculated before.

The Equations 24-26 show the concentration profiles of gases and solid, and from these equations we can compute "b" at each time and position. Then from Equations 20 and 21 we can compute the new  $M_A$  and

$M_C$  from "b" at the same position but at past time increment.

Now by replacing the Equation 26 in 17 and integrating with the initial Condition 12 we have:

$$1 - b_A = \frac{\psi_A}{\psi_A + \psi_C} (1 - \exp [-(\psi_A + \psi_C) \cdot \theta]) \quad (27)$$

The above equation is the amount of solid reaction due to gas "A". The conversion of the solid at each time can be calculated from:

$$X = 1 - 3 \int_0^1 b \cdot y^2 \cdot dy \quad (28)$$

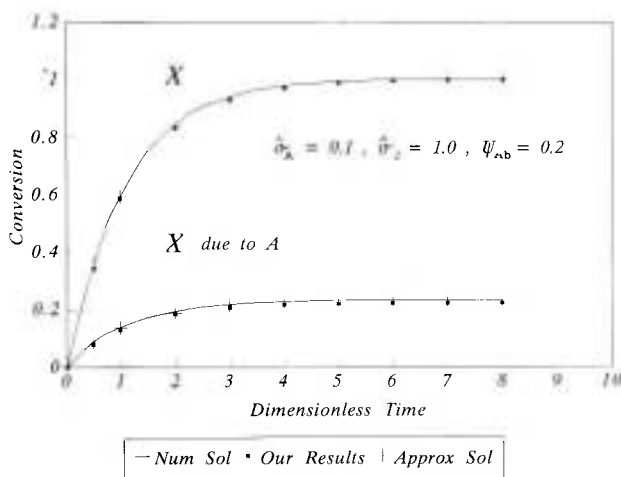
and the conversion due to gas "A" can be calculated from:

$$X_A = 1 - 3 \int_0^1 b_A \cdot y^2 \cdot dy \quad (29)$$

Finally, overall selectivity of system can be calculated from:

$$S_0 = \frac{X_A}{X - X_A} \quad (30)$$

Our solution technique is developed for the case



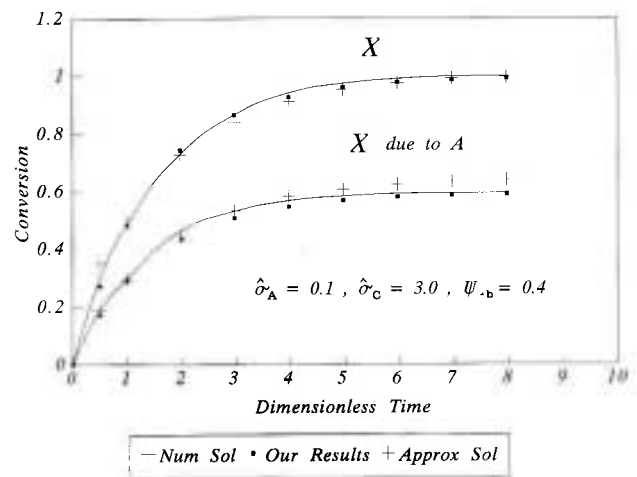
**Figure 1.** Comparison of our results with numerical and approximate solutions of Sohn & Braun [4], for conversion-time behavior at a small value of  $\hat{\sigma}_A$  and an intermediate value of  $\hat{\sigma}_C$ .

where both the diffusion and chemical reactions are important. But when "b" becomes small by the progress of reactions, the modified moduli  $M_A$  and  $M_C$  also become small even for high original moduli  $\hat{\sigma}_A$  and  $\hat{\sigma}_C$  (diffusion control regime). However, with small  $M_A$  and  $M_C$  the process is controlled by the reaction, and the diffusion is not important anymore. To avoid this difficulty we use the same technique as it is used by Evans and Ranade [16] for adjusting their own approximate solution. In this technique the approximate solution is compared with the numerical solution. Then the parameters of the approximate solution are adjusted. In this work this technique shows that the value of "b" in the calculation of  $M_A$  and  $M_C$  should not be less than 0.4.

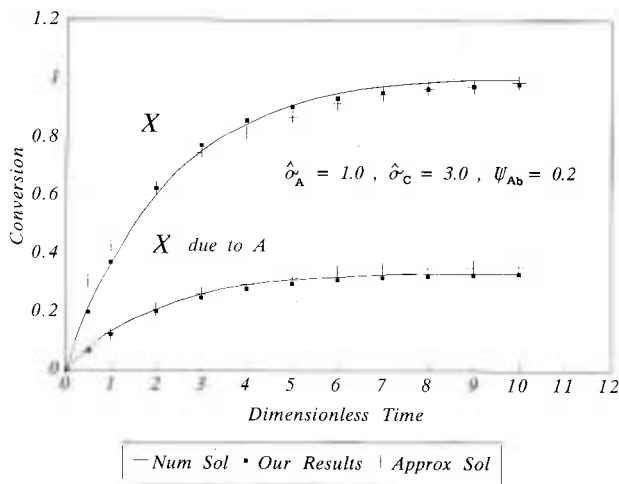
By this method we get reasonable results as will be presented in the following section.

## CONCLUSIONS

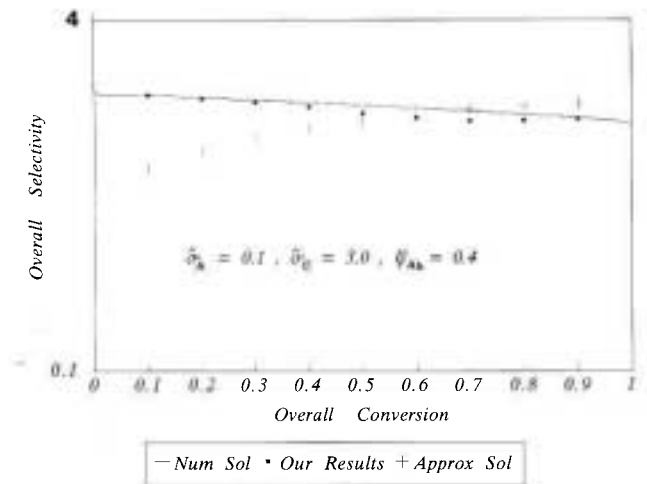
In this work the coupled partial differential equations of simultaneous reactions are solved using a new approximate solution called quantized method. The predicted conversion-time behaviors are compared with the numerical and the approximate solutions of



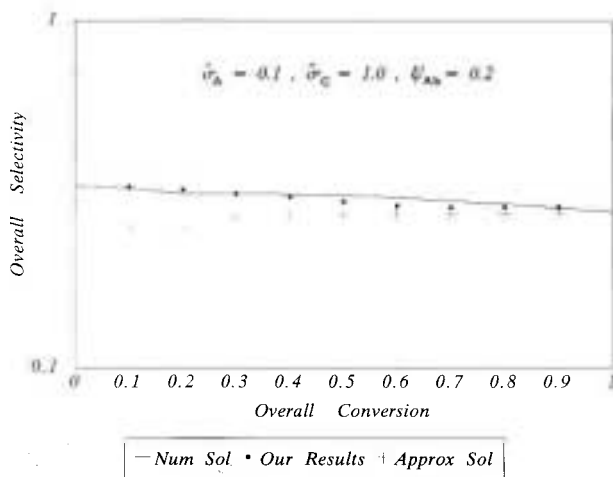
**Figure 2.** Comparison of our results with numerical and approximate solutions of Sohn & Braun [4], for conversion-time behavior at a small value of  $\hat{\sigma}_A$  and a large value of  $\hat{\sigma}_C$ .



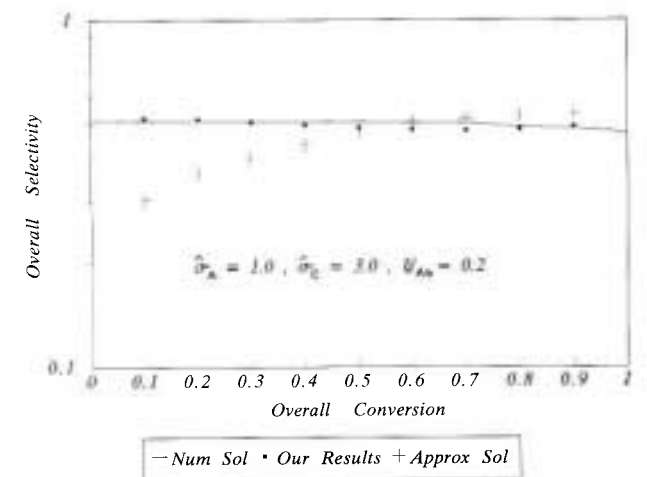
**Figure 3.** Comparison of our results with numerical and approximate solutions of Sohn & Braun [4], for conversion-time behavior at an intermediate value of  $\hat{\sigma}_A$  and a large value of  $\hat{\sigma}_C$ .



**Figure 5.** Comparison of our results with numerical and approximate solutions of Sohn & Braun [4], for overall selectivity at a small value of  $\hat{\sigma}_A$  and a large value of  $\hat{\sigma}_C$ .



**Figure 4.** Comparison of our results with numerical and approximate solutions of Sohn & Braun [4], for overall selectivity at a small value of  $\hat{\sigma}_A$  and an intermediate value of  $\hat{\sigma}_C$ .



**Figure 6.** Comparison of our results with numerical and approximate solutions of Sohn & Braun [4], for overall selectivity at an intermediate of  $\hat{\sigma}_A$  and a large value of  $\hat{\sigma}_C$ .

Sohn and Braun [4]. Figures 1-3 present this comparison for various combinations of  $\hat{\sigma}_A$ ,  $\hat{\sigma}_C$ ,  $\psi_{Ab}$ . In these figures there is a good agreement between our results and those obtained by the numerical solution.

Figures 4-6 show that our results predict overall selectivity of the system more accurately than the approximate solution of Reference [4].

This method gives a new mathematical expression, which can be used for the quick prediction of the conversion-time behavior and the selectivity of the

simultaneous reactions. Therefore, the model parameters can be estimated from the experimental data with reduced computational works.

#### NOMENCLATURE

$A_p$  = external surface area of the pellet

$b = \frac{C_B}{C_{B0}}$  = dimensionless solid concentration

$b_A = \frac{C_{B0}}{C_A}$  = dimensionless solid concentration if we have only gas "A"

$C_N$  = concentration of gas "N" in the pellet

$C_{Nb}$  = concentration of gas "N" in the bulk stream

$C_B$  = solid concentration

$C_{B0}$  = initial solid concentration

$D_{eN}$  = effective diffusivity of gas "N" in the pellet

$f(b) = [-\ln(b)]^{1/n}$

$$f'(b) = \frac{\partial f(b)}{\partial b}$$

$Fp$  = shape factor of the pellet

$K_1, K_2$  = rate constants for Reactions 1 and 2 respectively

$K_m$  = external mass transfer coefficient

$k_1, k_2$  = equilibrium constants for Reactions 1 and 2 respectively

$M_A$  = modified Thiele modulus defined by Equation 20

$M_C$  = modified Thiele modulus defined by Equation 21

$n$  = a positive integer in the Equation 9

$r$  = distance from the center of the pellet

$S_0 = \frac{X_A}{X - X_A}$  = overall selectivity

$Sh^* = \frac{K_m}{D_{eA}} \left( \frac{Fp \cdot Vp}{Ap} \right)$  = modified Sherwood number

$t$  = time

$X$  = solid conversion

$X_A$  = solid conversion due to gas "A"

$y = \frac{r \cdot Ap}{Fp \cdot Vp}$  = dimensionless position

$\epsilon$  = pellet porosity

$\theta = [v_{B1} \cdot k_1(C_{Ab} - C_{Pb}/K_1) + v_{B2} \cdot k_2(C_{Cb} - C_{Qb}/K_2)] \cdot t$  = dimensionless time

$v_N$  = stoichiometric coefficient of "N"

$\rho_B$  = true molar density of solid reactant "B"

$$\hat{\sigma}_A = \frac{Fp \cdot Vp}{Ap} \sqrt{\frac{k_1 \cdot \rho_B(1 - \epsilon)(1 + 1/K_1)}{2D_{eA} \cdot Fp}} \quad \text{Thiele}$$

modulus for Reaction 1

$$\hat{\sigma}_C = \frac{Fp \cdot Vp}{Ap} \sqrt{\frac{k_2 \cdot \rho_B(1 - \epsilon)(1 + 1/K_2)}{2D_{eC} \cdot Fp}} \quad \text{Thiele}$$

modulus for Reaction 2

$$\psi_A = \frac{v_{B1} \cdot k_1(C_A - C_P/K_1)}{v_{B1} \cdot k_1(C_{Ab} - C_{Pb}/K_1) + v_{B2} \cdot k_2(C_{Cb} - C_{Qb}/K_2)}$$

dimensionless concentration of gas "A"

$\psi_{Ab}$  = dimensionless concentration of gas "A" in the bulk stream

$$\psi_C = \frac{v_{B2} \cdot k_2(C_C - C_Q/K_2)}{v_{B1} \cdot k_1(C_{Ab} - C_{Pb}/K_1) + v_{B2} \cdot k_2(C_{Cb} - C_{Qb}/K_2)}$$

dimensionless concentration of gas "C"

$\psi_{Cb} = 1 - \psi_{Ab}$  = dimensionless concentration of gas "C" in the bulk stream

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