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Predicting reaction rates for non-catalytic fluid–solid reactions in presence of structural changes in the solid phase

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Abstract

Non-catalytic fluid–solid reactions are of common occurrence in chemical and metallurgical industries, pollution abatement, manufacture of "skeletal" catalysts like Raney nickel, to name a few applications. A new version of the grain model for analyzing the kinetics of this category of reactions has been presented in this paper. The model allows variation with conversion in the size distribution of the grains constituting the reactant solid particulates. This methodology has built in automatic variation of porosity, specific surface area and other pertinent structural parameters characterizing the porous particle and does not require a priori assumption of any relationship between porosity and conversion, thus widening the scope of model applications.

The model was tested successfully by applying it to predict accurately the conversion–time behavior for well-known examples of gas–solid reactions wherein, given the density difference between the product and the reactant, grains grow and the reactions are known to "die-off" prematurely. The model also predicted remarkably well the final structural properties of Raney Ni catalyst particles in a laboratory process of its preparation from Raney Ni–Al alloy by selective leaching of Al with alkali.

Keywords: Fluid–solid reactions; Structural changes; Grain size distribution

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1. Introduction

Non-catalytic gas–solid reactions are of common occurrence in chemical and metallurgical industries. In the context of pollution abatement the reaction of zinc oxide with hydrogen sulfide has been used in the desulfurization of hydrocarbon gases in ammonia synthesis [1]. The use of low-cost limestone and dolomite as sorbents in processes of sulfur dioxide removal from flue gases has been of considerable interest [2]. In the manufacture of "skeletal" catalysts like Raney nickel, selective dissolution of aluminum from the Ni–Al alloy by treatment with alkali is conducted so as to produce the product with desired structural properties. The standard analysis of the reaction rates of the fluid–solid reactions of the above types in terms of the time-honored shrinking core model has been partially supplanted by a more structurally conscious grain model due to Szekely et al. [3].

While the original grain model served the purpose of rate analysis fairly well for a number of reactions where the assumption that the original grain structure of the pellet remains intact during the reaction holds true, this is far less satisfactory in situations where structural changes in the solid phase are simply unavoidable.

With reference to the well-known example of the reaction between CaO and SO_2, due to the growing layer of the product $CaSO_4$ (having a density of about a third of the reactant CaO) the effective grain sizes grow as the reaction progresses, causing the overall pellet porosity to drop significantly. By the same token the intra-grain diffusional resistances also grow. In general, the grains near the periphery would grow relatively more than those near the center of the pellet as a result of the concentration gradient of SO_2 and in some cases can completely block further diffusion of SO_2. This may result in what has been termed in the literature as "die-off" of the reaction [4] at even 50–60% solid conversion though the overall average porosity is not necessarily zero. Sintering when present along with the conversion may accentuate the process. The grain model fails to account for these structural changes and generally over-predicts the conversion substantially. In the Raney Ni catalyst preparation practically non-porous Ni–Al alloy phase, consisting of grains of possibly variable sizes and composition, is gradually converted to an increasingly porous product [5]. A constant grain property model can, in this case, never hope to

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Nomenclature

A	fluid reactant
B	solid reactant
b, c	stoichiometric coefficients
C	solid product
C_A	fluid concentration (kmol/m^3)
D_A	bulk diffusivity of A (m^2/s)
D_C	grain core diameter (m)
D_e	effective diffusivity of A within pellet (m^2/s)
D'_e	effective diffusivity of A within the porous product layer (m^2/s)
D_I	original grain diameter (m)
D_P	grain diameter (m)
F	number of grains with sizes between D_P and $D_\mathrm{P} + \Delta D_\mathrm{P}$
k	pseudo-first-order surface reaction rate constant (m/s)
R	radial coordinate (m)
R_P	pellet radius (m)
t	time (s)
X	volume fraction of grains with sizes between D_P and $D_\mathrm{P} + \Delta D_\mathrm{P}$

Greek letters

ε	pellet porosity
ρ	molar density (kmol/m^3)

Subscripts

B	reactant B
C	product C
f	fluid
s	solid

Superscript

b	bulk

predict the structural properties like specific surface area, pore volume of the activated catalyst.

There has been in the past limited attempts [6,7] to modify the original grain model to reflect the structural changes in the context of specific gas–solid reactions with dramatic density changes. However, the assumption of a locally uniform grain size was preserved which amounted to a priori specification of a linear relationship between porosity and conversion. This assumption, which may have been justified in the specific example cases, comes in the way of generalizing the grain model and presaging its applications to other reactions where such a relationship may not necessarily hold. This is especially so for pellets composed of two or more types of grains with variable composition (as for a Raney Ni–Al alloy). In reality, grains may, in general, exist as a distribution of sizes even if within a narrow range. In the event of changing grain sizes the size distribution as a whole would undergo change. Even when the distribution is a relatively "monodisperse" one, to begin with, it is known from the literature on the dissolution of polydisperse particulates that the polydispersity of the distribution may increase or the distribution as a whole may shift (see, for example, Leblanc and Fogler [8]). It is, therefore, not quite correct to consider structural changes in the pellet in terms of a representative grain size alone, as both the mean size and the spread of the distribution around the mean, in general, can change with time.

In this paper we present a new generalized grain-structured model for non-catalytic fluid–solid reactions wherein changes in the grain size distribution has been considered simultaneously with the grain level and the pellet level mass balances. The model accounts for both the intra-grain and intra-pellet diffusion of the fluid reactant along with the surface reaction on the receding grain core. The significant advantage of this model is that it automatically computes the changing macro-porosity (intra-pellet) and the intra-pellet diffusivity with conversion and does not require assumption of any arbitrary a priori relationship as in the past work. After validating the model results against published experimental data for two gas–solid reactions showing the "die-off" phenomena, the model framework is shown to be easily extendable to another type of fluid–solid reactions, where the pellet porosity is experimentally found to increase with conversion.

2. New grain model

2.1. Model assumptions

1. Consider a porous spherical solid particle or pellet constituted initially of a large number of non-porous spherical grains.
2. The pellet retains its spherical shape and its initial size in course of the reaction.
3. The initial set of grains is characterized by a number-size or a volume-size distribution. In the present work a Rosin-Rammler-type volume-size distribution was assumed to be specified. As is well known [9] this distribution is completely described by two parameters, namely, a characteristic diameter size and the polydispersity index.
4. The fluid diffuses radially through the granular interstices (macro-pores) within the pellet and as it comes in contact with the solid reactant a first-order reaction such as given below ensues whose rate is first order with respect to the local fluid concentration:

   $$\mathrm{A}_{(\mathrm{f})} + b\mathrm{B}_{(\mathrm{s})} \rightarrow c\mathrm{C}_{(\mathrm{s})}$$

5. The solid reactant core in the constituent grains recede radially inward as porous product solid starts forming layers over the core. The thickness of this layer is

determined by the ratio (Z^*), defined as the volume of the solid product C produced per unit volume of B reacted:

$$Z^* = \frac{\rho_B/b}{\rho_C/c} \tag{1}$$

The actual particle size D_P may increase, decrease or remain the same depending upon the value of the ratio Z^*:

$$D_P = [Z^* D_I^3 + (1 - Z^*) D_C^3]^{1/3} \tag{2}$$

6. Pseudo-steady-state approximation is valid and the grains react according to the shrinking core model with the overall rate of reaction being controlled by both the product layer diffusion and the chemical reaction.
7. The reaction takes place under isothermal conditions.
8. No sintering occurs.

2.2. Model equations

The specific continuity equations for the reactant fluid and the solid along with their associated initial and boundary conditions are as follows:

$$\frac{D_e}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial C_A}{\partial R}\right) = 6(1-\varepsilon)kC_A\sum_{\text{all } D_P}\frac{(D_C^2/D_P^3)X(D_P,t)}{[1+(kD_C/2D'_e)(1-(D_C/D_P))]} \tag{3a}$$

subject to

$$R = R_P, \qquad C_A = C_A^b \tag{3b}$$

$$R = 0, \qquad \frac{\partial C_A}{\partial R} = 0 \tag{3c}$$

$$\frac{dD_C}{dt} = -\frac{2bkC_A}{\rho_B\left[1+\frac{kD_C}{2D'_e}\left(1-\frac{D_C}{D_P}\right)\right]}, \quad t = 0,\ D_C = D_I \tag{4}$$

The above equations completely generalize the traditional grain-pellet model with constant grain property assumption, as originally introduced by Szekely and coworkers [10,11]. Interestingly, in the original formulation of Szekely and Evans [10], the grains were conceived to acquire a product layer with the progress of conversion but offering no diffusional resistance (D'_e large) and without any density change (hence $Z^* = 1$). Georgakis et al. [6] in their version of the modified grain model accounted for the intra-grain diffusion and also allowed Z^* to be different from unity. However, the grain sizes were assumed to be uniformly distributed.

In terms of the specification of an initial grain size distribution consistent with measurements like specific surface area, pore volume, etc., the instantaneous grain size distribution can be easily computed by solving the following population balance equation:

$$\frac{\partial F(D_P,t)}{\partial t} + \frac{\partial}{\partial D_P}\left[(1-Z^*)\frac{D_C^2}{D_P^2}\left(\frac{dD_C}{dt}\right)F(D_P,t)\right] = 0 \tag{5}$$

At start ($t = 0$) an initial grain size distribution $F(D_P, 0)$ is specified as follows:

$$F(D_P,0) = N(0)\frac{n}{D_P}\left(\frac{D_P}{\bar{D}}\right)^{n-1}\exp\left(-\left[\frac{D_P}{\bar{D}}\right]^n\right) \tag{6}$$

2.3. Solution procedure

The population balance equation was solved by an adaptation of the classical method of characteristics as demonstrated in an earlier paper [12], given an initial grain size distribution. The rate of change of the diameter of the grain core is a function of the local radial concentration of the diffusing fluid, which in turn is calculated by solving the diffusion equation as above. The resulting concentration profile is given by

$$\frac{C_A}{C_A^b} = \frac{R_P}{R}\frac{\sinh(3\Phi_S R/R_P)}{\sinh(3\Phi_S)} \tag{7}$$

with the corresponding Thiele modulus defined as

$$\Phi_S = \frac{R_P}{3}\left[\frac{6(1-\varepsilon)k}{D_e}\times\sum_{\text{all } D_P}\frac{(D_C^2/D_P^3)X(D_P,t)}{[1+(kD_C/2D'_e)(1-(D_C/D_P))]}\right]^{1/2} \tag{8}$$

In the actual computation, which has been implemented in a computer program, the grain size distribution prevailing at each radial section was calculated by solving the population balance at the local conditions. About 10–12 radial shells used in the present work were found to give reliable results. The radial porosity profile was calculated based on the local grain size distribution. The gross (pellet wide) grain size distribution was then updated by combining the locally computed ones.

The overall porosity of the pellet was then computed from the following equation:

$$1 - \varepsilon = \frac{(\pi/6)\sum_{\text{all } D_P} D_P^3 F(D_P,t)\Delta D_P}{4\pi R_P^3/3} \tag{9}$$

The effective diffusivity within the pellet was calculated by the following formula based on the random pore model and as used by other workers [7]:

$$D_e = \varepsilon^2 D_A \tag{10}$$

3. Results and discussions

3.1. Reaction between CaO and SO_2

One of the most striking demonstrations of the deficiency of the original form of the grain model occurs when one tries to apply the model to cases of gas–solid reactions where the molar density of the product is very different from that of the reactant. As evident from the definition of the factor Z^* above, unless the stoichiometric factors balance the disparity in the densities, the changes in grain sizes during the reaction would be appreciable. For instance, for the case of sulfation of lime (or limestone directly), a reaction that has attracted a lot of attention in the literature the factor is about 3.1. Thus as the reaction progresses, not only does the gaseous reactant SO_2 has to diffuse through the growing sulfate layer to reach the lime core in each grain, the resulting enlargement of the grains would cause a reduction in the pellet porosity.

Published experimental data [13] on the extent of sulfation (conversion of CaO) with time had been used by Georgakis et al. [6] with their version of the grain model. We used the gas concentration, the bulk diffusivity of the gaseous reactant in the pellet and the reactant/product densities, the pellet diameter and its initial porosity as reported therein (Table 1 in their paper). The mean grain diameter reported (typical) in this table (2×10^{-7} m) seems a little too high compared with those reported in the literature. In the case of ZnO–SO_2 reaction measured specific surface area of the initial pellet could be shown to be consistent with monodisperse grains of mean size that is almost an order of magnitude less. Szekely et al. [14] reported a mean grain size of 4.5×10^{-8} m in the case of nickel oxide reduction. In absence of any further data we have assumed a relatively monodisperse initial grain size distribution ($n = 7$) giving a mean grain diameter of about $\sim 5 \times 10^{-8}$ m.

The values for the reaction rate constant (k) and the diffusivity through porous product layers (D'_e) were both listed by Georgakis et al. [6] for the case of CaO–SO_2 reaction, which in all probability were "adjustable" parameters (as nothing was mentioned about their source). In the present work, attempt was made to predict the entire set of experimental data [13] with one pair of values for k and D'_e. Both values turn out to be quite different from those used by Georgakis et al. More particularly, the diffusivity through the product layer used in this work is several orders of magnitude lower (8×10^{-15} m^2/s) than used by them. Ranade and Harrison [7] had found for another similar reaction (between ZnO and H_2S) that fitting their data required just such low values for the intra-grain diffusivity and argued that this might be rationalized in terms of solid-state diffusion mechanism which may be suggested by their significant temperature sensitivity as observed in the data of Gibson and Harrison [4] on the latter system.

With the above proviso the new grain model was used to calculate the conversion–time behavior for three pellet radii (namely, 2.82×10^{-4}, 4.5×10^{-4} and 5.6×10^{-4} m) and the calculated results compared with the experimental data due to Hartman and Coughlin [13] in Fig. 1. As evident from the figure the model not only predicts the rates at low times but even the so-called "die-off" at longer durations quite accurately, further justifying the use of parameter values as discussed above.

Another set of conversion–time data for the same reaction due to Borgwardt [15] was available in the literature and summarized by Georgakis et al. [6]. The data including the bulk gas diffusivity through pores were used in the model directly, rate constant remaining the same as used for the data of Hartman and Coughlin [13]. The product layer diffusivity, however, had to be slightly modified from that in the case of Hartman and Coughlin's data above (3×10^{-14} m^2/s) in order to get the best fit to a set of data from an altogether different source. The model predictions were compared with the reported experimental data in Fig. 2 for three pellet radii (namely, 0.42×10^{-4}, 1.25×10^{-4} and 6.5×10^{-4} m). Again the match appears to be remarkably good for both the short and the long exposures.

The observed reaction "die-off" such as shown above (for a 0.565×10^{-3} m CaO pellet it has been estimated by Hartman and Coughlin [2] that as conversion rises from 11.5 to 35% the reaction rate drops in about 30 min by a factor of 80!) occurs because the grains in the outer periphery of the pellets have better chance of growing to start with due to higher gaseous reactant concentration locally. The growing grains eventually come to occupy practically all the inter-grain space available initially and thereby blocking almost all pores in the peripheral shells. This is reflected in the changes in the radial profiles of the local porosities in the pellet with time (Fig. 3).

Finally in Fig. 4 we have plotted the predicted terminal values of the pellet porosity for all the six cases above against the maximum conversion attained in each case. In the same graph are included the experimental data on the dependence of the porosity of the sulfated particles on the conversion to sulfate, collected for a number of limestone types and sizes as reported by Hartman and Coughlin [2]. It must be remembered that the calculations and the experimental observations do not necessarily refer to corresponding runs. While quantitatively speaking the model appears to be slightly over-predicting the porosity at all conversion levels, the observed trend of variation has been reflected quite well. Most importantly, this change in the pellet property with conversion is obtained automatically as a part of the calculation and not assumed a priori.

3.2. Reaction between ZnO and H_2S

This reaction studied originally by Gibson and Harrison [4] is another example of progressive resistance to intra-pellet diffusion of the gaseous reactant (H_2S) during reaction, though not as dramatic as in the previous example, which can be explained in terms of similar growth in sizes of the peripheral grains during reaction. In this instance,

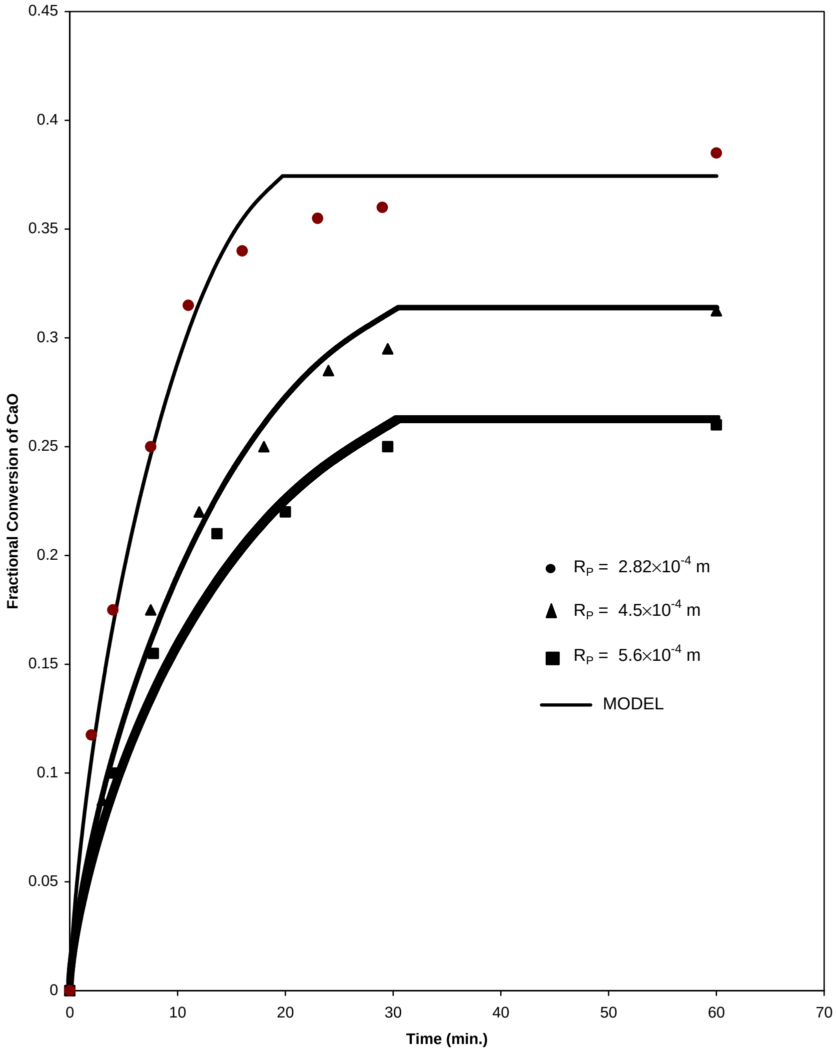

Fig. 1. Comparison of predicted rate of conversion of CaO with experimental data [13].

at higher temperatures sintering adds to the grain size enlargement. But as the authors show, below 400 °C the size growth is entirely due to density change during reaction.

Ranade and Harrison [7] provided all the necessary data regarding the gas concentration, the reactant and product densities, initial pellet porosity as well as the specific surface area. Initial grain size distribution (mean grain diameter 3×10^{-8} m) was chosen to reproduce values for these initial pellet properties. The estimate of the rate constant and the gas diffusivity (calculated by combining the bulk and the Knudsen diffusivities) were obtained from Gibson and Harrison [4]. The values of the intra-grain diffusivity required to best fit the data were again very low but of the same order as used by Ranade and Harrison. No other independent and reliable estimate of this parameter seems to be available. The conversion (of ZnO)–time behavior predicted by the model at two low-temperature levels has been compared in Fig. 5 with the experimental data.

Interestingly, the data shows that while at 375 °C the conversion almost shuts off at ∼40% it could show an increasing (though at a decreasing rate) trend at 440 °C. The model predicts these results fairly closely.

3.3. Preparation of Raney Ni catalyst

The laboratory process of Raney Ni catalyst preparation consists in controlled leaching of the aluminum content from the Raney alloy material (usually consisting of Ni and Al in equal proportions) by treating it with concentrated sodium hydroxide solution. Chaudhari et al. [5] attempted to study the kinetics of this activation process carried out in batch experiments wherein the alloy powder in narrow size cuts was extracted with the alkali at various temperatures. While interpretation of their experimental data in terms of the model will be presented elsewhere, what is of interest here is that we have been able to adapt the present model to this case and to predict the changes in the key structural properties of an alloy pellet as Al is selectively leached out by the diffusing alkali and an increasingly porous pellet eventually results.

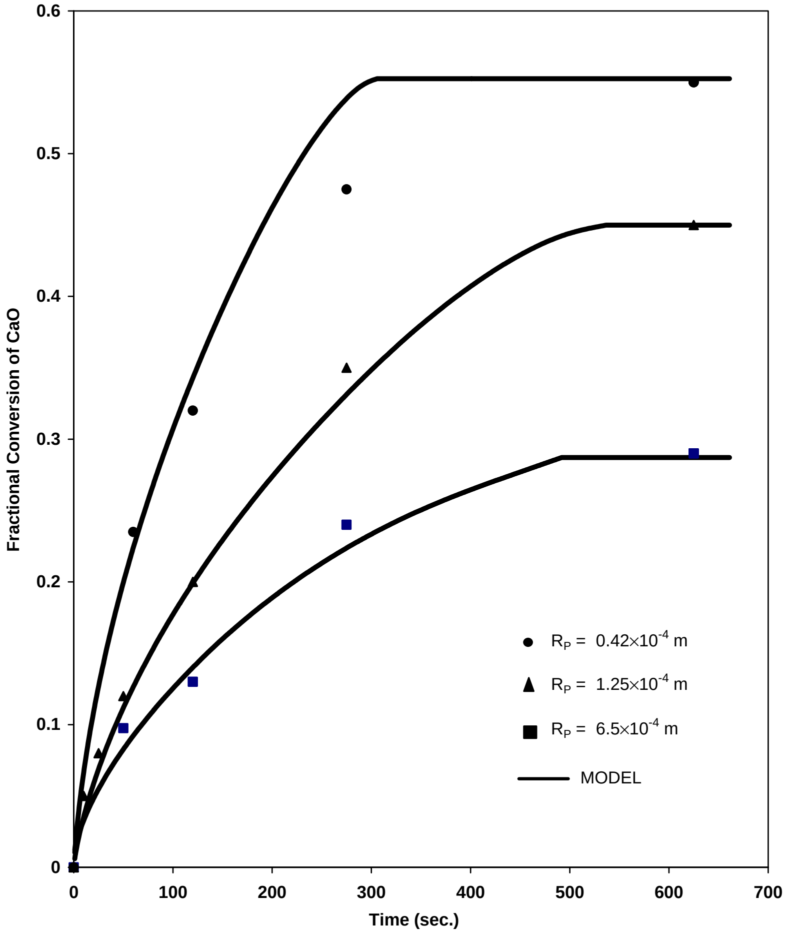

Fig. 2. Comparison of predicted rate of conversion of CaO with experimental data [15].

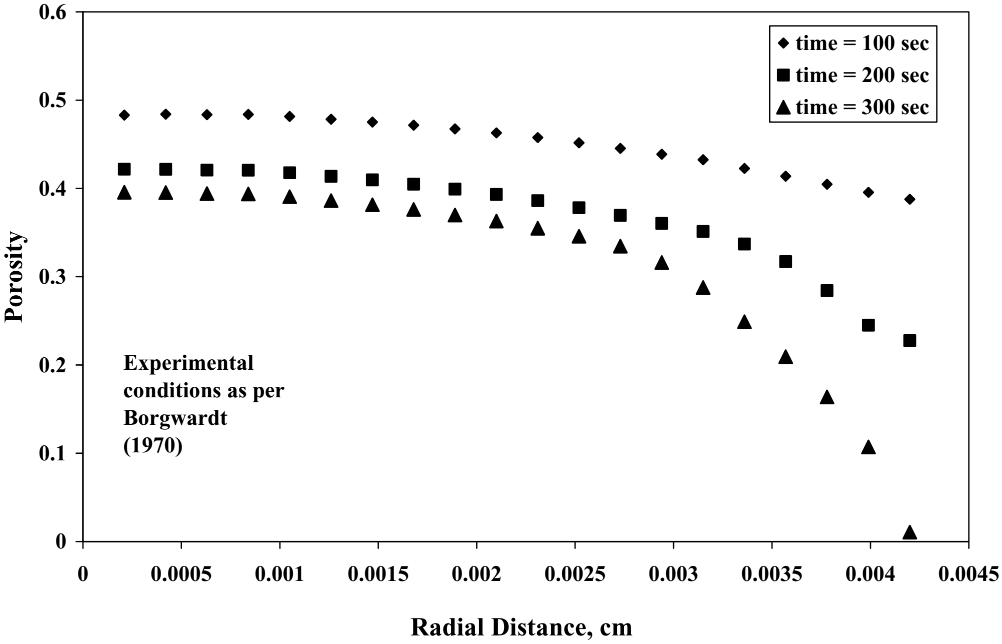

Fig. 3. Predicted radial porosity profile for CaO–SO_2 reaction.

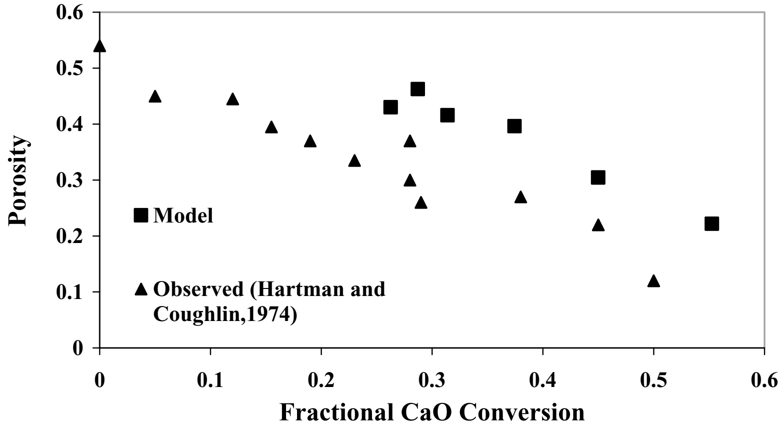

Fig. 4. Dependence of the pellet porosity on the CaO conversion.

It was assumed that the alloy pellet consisted of two kinds of grains, namely that of Ni and of Al (in reality different forms of alloys) which, in general, were characterized by different size distributions. These were chosen (Rosin-Rammler type as in the previous examples with different sets of values for n and $\bar{D}$ parameters) so as to result in observed porosity, specific surface area, pore volume per gram and such like properties of the fresh alloy particles. The alkali was assumed to diffuse into the interstices within the grains and selectively react with and consume the Al grains but not the Ni grains. The rate of Al consumption was taken to be controlled mainly by a pseudo-first-order surface reaction and no product layer formation was assumed. This simplified the form of the "linear" grain dissolution rate expression $\mathrm{d}D_\mathrm{p}/\mathrm{d}t$ especially as in this case $D_\mathrm{P} = D_\mathrm{c}$.

The Ni grains on the other hand were allowed to readjust their size distribution by another independent "linear" size growth law that was consistent with conjectures in the literature about partial dissolution and recrystallization of the Ni alloys in alkaline medium and/or phase transformation [5,16] that may accompany Al leaching. A simple power law model was chosen to represent this rate. The basic model equations are summarized in Appendix A. The necessary data for the model calculation were available [5]. The solution procedure was same as outlined earlier.

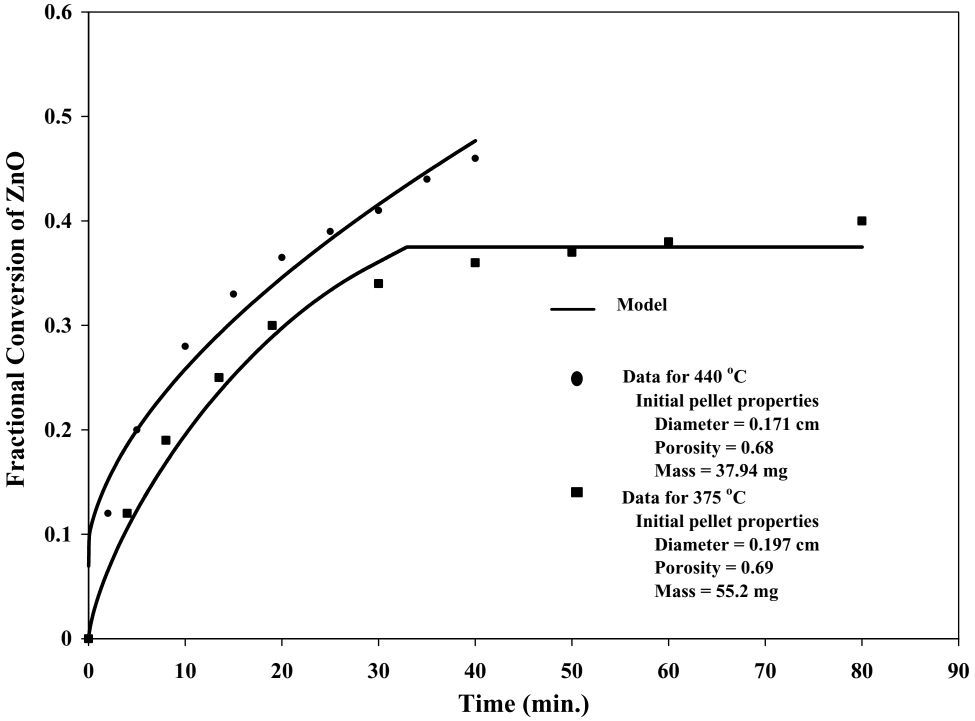

Fig. 5. Comparison of model predicted rate of conversion of ZnO with experimental data [7].

Table 1
Prediction of properties of Raney nickel catalyst prepared by selective dissolution of aluminum from Raney Ni–Al alloy

Properties	Raney Ni–Al alloy	Raney Ni	
		Experimental	Model
Ni (wt.%)	50.0	96.0	95.5
Al (wt.%)	50.0	4.0	4.5
Particle density (g/cm^3)	3.99	3.32	3.22
Porosity	0.027	0.59	0.602
Pore volume (cm^3/g)	0.007	0.178	0.187
Surface area (m^2/g)	–	82	82.07
Mean pore diameter (Å)	–	61	45.6

Starting with a typical Raney Ni–Al alloy pellet of 45 μm diameter and standard structural properties and Ni–Al composition as those of commercial alloy particles, the model was then used to predict the density, porosity, pore volume and the specific surface area of the final porous pellet of Ni–Al composition as in typical Raney Ni catalyst. The calculated properties match quite closely with the reported (typical) values as shown in Table 1.

4. Conclusions

In this paper a new and completely generalized version of the grain model of fluid–solid reactions has been presented that allows consideration of the changes in a distributed variable, namely, the grain size distribution with conversion. This methodology has built in the automatic variation of porosity, specific surface area and other pertinent structural parameters characterizing a porous pellet and allows variation of the effective intra-pellet diffusivity as well. This obviates the need for a priori assumption of any relationship between porosity and conversion. This will also presage the future applications of the model to particles composed of more than one kind of grains of variable initial sizes and composition.

The model was tested successfully by applying it to predict accurately the conversion–time behavior for two well-known examples of gas–solid reactions wherein the molar density of the solid product being considerably lower than that of the reactant solid, the constituent grains, especially in the outer layers of the pellet, grow and the reactions are known to “die-off” prematurely.

It was also shown that the model with marginal modifications could predict remarkably well the final structural properties of Raney Ni catalyst particles in a laboratory process of its preparation from Raney Ni–Al alloy by selective leaching of Al with concentrated alkali.

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Appendix A. Adapting the model to the case of preparation of Raney Ni catalyst

The instantaneous grain size distribution has been computed by solving the following population balance equation:

$$\frac{\partial F(D_\mathrm{P}, t)}{\partial t} + \frac{\partial}{\partial D_\mathrm{P}}[R(D_\mathrm{P})F(D_\mathrm{P}, t)] = 0 \qquad (\mathrm{A.1})$$

where the “linear” dissolution rate law is given by

$$R(D_\mathrm{P}) = -\frac{2kC_\mathrm{A}}{\rho_\mathrm{B}} \quad \text{for the Al grains} \qquad (\mathrm{A.2a})$$

and

$$R(D_\mathrm{P}) = \alpha D_\mathrm{P}^{\beta} \quad \text{for the Ni grains} \qquad (\mathrm{A.2b})$$

The radial profile of liquid reactant concentration is obtained by solving the following continuity equation:

$$\frac{D_\mathrm{e}}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial C_\mathrm{A}}{\partial R}\right) = 6(1-\varepsilon)kC_\mathrm{A}\sum_{\text{all } D_\mathrm{P}}\frac{X(D_\mathrm{P}, t)}{D_\mathrm{P}} \qquad (\mathrm{A.3})$$

subject to

$$R = R_\mathrm{P}, \qquad C_\mathrm{A} = C_\mathrm{A}^\mathrm{b} \qquad (\mathrm{A.4a})$$

$$R = 0, \qquad \frac{\partial C_\mathrm{A}}{\partial R} = 0 \qquad (\mathrm{A.4b})$$

ε and X in Eq. (A.3) refer to all grains within a shell irrespective of the grain type.

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