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Gas–solid reaction modeling as applied to the fine desulfurization of gaseous feedstocks

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Abstract

The paper considers mathematical modeling in relation to the removal of low concentrations of impurities by gas–solid reactions in a fixed bed of absorbent. Models describing the following process mechanisms are analyzed: (1) gas diffusion through the outer shell of the reacted absorbent; (2) chemical reaction at the interface between the reacted shell and the non-reacted core; (3) reacted-shell diffusion together with the interface chemical reaction; (4) reacted-shell diffusion and reaction together with diffusion in the bulk of the internal non-reacted core. For an isothermal plug-flow reactor with spherical particles of absorbent, solutions by quadrature or even the exact ones are derived for each of the models. The solutions are analyzed for the process of gas sweetening over zinc oxide absorbents: $H_2S(g) + ZnO(s) = H_2O(g) + ZnS(s)$. It is shown that the models may be distinguished through analysis of experimental gas content versus time data at the outlet of the absorbent packed beds rather than on the basis of conversion versus time curves. The requirements for experimental distinction of the models are determined. It is shown that model (3), describing reacted-shell diffusion together with interface chemical reaction, is the most adequate for the design of zinc oxide beds.

Keywords: Feedstocks; Gas–solid reaction modeling; Desulfurization

1. Introduction

Many commercial processes use gas–solid reactions for the fine purification of gas streams. For example, hydrocarbon gaseous feedstocks such as natural gas, petroleum associated gas, naphtha, etc., are purged of sulfur (sweetened) prior to steam reforming over porous zinc oxide absorbents. The design of absorption units involves setting a limit on the maximum permissible concentration of impurity in the outlet flow from the absorbent bed. Typical units employ rather large beds, such that the initial outlet concentration of the impurity is much lower than the allowable maximum. The time between the absorbent start-up and the appearance of the maximum concentration of impurity in the bed outlet determines the absorbent breakthrough (or service) time. Correct prediction of the breakthrough time is critical for unit design and operation.

From the equation for a gas–solid reaction, one can determine the maximum amount of impurity potentially saturated over a given volume of the absorbent (the so-called "stoichiometric capacity", which is hard to achieve in reality, supposedly due to limitations imposed by intraparticle solid-state diffusion). The breakthrough time can then be estimated as the ratio of this amount to the mass flow rate of the impurity (see below about "static time of exhausting"). However, the accuracy of such an estimate, which assumes steep absorption fronts, is rarely sufficient for practical purposes. The actual breakthrough time can be much shorter than that estimated in this way, due to a widening of the absorption front as a result of various diffusion processes and the limited rate of the gas–solid reaction, especially in the case of modern high-performance units.

While the general theory of gas–solid reaction processes has been well developed and documented in many publications since the mid-1950s (see, for example, ref. [2]), few systematic discussions about the practically important application of fine purification of gaseous impurities have hitherto been reported.

The basis for the following consideration is a well-known shrinking-core model [2]. This model allows one to determine the instantaneous local rate of reaction under various limitations imposed by process control mechanisms. In a previous publication [1], we considered a plug-flow reactor model in relation to the removal of sulfur in a zinc oxide bed. It was shown that the system of differential equations can be reduced to two integral and one algebraic equation. The computational procedure based on this approach is simpler than one based on solution of the original system of differential equations. Also, it represents a convenient form for evaluating the process parameters. In

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Nomenclature

c	Gas impurity content per unit volume (kg/m^3)
c_0	Inlet gas impurity content per unit volume (kg/m^3)
D^*_O, D^*_S	Gas impurity diffusivities in the core and the outer layer of a granule, respectively, (m^2/s)
$E_\mathrm{sp} = c_0 t/P_0$	Specific exposure (s)
k	Rate coefficient per unit volume of unreacted core (s^{-1})
$K = \sqrt{kD_\mathrm{O}}$	Rate coefficient per unit surface area of the unreacted core (m/s)
P	Local adsorptive capacity per unit bed volume (kg/m^3)
P_0	Initial local adsorptive capacity per unit bed volume (kg/m^3)
R	Granule radius (m)
t	Running time (s)
u	Gas velocity (m/s)
V	Space velocity (h^{-1})
w_b	Gas–solid reaction local absorption rate per unit bed volume (kg/(m^3 s))
x	Penetration depth into the absorbent bed downstream of the gas flow (m)
$\bar{X}$	Average conversion of the solid phase in a plug-flow reactor
z	Integration variable

Greek symbols

ε	Bed porosity
$\eta = P/P_0$	Dimensionless local adsorptive capacity per unit bed volume
η_0	Value of η in the frontal bed layer
η_1	Value of η in the rear bed layer
$\nu = c/c_0$	Dimensionless gas impurity content
$\rho_0 = R\sqrt{k/D^*_\mathrm{O}}$	Dimensionless granule radius
$\tau_\mathrm{ac} = V^{-1}$	Average contact time (s)
$\tau_\mathrm{D} = \frac{R^2}{6(1-\varepsilon)D^*_\mathrm{S}}$	Diffusion time scale (s)
$\tau_\mathrm{K} = R/(1-\varepsilon)K$	Kinetic time scale (s)

this previous publication [1], we determined an analytical solution for a situation in which a process is controlled by diffusion within the pores of a reacted shell of an absorbent particle and by reaction together with diffusion in the bulk of the non-reacted core.

In this publication, we consider four models for a plug-flow reactor, which differ with respect to their process control mechanisms and their mathematical complexity. The laboratory test conditions necessary for distinguishing between the models are discussed in relation to the essential requirements for sulfur absorber design. The least complex model that adequately describes the process is recommended for design purposes.

The introduction of the specific exposure, E_sp, in the following allows the results to be presented in a uniform manner.

2. Process models

2.1. Model 1

Only diffusion of the impurity through the exhausted external shell of the reacting granule is considered as rate controlling. The absorbent in the bed is described by two parameters: adsorptive capacity (P_0) and diffusion time scale (τ_D).

The well-known expression for local absorption rate is:

$$w_\mathrm{b} = \frac{c_0}{\tau_\mathrm{S}}\nu\varphi_1(\eta), \quad \varphi_1(\eta) = 0.5(\eta^{-1/3} - 1)^{-1}, \quad \tau_\mathrm{S} = \tau_\mathrm{D}.$$

Using results from ref. [1], we have the following pattern of bed behavior. When the frontal bed layer is still reacting ($\eta_0 > 0$),

$$E_\mathrm{sp} = \tau_S T_1(\eta_0), \quad \tau_\mathrm{ac} = \tau_\mathrm{S}[I(\eta) - I(\eta_0)],$$
$$\eta = [1 - \nu(1 - \eta_0)],$$

$$T_1(x) = 1 - 3x^{2/3} + 2x,$$
$$I(x) = 3\ln(1+x^{1/3}+x^{2/3}) - 2\sqrt{3}\left(\arctan\frac{1+2x^{1/3}}{\sqrt{3}} - \frac{\pi}{6}\right).$$

The time of full exhausting of the frontal bed layer is finite and corresponds to $E_\mathrm{sp} = \tau_\mathrm{S}$, as in ref. [2]. After this moment

$$E_\mathrm{sp} = \tau_\mathrm{ac} + \tau_\mathrm{S}[1 - I(1 - \nu)].$$

The so-called "static time of exhausting", which is frequently used for rough estimations of service time, corresponds to $E_\mathrm{sp} = \tau_\mathrm{ac}$.

At first, $v = 0$ at the bed outlet for a certain time. After the moment corresponding to $E_\mathrm{sp} = \tau_\mathrm{S} + \tau_\mathrm{ac}$ (time of full bed exhausting), $v = 1$.

2.2. Model 2

Only chemical reaction at the interface with the non-reacted core, and not the diffusion of the impurity through the exhausted external shell of the reacting granule, is considered as rate controlling. The reaction is first-order with respect to gas impurity content, and its overall rate is proportional to the surface area of the interface. The absorbent in the bed is described by two parameters: adsorptive capacity P_0 and kinetic time scale τ_K.

The well-known expression for local absorption rate is:

$$w_\mathrm{b} = \frac{c_0}{\tau_\mathrm{S}}\nu\varphi_2(\eta), \quad \varphi_2(\eta) = 3\eta^{2/3}, \quad , \tau_\mathrm{S} = \tau_\mathrm{K}.$$

Using results from ref. [1], we have the following pattern of bed behavior. When the frontal bed layer is still reacting ($\eta_0 > 0$),

$$E_\mathrm{sp} = \tau_\mathrm{S} T_2(\eta_0), \quad \tau_\mathrm{ac} = \tau_\mathrm{S}[F(\eta) - F(\eta_0)],$$
$$\eta = [1 - \nu(1 - \eta_0)],$$

$$T_2(x) = 1 - x^{1/3},$$
$$F(x) = \frac{1}{2}\ln\frac{(1-x)^{1/3}}{1-x^{1/3}} + \frac{1}{\sqrt{3}}\left(\arctan\frac{1+2x^{1/3}}{\sqrt{3}} - \frac{\pi}{6}\right).$$

The time of full exhausting of the frontal bed layer is finite and corresponds to $E_{\mathrm{sp}} = \tau_{\mathrm{S}}$, again as in ref. [2]. After this moment

$$E_{\mathrm{sp}} = \tau_{\mathrm{ac}} + \tau_{\mathrm{S}}[1 - F(1 - \nu)].$$

At first ($t = 0$), $\upsilon = \exp(-3\tau_{\mathrm{ac}}/\tau_{\mathrm{K}})$ (minimal possible breakthrough value) at the bed outlet. After the moment corresponding to $E_{\mathrm{sp}} = \tau_{\mathrm{S}} + \tau_{\mathrm{ac}}$ (time of full bed exhausting), $\upsilon = 1$.

2.3. Model 3

Both diffusion and reaction at the core interface are considered as rate controlling. All three of the aforementioned absorbent parameters are needed here, namely P_0, τ_{D}, and τ_{K}.

The expression for local reaction rate is also well known:

$$w_{\mathrm{b}} = \frac{c_0}{\tau_{\mathrm{S}}}\nu\varphi_3(\eta), \quad \varphi_3(\eta) = 0.5\left[\frac{\tau_{\mathrm{D}}}{\tau_{\mathrm{S}}}(\eta^{-1/3} - 1) + \frac{1}{6}\frac{\tau_{\mathrm{K}}}{\tau_{\mathrm{S}}}\eta^{-2/3}\right]^{-1},$$

$$\tau_{\mathrm{S}} = \tau_{\mathrm{D}} + \tau_{\mathrm{K}}.$$

As in the previous cases, the results from ref. [1] allow a description of the pattern of the bed behavior.

When the frontal bed layer is still reacting ($\eta_0 > 0$),

$$E_{\mathrm{sp}} = \tau_{\mathrm{D}} T_1(\eta_0) + \tau_{\mathrm{K}} T_2(\eta_0),$$

$$\tau_{\mathrm{ac}} = \tau_{\mathrm{D}}[I(\eta) - I(\eta_0)] + \tau_{\mathrm{K}}[F(\eta) - F(\eta_0)],$$

$$\eta = [1 - \nu(1 - \eta_0)].$$

The time of full exhausting of the frontal bed layer is also finite and corresponds to $E_{\mathrm{sp}} = \tau_{\mathrm{S}}$, as in the case of a single granule in ref. [2]. After this moment

$$E_{\mathrm{sp}} = \tau_{\mathrm{ac}} + \tau_{\mathrm{D}}[1 - I(1 - \nu)] + \tau_{\mathrm{K}}[1 - F(1 - \nu)].$$

The minimum possible breakthrough value is the same as for Model 2; $\upsilon = 1$ after the time of full exhausting of the bed, i.e. after the moment corresponding to $E_{\mathrm{sp}} = \tau_{\mathrm{S}} + \tau_{\mathrm{ac}}$.

2.4. Model 4

Absorption is considered to occur in the bulk of the non-reacted core, its rate being proportional to the gaseous admixture content, the admixture being transported through the pores of the core by diffusion. Such complication of the model results in an extra parameter being needed for the absorbent, namely the dimensionless granule radius, ρ_0.

In this case, for local reaction rate, we obtain [1]:

$$w_{\mathrm{b}} = \frac{c_0}{\tau_{\mathrm{S}}}\nu\varphi_4(\eta), \quad \varphi_4(\eta) = 0.5\left\{\frac{\tau_{\mathrm{D}}}{\tau_{\mathrm{S}}}(\eta^{-1/3} - 1) + \frac{\tau_{\mathrm{K}}}{\tau_{\mathrm{S}}}\frac{\rho_0}{6\eta^{1/3}[\rho_0\eta^{1/3}\coth(\rho_0\eta^{1/3}) - 1]}\right\}^{-1}, \quad \tau_{\mathrm{S}} = \tau_{\mathrm{D}} + \tau_{\mathrm{K}}.$$

For this model, the description of bed behavior is more complicated:

$$E_{\mathrm{sp}} = \tau_{\mathrm{D}} T_1(\eta_0) + \frac{\tau_{\mathrm{K}}}{\rho_0}[L(\rho_0) - L(\rho_0\eta_0^{1/3})],$$

$$\tau_{\mathrm{ac}} = \tau_{\mathrm{S}}\int_{\nu}^{1}\frac{\mathrm{d}z}{z\varphi_4[1 - z(1 - \eta_0)]},$$

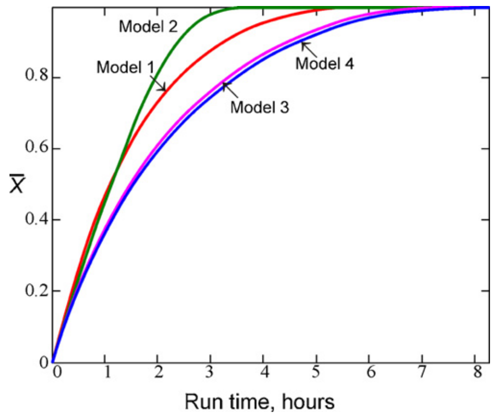

Fig. 1. Comparison of calculated average conversions, $\bar{X}$, of the solid phase throughout the bed vs. time dependences using various gas–solid reaction models for $\tau_{\mathrm{ac}} = 0.5$ s. Models: 🟥 1; 🟩 2; 🟪 3; 🟦 4.

$$L(x) = \ln(x\cosh x - \sinh x).$$

Neither time of full exhausting is finite. At the bed outlet

$$\nu(t = 0) = \exp\left[-3\frac{\tau_{\mathrm{ac}}}{\tau_K}\left(\coth\rho_0 - \frac{1}{\rho_0}\right)\right].$$

Results from ref. [1] also allow us to obtain a simple expression for the average conversion of the solid phase in a plug-flow reactor:

$$\bar{X} = \frac{1}{\tau_{\mathrm{ac}}}\left[E_{\mathrm{sp}} - \tau_{\mathrm{S}}\int_{\eta_1}^{1}\frac{\mathrm{d}z}{\varphi_i(z)}\right], \quad i = 1, 2, 3, 4$$

The integral here can be expressed analytically for all of the models in question.

3. Comparison of the models

According to ref. [2], the difference in conversion–time curves for the reaction of a single spherical particle with a surrounding fluid in the cases of diffusion through an exhausted shell and chemical reaction as rate-controlling steps is not great and may be masked by the scatter in the experimental data.

In practice, most gas–solid processes in the treatment of gases using fixed solid-particle beds take place in plug-flow reactors. In order to delineate a “model-sensitive” criterion for gas–solid reactions, the time dependences of some process characteristics were calculated using expressions pertaining to the aforementioned models. Bed parameter values were chosen as being typical of the reaction of small amounts of gaseous H_2S with pellets of commercial ZnO-based absorbent. The values obtained as described in ref. [1] were: $c_0/P_0 = 7 \times 10^{-5}$, $\tau_{\mathrm{D}} = 1.03$ s, $\tau_{\mathrm{K}} = 0.55$ s, $\rho_0 = 9.5$.

Fig. 1 shows the average conversion, $\bar{X}$, of the solid phase throughout the bed versus time. Similarly to the case of a single granule [2] (in our consideration, it corresponds to the frontal

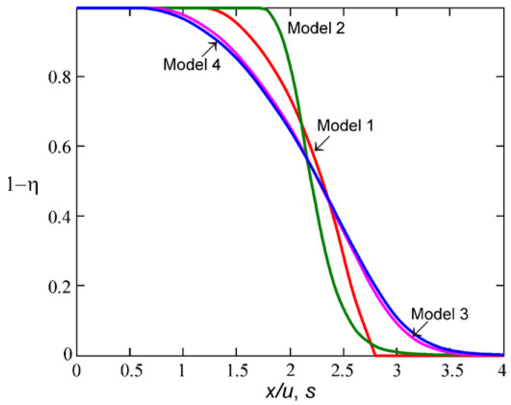

Fig. 2. Calculated solid-phase local conversion profiles along the gas flow for $\tau_{ac} = 4$ s at the moment corresponding to $E_{sp} = 2.23$ s. Models: 🟥 1; 🟩 2; 🟪 3; 🟦 4.

bed layer conversion), one can scarcely discern any significant qualitative difference in the shapes of these curves, especially if the data are subject to scatter. At $\tau_{ac} > 0.5$ s, the difference is even less.

Local conversion profiles may be used to characterize absorbents [3]. Fig. 2 depicts such profiles as calculated $(1 - \eta)$ versus (x/u) plots. After full (or practically full in the case of Model 4) exhausting of the frontal bed layer, as it is presented here, these profiles are moving uniformly deep into the absorbent bed downstream of the gas flow. As in the case of the average conversion curves, these profiles are qualitatively indistinguishable.

Thus, it would appear that solid–phase conversion data are not sufficiently "model-sensitive". So, the other process characteristic, namely gas composition, should be tested for the role of the criterion that we need. The so-called "breakthrough curves" were constructed by calculating impurity content versus run time dependences for several values of contact time, or in other words, of space velocity. The results are presented in Fig. 3a–c.

Unlike for solid–phase conversion, the shapes of the "breakthrough curves" in Fig. 3a and b are distinctly different, especially for Model 2, except for those for Models 3 and 4. As for the "breakthrough curve" generated by Model 1, although it differs qualitatively from those generated by Models 3 and 4 at low values of τ_{ac}, these curves might be confused when the data are subject to scatter. So, the average value of τ_{ac} seems to be optimal for the case of a typical sulfur absorbent. In general, the best value of τ_{ac} is most likely to be chosen close to the value of τ_S.

4. Discrimination of the models

In order to verify the conclusions reached in the preceding section and to evaluate the applicability of these models in describing the fine desulfurization of gases over solid absorbents, the above-mentioned expressions for the models in question were used to fit the results of laboratory tests on a commercial ZnO-based sulfur absorbent (test conditions: sample mass: 1.4 g, gas flow: 4.34 dm^3 h^{-1} of H_2 + 1.83 vol% H_2S mixture at atmospheric pressure and 400 °C) as referred to in ref. [1]. Experimental data were obtained as the difference between the inlet and outlet H_2S contents versus time of sulfurization.

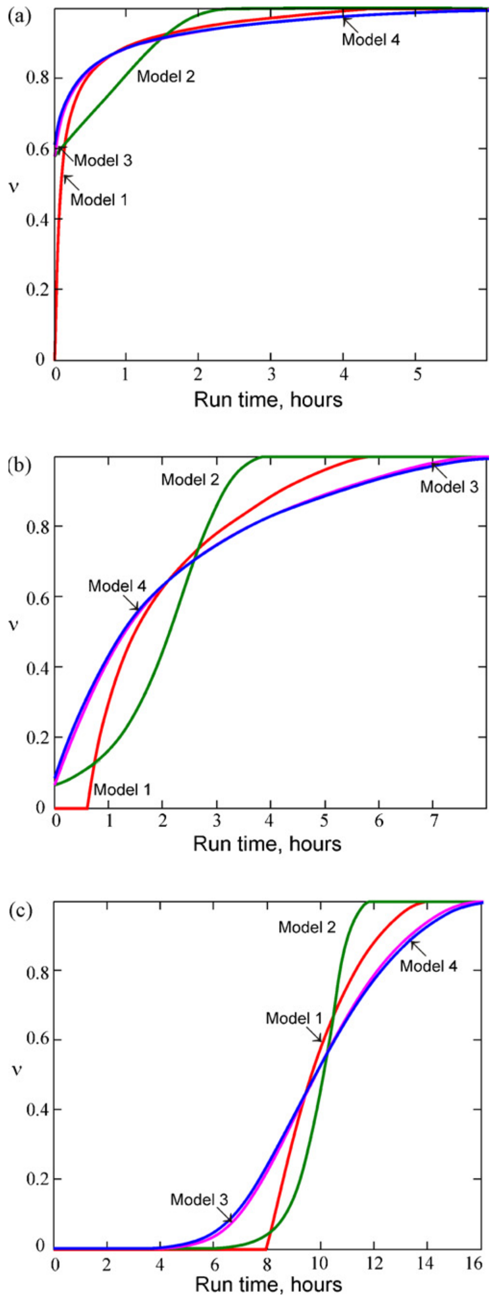

Fig. 3. Comparison of calculated υ vs. time plots. (a) $\tau_{ac} = 0.1$ s; (b) $\tau_{ac} = 0.5$ s; (c) $\tau_{ac} = 2.5$ s. Models: 🟥 1; 🟩 2; 🟪 3; 🟦 4.

Fig. 4 shows these experimental data together with the breakthrough curves, as calculated for each model using its own set of parameter values providing the best possible fit.

Obviously, Models 1 and 2 fail to provide an adequate fitting of the laboratory data. Moreover, the curve shapes provided by these models show qualitative differences.

On the contrary, Models 3 and 4 approximate the data almost precisely and the curves merge. It therefore seems that ρ_0 is a superfluous parameter here.

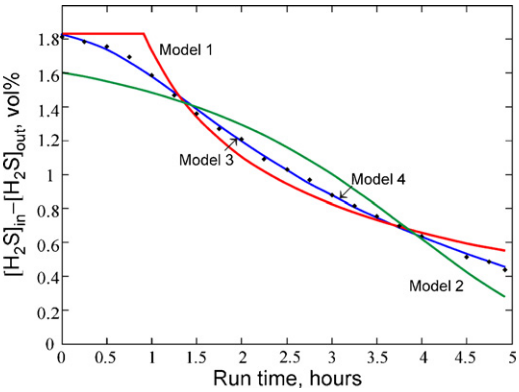

Fig. 4. Comparison of calculated breakthrough curves resulting from fitting of laboratory test data using the formulae for Models 1, 2, 3, and 4. Models: 🟥 1; 🟩 2; 🟪 3; 🟦 4; ♦ – test data.

So, as far as experimental data of this type are concerned, Model 3 should be chosen for modeling the process in question.

5. Conclusions

Solid-phase conversion–time data in any form are inadequate for discrimination of the rate-controlling step when a shrinking-core model is used to describe a gas–solid reaction in an absorbent bed.

On the contrary, time-dependent data concerning the impurity content in the gas flow leaving an absorbent bed have been found to be sensitive to the nature of the rate-controlling step.

In the case of the fine desulfurization of gases over commercial solid ZnO-based absorbents, the two simplest models considered, which assume only diffusion through the exhausted outer shell or only reaction at the interface with the unreacted core to be rate controlling, fail to provide adequate fitting of laboratory test data. Thus, both of these steps need to be taken into account for a full and proper description of the process.

On the other hand, a more complicated approach, considering both diffusion and chemical reaction in the bulk of the unreacted core (in addition to diffusion through the exhausted outer shell) and thus introducing an additional parameter for the description of the gas–solid reaction, does not improve data fitting and is thus deemed useless for practical application in the field.

The contact time for laboratory tests of commercial ZnO-based absorbents should be of the order of 1 s.

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