

Effect of sulphur removal catalyst granules properties on the commercial-scale bed macrokinetics

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Abstract

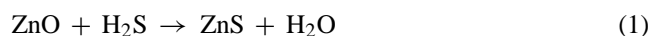
The results of exact solution of the nonlinear equations set for the case of first order reaction rate with respect to gaseous admixture and for a particular model of the gas-porous solid reaction in flow are presented. Along with the expressions derived from an improved shrinking core model they are used to study the effect of sulphur removal catalyst granules properties on the commercial-scale bed macrokinetics. It is shown that sulphur removal catalyst bed dynamics are mainly determined by the size of granules and the value of effective diffusivity of hydrogen sulphide in sulphurized granule shell. The results allow a reasonable choice of sulphur removal catalyst to be made and to estimate bed service time under various operating conditions. They will be also useful when analysing other similar processes.

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1. Introduction

At present fine natural gas purification from H₂S and small amounts of other sulphur compounds occurs via its irreversible reaction with granules of high surface area zinc oxide



The process is usually carried out at operating pressure within the range of 1–45 atm, temperatures within the range of 260–395 °C and space velocities within the range of 300–2000 h⁻¹. The integral average total content of sulfur amounts now at different plants from 0 up to 40 ppm, and maximal one reaches up to 50 ppm. Maximum permissible sulfur content in the purified gas varies from 0.1 to 0.5 ppm.

The key feature distinguishing sulphur absorption from steady catalytic processes, besides essential nonstationarity, is its multilevel structure: reaction fronts in gas and solid phases simultaneously and interdependently move through the bed, granules and particles of ZnO; hydrogen sulphide diffuses through granule pores to a surface of particles aggregates, then sulphur through intercrystalline gaps in primary

particles reaches crystallites surfaces, whence its diffusion into a crystallite begins; oxygen, first as atoms, and through pores as part of H₂O, makes the same path in the opposite direction.

Digital simulation of such multilevel adjoint problem is too intricate. Even the results of direct numerical solution for two upper levels only [1] can hardly be applied to another specific area. In some cases getting not too exact but explicit expressions may be preferable.

2. Process model

It has been shown in [2], that the adjoint problem of modeling the reaction between minor admixture of H₂S in gas and the bed of porous granules of ZnO-based adsorbent (accepting first order of reaction rate with respect to H₂S content) can be separated into two independent ones: the expression for local reaction rate in the adsorbent bed is found by the analysis of absorbed sulphur front movement through a granule in a quasistationary approximation within the framework of shrinking core model (Fig. 1), and then used in the problem of sulphur fronts movement through gas phase and adsorbent bed. The second problem in the simplest (one-dimensional) case is reduced to the set of two differential partial equations

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Nomenclature

c	gas sulphur content per unit volume (kg/m ³)
c_b	gas sulphur content per unit volume in the bed (kg/m ³)
c_{g1}, c_{g2}	gas sulphur content per unit volume of granule pores in the core and outer layer, respectively (kg/m ³)
c_0	the instantaneous inlet gas sulphur content (kg/m ³)
D_O^*, D_S^*	H ₂ S diffusivities in the core and outer layer, respectively (m ² /s)
$k = k(P_{0g})$	effective constant of reaction (1) in the core (s ⁻¹)
$K_{dr}(\eta)$	variable efficiency factor of reaction inside a granule
$K_{dr \min}$	$K_{dr}(\eta)$ minimal value
l_0	characteristic length (m)
L	bed length
P	local sulphur absorption capacity per unit bed volume (kg S/m ³)
P	value numerically equal to pressure in atm
P_0	initial sulphur absorption capacity per unit bed volume (kg S/m ³)
q	rate coefficient in Bohart–Hinshelwood model (m ³ /(kg s))
$Q = qP_0$	dynamic characteristic of absorbent (h ⁻¹)
r	radial coordinate in granule (m)
r_1, R	radii of core and granule, respectively (m)
t	time (s)
t_{br}	time of run before breakthrough of permissible content of H ₂ S at the bed outlet (s)
$t_0 = \frac{P_0}{uc_0} l_0$	characteristic time (s)
T	absolute temperature (K)
u	gas flow velocity (m/s)
V	space velocity (h ⁻¹)
w_b	rate of reaction (1) per unit bed volume (kg/(m ³ s))
x	coordinate along the gas flow (m)
Δx	characteristic width of absorbed sulphur front (m)
y, z	integration variables

Greek symbols

$\bar{\alpha}$	utilization factor of the bed total sulphur capacity
ε	bed porosity
η	$\frac{P}{P_0}$
η_0	$\eta(s=0)$
λ	$\sqrt{\frac{D_O^*}{k}}$ (m)
τ	$\frac{s}{t_0}$

v	$\frac{c}{c_0}$
ξ	$\frac{u\sigma}{l_0}$
ρ_0	$\frac{R}{\lambda}$
$\varphi(\eta)$	$\frac{l_0}{u} f(\eta P_0)$
χ	$\frac{D_S^*}{D_O^*}$

Superscript

(1)	value at atmospheric pressure
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of hyperbolic type with nonlinear right members:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = -w_b, \quad \frac{\partial P}{\partial t} = -w_b, \quad (2)$$

If the flow is steady and uniform ($u = \text{const.}$), new pair of variables, instead of t and x , may be introduced:

$$\sigma = \frac{x}{u}, \quad s = t - \frac{x}{u},$$

and the set (2) turns into

$$\frac{\partial c}{\partial \sigma} = -w_b, \quad \frac{\partial P}{\partial s} = -w_b \quad (3)$$

with initial conditions

$$c(\sigma = 0) = c_0(s), \quad P(s = 0) = P_0(u\sigma). \quad (4)$$

If $w_b = cf(P)$, where $f(P)$ is an arbitrary non-negative function, such that $f(0) = 0$ and given below integrals exist, in the case of $P_0 \equiv \text{const.}$ problem (3) and (4) is reduced to two successive quadratures and one explicit relationship:

$$\int_{\eta_0}^1 \frac{dz}{\varphi(z)} = \frac{u}{P_0 l_0} \int_0^s c_0(y) dy, \quad (5)$$

$$\int_{\eta_0}^n \frac{dz}{\varphi(z)(1-z)} = \xi, \quad v = \frac{1-\eta}{1-\eta_0}.$$

The expression for characteristic length l_0 is chosen depending on the view of $f(P)$.

For simplicity we shall henceforth (excluding the case of Fig. 4) limit ourselves to the case of constant c_0 . If so, the characteristic time t_0 may be introduced, and the first integral in (5) equals simply τ .

Even in such general case it can be seen, in particular, that sulphurization front moves through bed not changing its form, unlike the front of gaseous admixture. Nevertheless, their velocities are equal and normalized patterns are similar, except $t = 0$; they merge when frontal layer of the bed is fully exhausted as shown in Fig. 2.

To get an expression for w_b it was assumed for shrinking core model that the reaction (1) occurs only within the unreacted core. We have in such case for core (assuming first

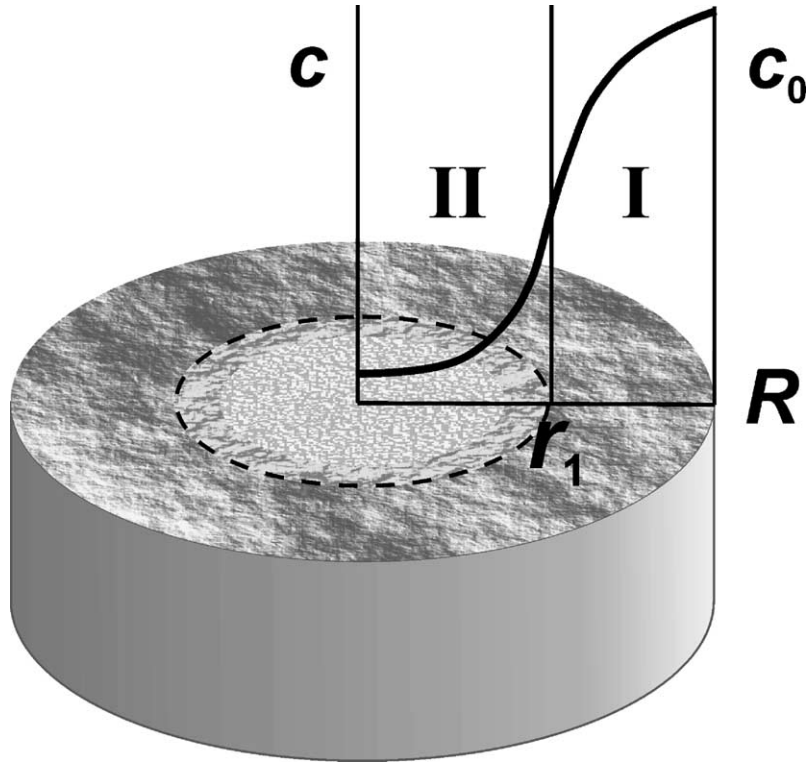


Fig. 1. The pattern of radial H₂S distribution in a partially sulphurized granule of ZnO-based sulphur absorbent. Zone I: uniformly sulphurized shell; zone II: unreacted core; dashed circle: the boundary between zones; solid line: the schematic plot of H₂S gas content vs. radius.

order of reaction rate with respect to H₂S content and spherical form of granule):

$$D_O^* \Delta_r c_{g1} = k c_{g1}, \quad \Delta_r c_{g1}(r = 0) = 0,$$

for outer (sulphurized) layer:

$$D_S^* \Delta_r c_{g2} = 0, \quad c_{g2}(r = R) = c_b,$$

core boundary conditions:

$$c_{g1} = c_{g2}, \quad D_O^* \nabla_r c_{g1} = D_S^* \nabla_r c_{g2},$$

rate of reaction (1) per unit bed volume:

$$w_b = \frac{3(1 - \varepsilon)}{R} D_S^* \nabla_r c_{g2}(r = R).$$

Taking into account that $\eta = (r_1/R)^3$, after elementary transformations we get

$$w_b = c \frac{6(1 - \varepsilon) D_S^*}{R^2} \varphi(\eta),$$

$$\varphi(\eta) = \frac{1}{2\{\eta^{-1/3} - 1 + \chi/(\eta^{1/3}[\rho_0 \eta^{1/3} \text{cth}(\rho_0 \eta^{1/3}) - 1])\}} \quad (6)$$

and it is convenient to choose

$$l_0 = \frac{uR}{6(1 - \varepsilon) D_S^*}.$$

3. Evaluation of parameters

Integrating numerically (5) taking into account (6) gives time dependence of gaseous admixture content at the bed outlet. Fitting some experimental data of such a dependence will give evaluations of sorbent properties.

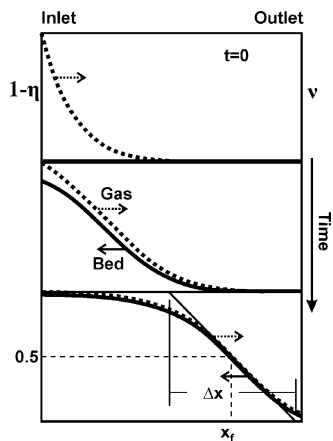


Fig. 2. Successive normalized patterns of sulphur distribution (“fronts”) in gas (H₂S, dotted line) and absorbent (ZnS, solid line) along the gas flow inside an absorbent bed. Dimension lines in the lower box define front width Δx . x_f is the x -coordinate of fronts flex points.

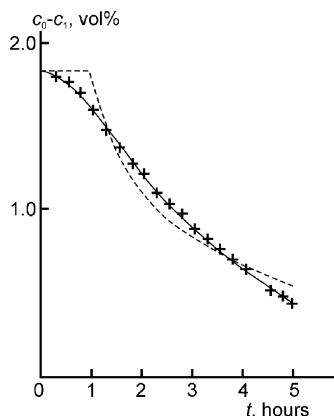


Fig. 3. Fitting of laboratory data (+) on commercial ZnO-based adsorbent sulphurization with $H_2S + H_2$ mixture using proposed (solid line) and usual (dashed line) models.

An example of such fitting is shown in Fig. 3 (solid line). Experimental technique is described in [2]. For comparison the usual version of shrinking core model taking into account only diffusion through outer layer was also tried for fitting (dashed line). It is seen that the latter failed to fit properly. As for the former, the following estimates were received for this sample of commercial extruded sulphur removal catalyst: $\rho_0 = 9.4$; $\chi = 0.63$; $k = 27 \text{ s}^{-1}$; $\lambda = 2.5 \times 10^{-4} \text{ m}$; $P_0 = 360 \text{ kg/m}^3$; $D_O^{*(1)} = 1.7 \times 10^{-6} \text{ m}^2/\text{s}$; $D_S^{*(1)} = 1.1 \times 10^{-6} \text{ m}^2/\text{s}$.

Estimated value of λ is in agreement with experimental results of [3]. P_0 value is confirmed by direct evaluation [2].

Values of diffusivities are roughly 10 times less than those for usual gas diffusion. Possible explanation is that, as was mentioned above, not only macropores, but also micropores and even intercrystalline gaps are involved in the process of hydrogen sulfide transportation to zinc oxide crystallites.

It should be emphasized that initial sulfur capacity for granules is less than its stoichiometric value.

For three commercial removal catalyst (named Abs1, Abs2, Abs3) the above mentioned parameters were also obtained and used for simulation of their runs in industrial units. Fig. 4 shows the results of this simulation compared with measured contents of H_2S in outlet gas.

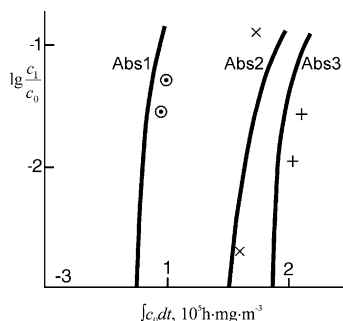


Fig. 4. Calculated breakthrough curves (solid lines) compared with commercial runs data of Abs1 (O), Abs2 (x) and Abs3 (+) adsorbents. x - and y -coordinates are chosen according to (5).

4. Analysis of bed behavior

Further study has showed that these data are typical. Let us present w_b as follows:

$$w_b = k \frac{1 - \varepsilon}{P_0} K_{dr}(\eta) c P.$$

$K_{dr}(\eta)$ can be regarded as a variable efficiency factor of reaction inside a granule, related to pore-diffusion resistance. The pattern of this factor dependence on the local value of the residual sulphur capacity fraction η for typical values of model parameters (Fig. 5), namely, its approximate constancy over a wide range of η values, allows to try Bohart–Hinshelwood model [4,5] to analyse the process under consideration.

In this model, being the simplest case of (3) and (4) with $w_b = qcP$, $q = \text{const.}$, the set (5) turns into explicit analytical expression, and for such important process variables as utilization factor $\bar{\alpha}$ of the total bed sulphur capacity and a time t_{br} before appearance of maximum permissible H_2S content at the unit outlet, as well as for some others, simple analytical expressions were obtained [4,5]:

$$\bar{\alpha} = 1 - \frac{V}{Q} \ln \left(\frac{c_0}{c_1} - 1 \right), \quad t_{br} = \frac{P_0}{c_0 V} \bar{\alpha}. \quad (7)$$

For most known commercial sulphur removal catalysts the order of magnitude of Q values (at NTP) is 10^4 h^{-1} .

Sulphur (of ZnS) concentration front width Δx can be introduced as follows:

$$\Delta x = \left[\frac{\partial \eta(x_f)}{\partial x} \right]^{-1},$$

where x_f is the x -coordinate of this front flex point, i.e. $\partial^2 \eta(x_f) / \partial x^2 = 0$. In the Bohart–Hinshelwood model

$$\eta(x_f) = 0.5, \quad \Delta x \approx 4uQ^{-1} = 4LVQ^{-1}.$$

Then for a typical sulphur removal unit of 1360 t per day ammonia plant ($V \approx 600 \text{ h}^{-1}$) Δx amounts to $\approx 30\%$ of the total adsorbent bed length.

The velocity of this sulphur front movement, estimated as that of front flex point, for such a unit under usual up-to-date conditions has the order of magnitude of millimeters per day.

It needs to be emphasized, that estimations thus obtained of sulphur removal catalyst run and the rate of use of the bed sulphur capacity are inferior.

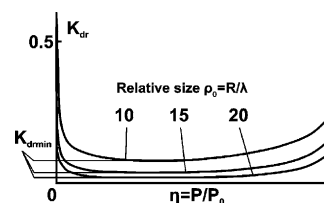


Fig. 5. Pore-diffusion caused efficiency factor K_{dr} for reaction inside a granule of ZnO-based adsorbent vs. residual sulphur capacity fraction η , calculated for $\chi = 0.5$ and $\rho_0 = 10, 15, 20$.

Taking into account the local rate structure (6) of reaction (1) and also characteristic values of granule parameters shows that minimum of $K_{dr}(\eta)$ is situated closely enough to $\eta = 0.3$. It allows, in particular, to receive from (7) an approximate expression (8) for $\bar{\alpha}$, containing, in addition to parameters in (7), an effective size R of absorbent granules, an effective diffusivity $D_S^{*(1)}$ (at normal pressure) of hydrogen sulphide in sulphurized granule shell and operating pressure \mathbf{P} (atm) in a sulphur absorber:

$$\bar{\alpha} \approx 1 - \frac{R^2 VT}{10D_S^{*(1)}} \left(1 + \frac{0.22}{\sqrt{\mathbf{P}}} \right) \ln \left(\frac{c_0}{c_1} - 1 \right), \quad (8)$$

To separate out the dependence on \mathbf{P} it was assumed, as usual, D_S^* (and D_O^*) $\sim \mathbf{P}^{-1}$.

The effective diffusivity in a porous solid essentially depends on parameters of the pore structure. When zinc oxide is converted to sulphide then molar volume increases almost by a factor of 1.7 and it results in significant decrease of porosity and, respectively, diffusivity [1].

Gas composition, in addition to a pore structure, also affects the value of effective diffusivity of hydrogen sulphide in sulphurized granule shell. For methane it is 1.3 times less than for H_2 , and for gases of higher molecular weight this ratio is even greater.

It can be easily seen from (8) that bed overall sulphur pick-up dependence on gas composition as well as on operating pressure and space velocity is in good qualitative accordance with corresponding data of [6].

At last, the combination $D_S^{*(1)}/T$ behaves itself as $T^{(0.75-1)}$.

5. Conclusions

Sulphur removal catalyst bed macrokinetics is mainly determined by the size of granules and H_2S diffusivity in their outer sulphurized layer.

Certainly, it can take place only in the absence of kinetic limitations of reaction (1) rate which is ensured with the production techniques of the up-to-date sulphur removal catalysts, enabling to obtain active zinc oxide with a surface area of 40–50 m^2/g and even more.

Despite the fact that usual version of shrinking core model also takes into account only diffusion through outer layer it is not adequate to the problem in question. Possible reason may be that though this version can be obtained from (6) if $k \rightarrow \infty$, such transition in (5) is incorrect.

If the value of effective diffusivity is obtained through data interpretation of H_2S sorption by ZnO granules, the expression (8) allows estimation of dynamic properties of an absorbent in certain range of granule sizes and operating conditions.

The approach proposed to sulphur absorbent bed modeling has been proved when calculating the reduced loading of the sulphur removal unit of the methanol plant [7].

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