

Heterogeneous Model for the Adsorption and Reaction on the Surface of highly-agglomerated Nanoparticles in a Fluidized Bed

*Jürgen Flesch, Thai Aerosil Co. Ltd., 21130 Rayong / Thailand
Jonah Klein, Degussa Corp., Mobile, AL, 36582 / USA
Dieter Kerner, Degussa AG, 63403 Hanau / Germany
Herbert Riemenschneider, Degussa Corp., Mobile, AL, 36582 / USA
Rainer Reimert, Universität Karlsruhe, 76131 Karlsruhe / Germany*

Introduction

Fumed oxides (SiO_2 , Al_2O_3 , TiO_2) are industrially produced in flame reactors. In the case of fumed silica, a chlorosilane-vapor (e.g. SiCl_4) is mixed with air and hydrogen and hydrolysis takes place in a flame at temperatures well above 1000°C . Nano-sized primary particles are formed, which sinter together to aggregates of sub-micron size. The morphology of these aggregates is determined by the reaction conditions in the flame reactor. Subsequently, these aggregates adhere to each other to form three-dimensional agglomerates, which can be in the several hundred micron range in size. The overall porosity of these agglomerates can exceed 98% and a fixed bed of such material has bulk densities of 20 to 100 g/l only. Due to the small primary particles, industrially produced fumed oxides have large specific surface areas of up to $400 \text{ m}^2/\text{g}$. On their large specific surface there are functional chemical groups, in case of fumed silica these are silanol (Si-OH) and siloxane (Si-O-Si) groups. Some of these functional groups (e.g. the silanol groups) can readily interact with other chemicals or they can be modified in the production process itself.

This unique morphology paired with a wide array of possible surface chemistry make fumed oxides a necessary compound in many products. Fumed silica for example is used in the silicone industry to provide the desired rheology and mechanical strength in silicone adhesives and silicon rubbers. Fumed alumina is used for example to treat ink-jet paper for improved ink-absorbance and fumed titania is used in cosmetic applications such as sun-protection. These same properties also require special considerations in the processing of these solids which often go beyond the conventional text-book knowledge for solids processing.

In the industrial processes for fumed oxide manufacturing, fluidized beds are used to remove the byproduct HCl from the fumed oxides (so called deacidification) or for chemical modification of the functions surface groups (e.g. to make a hydrophilic fumed silica hydrophobic). Whereas research on gas-/solids fluidized bed is extensive, the fluidization of fumed oxides has only been studied recently^{1,2,3}. Some fumed oxides can be fluidized well (e.g. fumed silica with large specific surface area) and the fluidization is characterized by large bed-expansion and no channeling. Whether bubbles are formed, depends on certain fluidization parameters, such as gas-distributor type or fluidization velocity⁴. This type of fluidization of nano-particles has been classified as agglomerate-particulate fluidization (APF)¹. On the other hand, some fumed oxides (e.g. fumed titania or fumed silica with low surface area) are difficult to fluidize and behave like Geldart B type solids with little bed expansion, channeling and if fluidization can be initiated, it shows strong bubbling. This type of fluidization behavior has been named agglomerate bubbling fluidization or ABF. The research group of Prof. Pfeffer at NJIT (e.g. Yu et. al.⁵) has investigated methods of assisted fluidization of such particles.

No reactor model has been reported so far, which can describe adsorption and chemical reaction of such low-bulk density particulate systems in fluidized beds. The presentation of such a

model and the comparison with experimental data for the deacidification of the fumed silica AEROSIL® 200 is the scope of this work.

Process-Model

Figure 1 shows a schematic of the reactor model for the batch fluidized bed employed in the experiments. The extended fluidized bed is divided in three phases. The first phase is the fluidized agglomerates, which are assumed to be spheres with constant diameter d_F and a porosity ε_F . These agglomerates are suspended in the suspension phase exhibiting the porosity ε_g . Solid free spherical bubbles of constant size make the third phase.

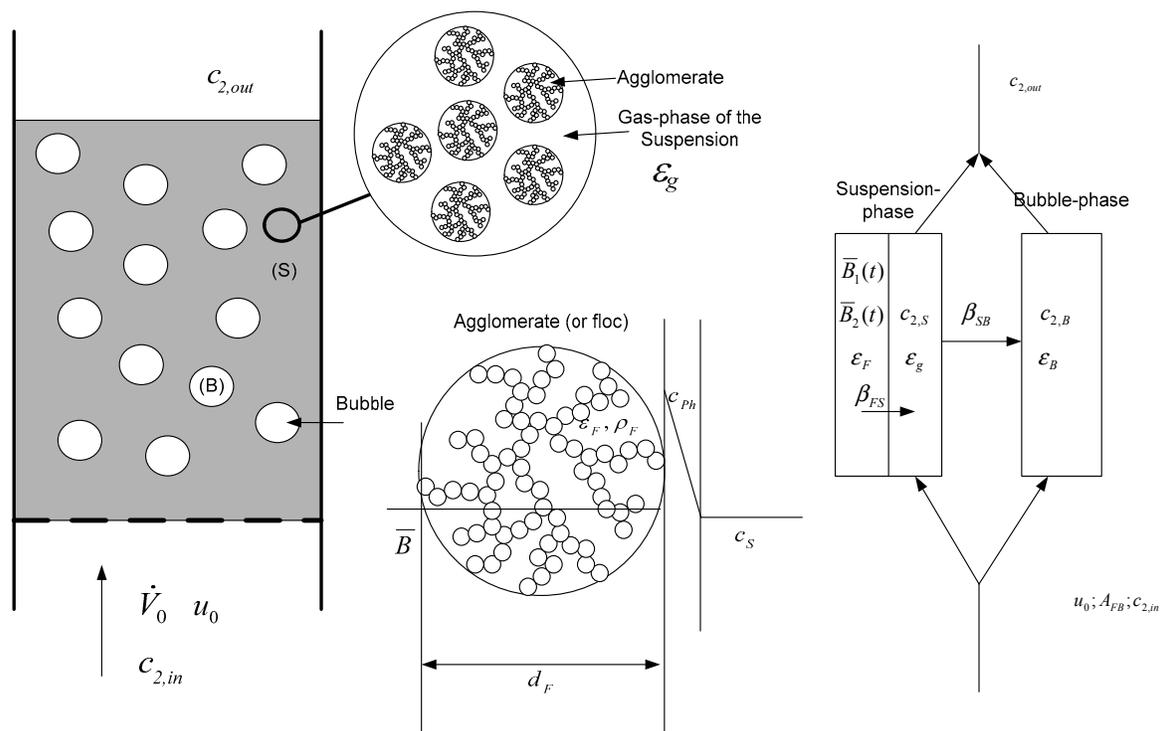


Figure 1: Schematic of the fluidized bed, the suspension phase and the agglomerate.

The fumed oxide agglomerates are fluidized with gas of the superficial velocity u_0 in the batch fluidized bed with the cross section A_{WS} . The total volume flow \dot{V}_0 is assumed to stay constant through the entire fluidized bed. For the deacidification of AEROSIL® 200, this fluidizing gas contains water vapor with the concentration $c_{2,in}$. All three phases are assumed to be back-mixed. Therefore, the mass-balance equations are only time-dependent and not a function of bed height and are not explained in detail here. The fluidized bed is considered isothermic. No energy-balance was included into the model.

Adsorption equilibrium and diffusion within the agglomerate

Physical adsorption of water takes place on the surface of the primary particles. The adsorption equilibrium is calculated using the linear Henry law, which was found applicable from experimental measurements over a wide range of temperatures.

$$\bar{B}_{2,phys} = K_c c_{2,Ph} \quad (1)$$

$\bar{B}_{2,phys}$ is the mass-fraction of physically adsorbed water on the surface of the primary particles. $c_{2,Ph}$ is the concentration in the gas-phase at the boundary of the agglomerate to the gas-phase of the suspension. The temperature-dependent Henry-coefficient K_c was measured in independent adsorption measurements⁴ and the temperature correlation was found to

$$K_c(T) = 7,85 \cdot 10^{-9} \frac{mg}{g \cdot mbar} \frac{RT}{\bar{M}} e^{4040K/T} \quad (2)$$

Zhu et. al.² have shown, that penetration of fluidization gas into the agglomerate is negligible and that the agglomerate can indeed be regarded hydro-dynamically as a non-penetrated sphere. There is also no diffusion limitation within the agglomerate which was checked experimentally by PFG-NMR measurements⁴. As a consequence, there is no concentration gradient within the agglomerate.

Chemical reaction at the surface of the primary particles

For the removal of chloride from the surface of the fumed silica the following chemical reaction is proposed



Experiments have shown an influence of the steam concentration in the fluidizing gas on the reaction kinetics⁴. A formal kinetic of second overall order is used to describe the chemical reaction for the deacidification. The exponent of 1/3 for the water mass-fraction is necessary to represent the influence of steam on the deacidification rate properly (as shown below).

$$\dot{R}_1 = -k_R \bar{B}_1 \bar{B}_2^{1/3} \quad (4)$$

In this equation \dot{R}_1 is the rate at which the Si-Cl groups (with the mass-fraction of \bar{B}_1) react with the adsorbed water \bar{B}_2 on the surface of the primary particles. k_R is the temperature dependent rate-constant. Experiments have shown, that there is a residual at the respective temperature non-removable mass-fraction $\bar{B}_{1,\infty}$. To account for this non-removable chloride content, the reaction kinetic term in equation (4) is modified by subtracting $\bar{B}_{1,\infty}$ from \bar{B}_1 .

$$\dot{R}_1 = -k_R (\bar{B}_1 - \bar{B}_{1,\infty}) \bar{B}_2^{1/3} \quad (5)$$

Mass transfer between phases

The resistance of the mass-transfer from the agglomerate to the gas-phase of the suspension phase and from there to the bubble phase is assumed to be in a boundary layer between each phase. The common linear kinetic expression for the mass-transfer is used.

$$\phi_{2,FS} = \beta_{FS} n_F a_F (c_{2,Ph} - c_{2,S}) \quad (6)$$

In this equation $\phi_{2,FS}$ is the mass-flux from the agglomerate to the gas-phase of the suspension, $n_F a_F$ the total surface area of the spherical agglomerates (not the primary particles), and β_{FS} the mass-transfer coefficient, which can be calculated using the Sherwood correlations for the flow around a single sphere. For the mass-transfer into the bubble phase the expression is analogous.

$$\phi_{2,SB} = \beta_{SB} n_B a_B (c_{2,S} - c_{2,B}) \quad (7)$$

Here, $n_B a_B$ is the total surface area for mass-transfer of all the bubbles.

Homogeneous and heterogeneous fluidized bed and other parameters

The transition from homogeneous to heterogeneous or bubbling fluidized bed is determined by the minimum bubbling velocity u_{mb} . The fluidized bed is homogeneous, if $u_{mf} \leq u_0 < u_{mb}$ and bubbling if $u_0 \geq u_{mb}$. The minimum bubbling velocity u_{mb} can be determined experimentally. Other model parameters, such as the agglomerate diameter d_F or the various porosities are determined from a mass-balance together with an analysis of the expansion behaviour of the fluidized bed. The method is shown in Zhu et al². The bubble diameter d_B is taken from a semi-empirical correlation of Darton et al⁶. The presented model allows the calculation of the overall mass transfer from the suspended agglomerates to the fluidizing gas as a function of time with chemical reaction and / or physical adsorption. It can be applied to both the homogeneous fluidized bed and the bubbling heterogeneous fluidized bed.

Results

The model results are compared to own experiments in a batch-fluidized bed. For these experiments the fumed silica AEROSIL® 200 was taken directly from a production process before the deacidification step, and with this material the influence of various parameters on the removal rate of HCl in a batch fluidized bed were studied⁴. Figure 2 and Figure 3 show a rather good representation of experimental data for the deacidification by the model. The temperature dependency of the chemical rate constant $k_R(T)$ in equation 5 can be written as

$$k_R(T) = k_0 \exp\left(-\frac{E_A}{RT}\right) \quad (8)$$

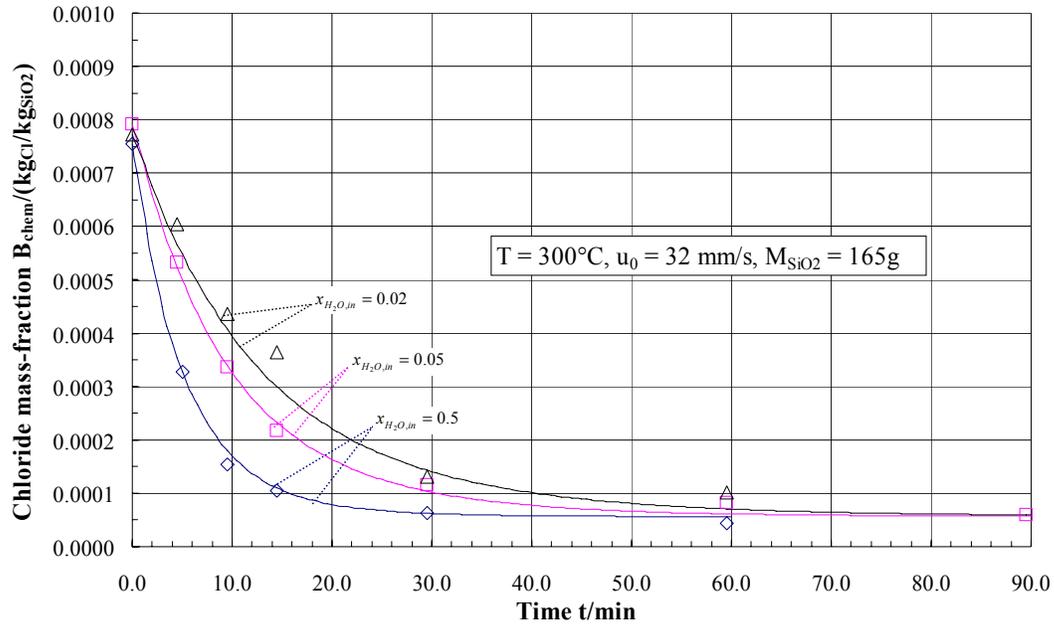


Figure 2: Representation of the experimental data for the deacidification of AEROSIL® 200 at different steam concentrations in the fluidizing gas by the model after parameter fitting.

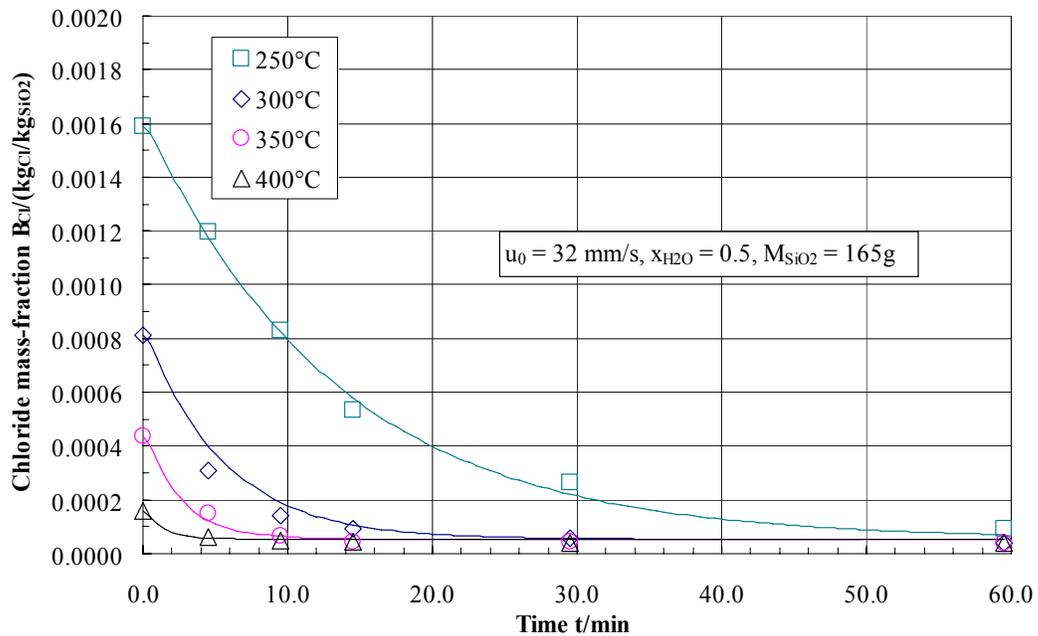


Figure 3: Representation of the experimental data for the deacidification of AEROSIL® 200 at different temperatures in the fluidized bed by the model after parameter fitting.

Fitting of the model to the experimental data in the measured range yields in an activation energy E_A of 51 kJ/mol and a pre-factor of k_0 of 87 kg/s. Other the deacidification rate influencing parameters, such as particle mass in the fluidized bed, initial Chloride mass-fraction or the influence of fluidization velocity and minimum bubbling velocity can be calculated with this model. If the ratio between the initial height to diameter of the fluidized bed is not too large (in our case $H_0/d_{ws} \cong 1$), the assumption of a back-mixed system is valid. More narrow fluidized beds may need some adjustment on the flow-pattern of the fluidizing gas towards plug-flow.

The same model was used to calculate the drying of fumed silica in a fluidized bed. Since there is no chemical reaction and therefore no rate constants to be determined, all parameters of the model are known and it can be used for predictive calculations. The results will be published in the future. For other treatments of fumed silica, such as surface treatment with silicone-oils, the proposed model should be applicable as well, if the rate expressions for the chemical surface reactions are determined experimentally.

Conclusions

A mathematical model was developed for adsorption and surface reaction on highly agglomerated nanoparticles in a fluidized bed. In applying this model to experimental data for the deacidification of fumed silica in a batch fluidized bed, a simple kinetic rate expression could be derived for the deacidification reaction, which is otherwise not obtainable. The temperature dependency of the rate-constant was also determined. All other parameters for the model can either be found through independent measurements (e.g. adsorption equilibrium or fluidizing characteristics) or in literature. The assumed flow pattern of complete back-mixing was found to be applicable, if the fluidized bed reactor has an initial height to diameter ratio of about one. For larger ratios (high fluidized bed with narrow diameters), an adaption of the flow pattern of the fluidizing gas might be necessary. The model can be used for sizing and optimizing of fluidized bed reactors in the production of fumed oxides.

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Symbols & Indices

A_{WS}	m^2	Cross section of the fluidized bed
a	m^2	Surface of a sphere (bubble or agglomerate)
\bar{B}_i	kg / kg	Mass-fraction of component i in the SiO ₂ particle
$\bar{B}_{1,\infty}$	kg / kg	Mass-fraction of Si-Cl which can not be removed at a given temperature
c	kg/m ³	Mass-concentration in a given phase
d	m	Diameter
E_A	kJ/mol	Activation energy
H_0	m	Height of fixed bed
K_c	m ³ /kg	Equilibrium constant for adsorption
k_0	kg/s	Pre-factor in Arrhenius equation
k_R	kg/s	Rate constant for chemical reaction
M_{SiO_2}	kg	Mass of SiO ₂ in the fluidized bed
\tilde{M}	g/mol	Molecular mass
n	-	Number of flocs or bubbles in the fluidized bed
R	J/(molK)	Gas constant
\dot{R}_i	kg/s	Reaction rate
T	°C	Temperature
t	s	time
u	m/s	Velocity
u_0	m/s	Superficial gas velocity
\dot{V}_0	m ³ /s	Volumenflow of fluidizing gas
x_{H_2O}	kg/kg	Mass-fraction of steam in the fluidizing gas
β	m/s	Mass-transfer coefficient
ε	-	Porosity
ϕ_i	kg/s	Mass-flux of component i

B	Bubbles or bubble-phase	out	exit of the fluidized bed
chem	Chemically bound component	Ph	Outer boundary of agglomerate
F	Agglomerate (floc)	phys	Physically bound component
FS	agglomerate to gas-phase suspension	S	Suspension or Suspension-phase
g	Gasphase of the Suspension- phase	SB	gas-phase suspension to bubble phase
in	Entrance of fluidized bed	FB	Fluidized bed
mb	Point of bubble formation	1	Component Si-Cl
mf	Minimal fluidisation	2	Component water