PARTICULATE FOULING IN MICRO-STRUCTURED DEVICES

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ABSTRACT

Micro-structured equipment is used for many applications in analytical or chemical reaction devices. A literature review shows the major fouling problems in micro-channels like clogging by gas bubbles, chemical reactions, corrosion, and particulate fouling. Experimental investigations of particle flow in micro-mixers indicate two major precipitation mechanisms of nanoscale particles, which are described by dimensionless numbers. Small particles reach the wall by diffusion and attach there for Peclet numbers smaller than $5 \bullet 10^6$. Larger particles touch the wall and accumulate in bent and curved flow, due to their inertia. The Stokes number describes the influence of the particle inertia in bent flow and has to be lower than 0.05 to prevent wall attachment. Additionally, surface properties have to be controlled and bends, curves, nozzles, and expansions have to be avoided to mitigate fouling.

INTRODUCTION

The application of micro-structured equipment is widely spread in analytical equipment, very common in laboratory devices, and now finds also applications in process engineering. This includes analytical microchips for biomedical applications or micro heat exchangers with straight laminar flow, mixing devices for various fluids with complex flow structures, and chemical micro-reactors for single phase or multiphase flow. In the last decade the development of micro parts for chemical engineering has made good progress: micro-mixers, micro heat exchangers and micro-reactors have been manufactured and tested. Companies like DuPont or BASF use micro parts for production or improvement and testing of their existing plants or processes. Fouling and blocking of the small passages with geometrical dimensions from 10 microns up to the millimeter size is the major problem during testing and operation of these devices, see Hessel et al. (2004). Although the problem is omnipresent in micro system technology, fouling still attracts too little attention in the technical-scientific investigation of micro systems.

This paper describes the actual state of the art of fouling in microstructures with special emphasis on devices for micro process engineering. An overview shows the recent activities in describing the fouling mechanisms in single phase or multiphase flow in process equipment with microstructures like micro-mixers, micro heat exchangers, and chemical micro-reactors. Emphasis is paid to the precipitation of particles and droplets at micro-channel walls, the blocking of micro-channels by the products of chemical reactions, and its consequences for proper operation. The deposition mechanisms are described with the help of dimensionless numbers. From the proper design and successful operation of microfluidic devices and micro-reactors, optimal strategies are derived to reduce or to prevent particle precipitation, fouling, or blocking in the micro-channels.

FOULING IN MICRO-STRUCTURED EQUIPMENT

Micro-channels in analytical equipment have to be filled with liquids at the beginning of their operation. A liquid has to replace the gas inside the channels, normally air. Due to the surface tension of the liquid and the wetting characteristics of the wall material, the liquid moves into the channel driven by capillary forces. Edges in channels are wetted earlier than plane surfaces, which may cause gas inclusions in the channels. This process was investigated by Goldschmidtböing et al. (2003), who gave an analytical correlation to estimate filling times. To overcome the clogging of small channels with air bubbles, the channels may be filled with CO_2 before the water filling. This gas dissolves easier in water than air and leads to the disappearance of the bubble after a short time. A proper channel design with no sharp edges, no small gaps and narrowing may prevent the formation of bubbles in small channels.

When priming micro-channel devices, any remaining gas bubbles may block the channels at unwanted locations, hinder the analytical process or increase the pressure loss to an intolerable value. Kohnle et al. (2002) propose a channel design with changes in cross section to overcome immobile gas bubbles in microfluidic devices. The combination of a high capillary channel with a small cross section and a low capillary channel with larger cross section increases the mobility of the gas bubble by a factor of about 6, which reduces the clogging risk. Optimization of the channel shape was a key to the successful gas phase synthesis of coated silicon nanoparticles from aerosols by Atwater et al. (2004). In particular, the avoidance of sharp expansions and dead zones produced a smooth flow and a long production time of the nanoparticles. Lipscomb et al. (2002) identified the control of the surface properties as a major parameter to

prevent fouling of proteins on a glass substrate. In their contribution they describe the fabrication details and some results with biological liquids. Other research groups work on functional coatings to prevent the adhesion of particles and molecules on the surface, see for example Fichtner et al. (2000). Functional surfaces are very specific to the system under consideration and difficult to transfer to more general problems.

Within one of our research projects a plate heat exchanger was designed and fabricated, see Fig. 1. With longer operation time of the heat exchanger with water, a slight corrosion of the alumina foil surface was observed which did not significantly affect the heat transfer or pressure loss. No experimental experience for longer than 50 hours has been gathered to present here. Blocking of the small channels leads to fluid maldistribution and to a diminished heat exchanger performance, i.e. less transferred heat. The recirculating flow in the structured channels increases heat transfer, but allows dead zones and particles attachment to the wall, too. This has to be investigated in future research studies.

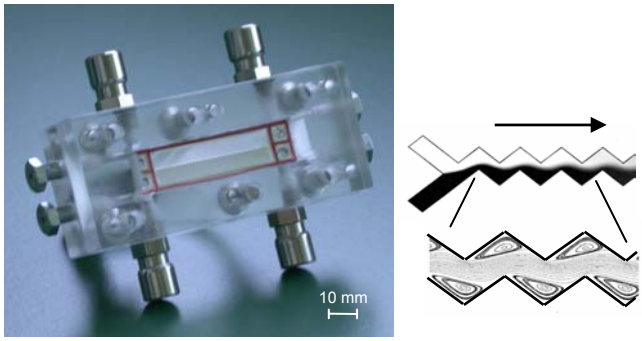

Fig. 1: Left: Micro-structured plate heat exchanger with alumina foil plate and silicone sealing within a PMMA mount with fluidic connections; Right: Schematic flow profile in zigzag channel with dead volumes, acc. Mengeaud et al. (2002).

Measuring of the velocity of luminescent particles for PIV (particle image velocimetry) has become a very common measurement technique in the last years, also for microfluidic devices. A working group in Bremen (Schlüter et al. 2004) measured the flow profile in smooth silicon channels and noticed no larger attachment of the luminescent particles at the wall. When using micro-structured devices from sintered metal powder, the luminescent particles adhered to the rough wall and disturbed the measurement considerably. The laser beam illuminates the attached particles, outshining the streaming particles and indicating zero velocity. The higher surface energy of the rough wall surface attracts the small particles and hinders them to detach from the wall. Another research group also reported the fouling problem during PIV measurement, see Adrian et al. (2004).

To mitigate fouling, a filtering of the inlet flows is recommended if it is possible. The filter size has to be adjusted to the smallest critical diameter of the micro-structured equipment. A high flow velocity in the micro-channels will hinder particle attachment to the wall and already attached particles may be washed away by the high shear gradient. For chemical reactions with severe fouling tendency, a separation layer of a clean fluid near the wall will hinder particles to get to the wall (Hessel et al. 2005). The impingement of two liquid jets and the fast reaction prohibits the fast contact of the reacting flow with the wall (Impinging Jet Micro Mixer). For analytical purposes disposable devices for singular use often circumvent the fouling problem. The device costs play the major role for disposables.

The major issue to control fouling in micro-channels is the proper design of the channel, of junction, expansions, nozzles, and the elimination of dead zones. A careful design of slender channels without sharp changes in cross sections will help a lot to prevent precipitation and attachment of particles. The underline this design strategy particulate fouling of particles with small diameter and different materials was investigated in micro-structured devices.

EXPERIMENTAL INVESTIGATION ON PARTICULATE FOULING

To get a more detailed view and to gain design criteria for particulate flow, our research group instigated the precipitation of monodisperse NaCl nanoparticles in a micro-structured device. The particles are generated by atomizing an aqueous NaCl solution, evaporation in a nitrogen carrier gas flow, drying, and selecting the desired particle diameter. Wengeler et al. (2005) describe the experimental and analytical setup in more detail, see Fig. 2.

The particle loaded flow enters the measurement setup at point (0), where the pressure difference PIR to the outlet flow is measured. For reference measurements, the entire particle flow can be sent with the three-way valve V1 to the particle counter with flow meter CPC. For testing the micro devices, the particle loaded flow is split-up into two equal flows and enters at (1) the micro-structured device. The other flow is filtered and enters the micro-mixer at (2). The flow rate of the second stream is adjusted with the help of the flow meter (FI) and the manual valve V2. After mixing, the entire flow leaves the device at (3) and enters the particle counter via the three-way valve V1.

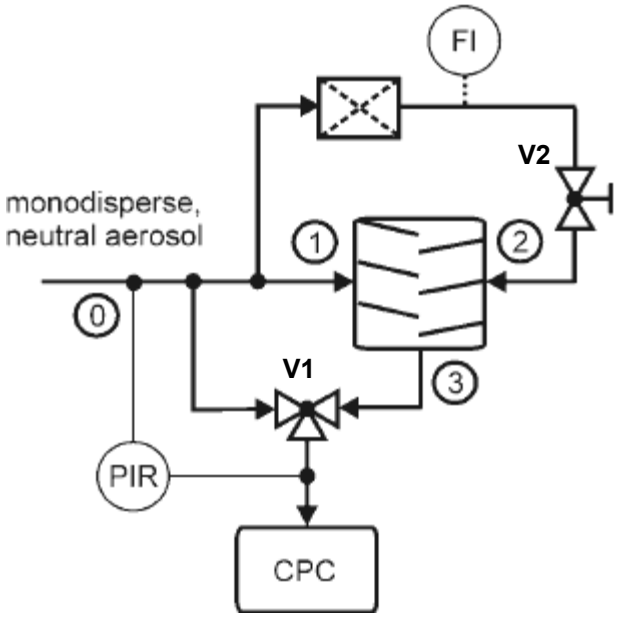

Fig. 2: Experimental setup used for the measurement of the particle deposition within the micro-mixer.

In Fig. 3 the passing probability p of a particle with a certain diameter is displayed of the particle diameter d_P. A probability of 1 means that all of the particles with this diameter pass through the device.

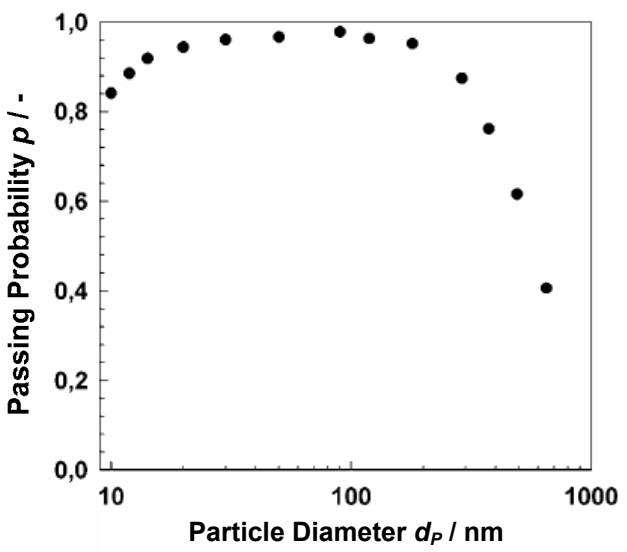

Fig. 3: Passing probability of the particles in the T-shaped micro-mixer (1000x500x300 µm, means mixing channel width x inlet channel width x channel depth) measured with monodispersed NaCl particles of varying size ($10 < d_P < 850$ nm) for a total flow rate of 0.3 ml/min and a mixing ratio of 1.35:1 (ratio of the inlet volume flows).

The total volume flow of 0.3 ml/min in the micro-mixer gives a mean velocity of 16.7 m/s in the mixing channel, a corresponding Re number of 417, and a mean residence time of about 1.4 milliseconds. The pressure loss over the mixing device was about 26 mbar without fouling. Fig. 3 indicates a dramatic decrease of the passing probability in the micro-mixer for particles larger than about 150 nm, which results from their relatively large mass and inertia. Particles with a diameter from 30 to 150 nm show a large passing probability, near 1. Smaller particles tend to attach to the wall due to diffusion; they follow the Brownian movement.

In Fig. 4, left side, a typical T-shaped micro-mixer is given with the outer dimensions of 20x20x1.0 mm. The chip is fabricated from silicon with DRIE etched rectangular cross section channels (deep reactive ion etching), and covered with a Pyrex glass lid. The fabrication process is explained in more detail by Engler et al. (2003).

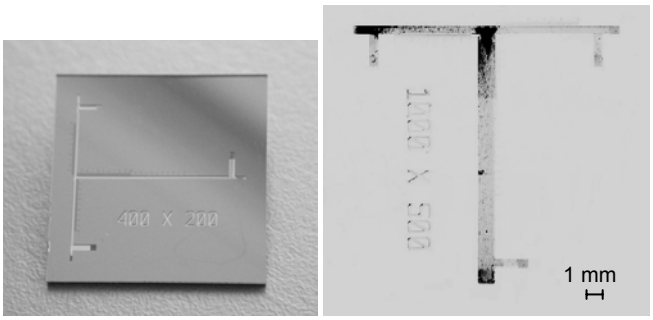

Fig. 4: Left: Clean T-shaped micro-mixer with RIE fabricated micro-channels, 200 µm inlet channel width, 400 µm mixing channel width; Right: Deposition structure of 200 nm NaCl particles (dark fields) in the micro-mixer 500 µm inlet channel width, 1000 µm mixing channel width.

The right image in Fig. 4 indicates clearly the main locations where the NaCl particles (200 nm) collect and attach to the wall. At the left inlet, the particulate flow turns into the drawing plane; larger particles cannot follow the bended flow and hit the wall. After about 2 mm in flow direction, the flow is laminar and parallel to the wall. Only a few particles reach the wall, mainly by diffusion. In the T-junction the two streams mix and form vortices. An analysis of the complex flow structures and vortex generation can be found in Kockmann et al. (2004). These vortices bring the particles to the wall and cause a strong attachment to the wall. After 2 to 3 mm into the mixing channel, the vortices are damped and straight laminar flow is adjusted again. The particles are flowing parallel to the wall and will attach only by diffusion. As indicated by the dark spots, larger particles may attach to the wall due to the diffusion effect also. At

the mixer outlet, there are also particles accumulated at the wall due to the bent flow.

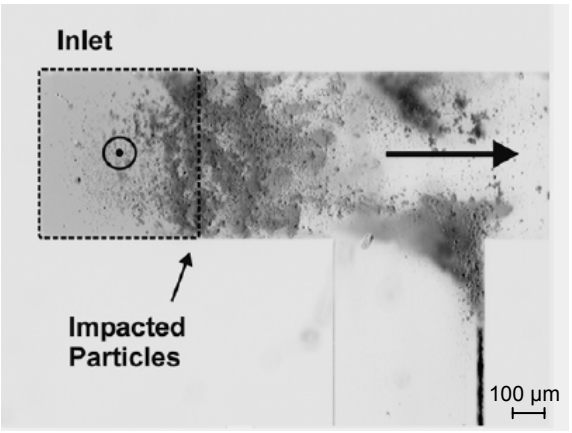

Fig. 5: Deposition structure of 200 nm NaCl particles in the inlet region of the micro-mixer; Detail of Fig. 4.

Fig. 5 shows the inlet (square hole) of the particulate flow into the micro-mixer, which clearly indicates the impact of the particles at the wall. The particulate flow comes from below and turns to the right in the drawing plane. Many particles are attached close to the inlet, but not directly over the inlet. This indicates the high angular flow velocity directly over the sharp bend, where the most particles accumulate. The channel directing downwards serves as a pressure measurement connection, where no flow is passing through. Many particles are located at the opposite side of the flow, which indicates the role of the particle inertia and the importance of the flow direction.

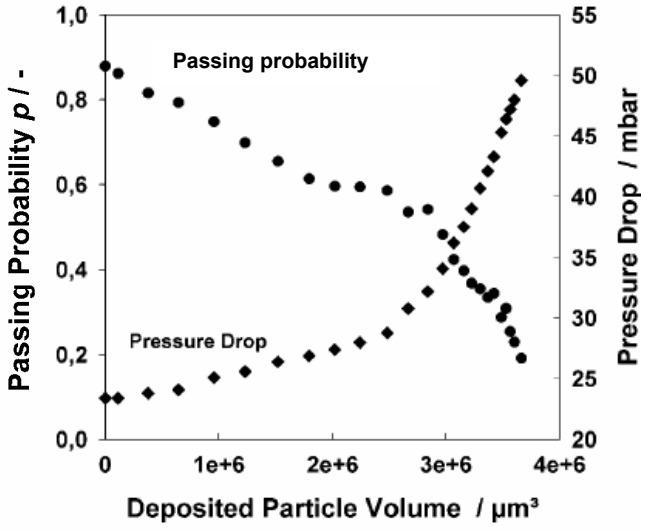

Fig. 6: Variation of the pressure drop and penetration efficiency of the micro-mixer caused by clogging with 200 nm NaCl particles as a function of the calculated deposited particle volume

The evolution of the passing probability of a particle through the micro-mixer and the correlated pressure drop over the device is shown in Fig. 6. With increasing attached particle volume the passing probability decreases, which indicates a smaller cross section at some locations and a more bended flow. This increases the pressure loss over the device that is the primary indication of blocking in a micro device.

DISCUSSION OF PARTICULATE FOULING OF AEROSOLS

The images of the deposited particles in micro-channels clearly indicate the major deposition at the channel curves, where lateral velocities occur. But also in straight channels some particles attach to the wall. The passing probability of particles flowing through micro-channels, displayed in Fig. 3, indicates two deposition mechanisms. The passing probability is nearly 1 for medium-sized particles with a diameter of about 30 to 200 nm. Small particles can follow the curved flow due to their little mass, but have to follow also the thermal fluctuations in the surrounding fluid. Larger particles attach to the wall in curved flow due to their inertia. The deposition process of particles from the flow to the wall is quite complex, but mechanism limits can be described with the help of dimensionless numbers. For more information on the dimensionless treatment of particle flow see Friedlander (2000).

The fluctuation of a particle is described by the particle diffusion coefficient D_P which is expresses as the ratio with the kinematic viscosity ν in the dimensionless Schmidt number *Sc*.

$$Sc = \frac{\nu}{D_P} \tag{1}$$

Small particle fluctuate with the surrounding fluid and possess a high diffusion coefficient. The ratio of the characteristic time of the flow t_F

$$t_F = \frac{d_h}{\overline{w}} \tag{2}$$

to the characteristic diffusion time

$$t_D = \frac{d_h^2}{D_P} \tag{3}$$

is proportional to the diffusion attachment of a small particle at the wall. The ratio is also called the dimensionless Peclet number which describes the motion of a particle by diffusion in a fluid flow. The Peclet number is also the product of the Reynolds number *Re* and Schmidt number *Sc*.

$$Pe = \frac{t_D}{t_F} = \frac{\overline{w}\, d_h}{D_P} \tag{4}$$

The experimental data show, that the deposition by diffusion happens for Peclet numbers $Pe < 5 \bullet 10^6$. For higher Pe numbers, the fluid velocity is too high or the particle is too large to let the particles attach to the wall by diffusion.

Larger particles with a diameter $d_P > 200$ nm attach to the wall in curved flow due to their inertia. The particle relaxation time t_P of small particles in a centrifugal field with laminar flow (Stokes flow) is described by the following term, see also Collins and Keswani (2004).

$$t_P = \frac{\rho_P \cdot d_P^2}{18\,\eta} \tag{5}$$

The dimensionless Stokes number Stk expresses the ratio of the particle relaxation time to the characteristic time of the fluid flow.

$$Stk = \frac{t_P}{t_F} = \frac{\rho_P \cdot d_P^2}{18\eta} \frac{\overline{w}}{d_h} \tag{6}$$

It can be concluded from experimental data that the inertia deposition happens for Stokes numbers $Stk > 0.05$. For Stokes numbers $Stk << 1$ the particle relaxation time is much shorter than the characteristic time of the flow; particles can follow the flow and do not attach to the wall. For larger Stokes numbers the inertia of the particle pushes the particles to the wall in curved flow.

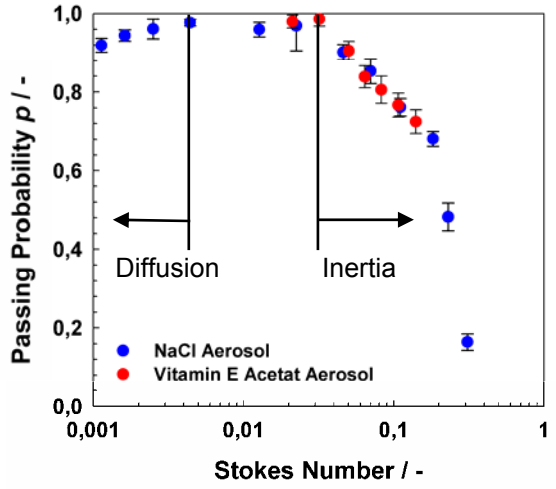

Fig. 7: Deposition mechanism of sodium chloride particles ($\rho_P = 2.16$ g/cm^3) and Vitamin E Acetate droplets ($\rho_P = 0.96$ g/cm^3) in micro-channels given with the Stokes number Stk.

To evaluate the influence of the Stokes number, the deposition of Vitamin E Acetate droplets was investigated in the same mixing device. In Fig. 7 the passing probability of sodium chloride particles ($\rho_P = 2.16$ g/cm^3) and Vitamin E Acetate droplets ($\rho_P = 0.96$ g/cm^3) are displayed with the Stokes number. The passing probability for the inertia deposition agrees very well for both particle materials. This indicates the central role of the Stokes number for the inertia deposition of aerosol particles.

The particle diameter where the inertia becomes important for deposition is about $d_P = 200$ nm for sodium chloride particles (NaCl) and about $d_P = 340$ nm for Vitamin E Acetate droplets.

The future investigations of particulate flow in micro-channels include the numerical simulation of particle motion with the flow. First results by Wengeler et al. (2005) show a good correlation between experimental and numerical data. The mitigation of particle attachment is one of the major design issues for the layout of micro reactors with particulate flow. The typical flow velocities and channel curves have to be adjusted to the particle size and properties. Additionally, sheath flow at the walls in critical regions and special surface treatment can help to avoid the particle attachment to the wall.

CONCLUSIONS

We have performed a literature study and some experimental investigations to identify the major fouling processes in micro-structured equipment. Besides chemical reactions and combined precipitation processes, particulate fouling and gas bubble clogging are the major reason for the blocking of micro-channels. The attachment of nano-sized NaCl particles is governed by diffusion for small particles (< 30 nm) and inertia for larger particles (> 200 nm). Particles with a diameter in between are very probable to pass through micro-channels, even if they are bent or curved. Two dimensionless numbers describe the deposition process. The Peclet number Pe has to be smaller than $5 \bullet 10^6$ to prevent particle deposition by diffusion. The Stokes number Stk has to smaller than 0.05 to avoid particle deposition at the wall by inertia. The important role of the Stokes number was experimentally shown with the deposition investigation of nano-sized NaCl particles and Vitamin E Acetate droplets.

From the literature survey and own experimental data, design rules are concluded for the appropriate layout of microfluidic devices. A proper channel design without sharp bends, nozzles, expansions, or junctions is essential to mitigate fouling. Larger channel diameters that allow high flow velocities, and smooth surfaces also help to mitigate precipitation. Due to the complex flow and great variety of different applications, a fouling-sensitive design and the collection of more experimental data will help for the successful operation of micro-structured devices.

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NOMENCLATURE

d_h	hydraulic diameter, m
d_P	particle diameter, m
Pe	Peclet number, -
Re	Reynolds number, -
Sc	Schmidt number, -
Stk	Stokes number, -
t_D	characteristic diffusion time, s
t_F	characteristic flow time, s
t_P	particle relaxation time, s
$\overline{w}$	mean velocity, m/s
η	dynamic viscosity, Pa s
ν	kinematic viscosity, m^2/s
ρ_P	particle density, kg/m^3

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