PHOTOCATALYTIC DEGRADATION ABILITY OF CEMENTITIOUS MATERIALS: A MODELING APPROACH

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Abstract

Concrete technology is a subject of continuous development and improvement. One of the very recent contributions to durability and sustainability of concrete is the self-cleaning ability. This effect can be achieved by applying photocatalytic materials to the concrete mix.

In earlier work a test setup was developed for the quantitative assessment of the air-purifying ability of paving stones [1]. Using this setup and the involved test procedure it is now possible to compare the performance of different active cementitious substrates.

Furthermore, with the help of this innovative setup, the influences on the degradation efficiency are studied and a basic reaction model is derived. This model follows the Langmuir-Hinshelwood kinetics and is in good agreement with the measurement results obtained. By means of this model an adsorption equilibrium constant as well as a reaction rate constant are derived. These two general measures are sufficient for a comprehensive description of the photocatalytic performance of the system. It will be shown that these measures include the kinetics of the system being the reactor dimensions, residence time, volumetric flow and pollutant concentration. In addition, the inclusion of the two most important external influences, the UV-irradiance and relative humidity, is discussed. Based on the measurements of their influences on the photocatalytic performance, a modification of the total reaction rate calculation is proposed.

1. INTRODUCTION

Despite intensifying immission control requirements and the increased installation of emission reduction systems, the air pollution and in particular the exhaust gas pollution by nitrogen oxides (NO) will be a serious issue in the near future. The by far largest polluters are traffic and industrial flue gases. In this respect attempts regarding the active reduction of nitrogen oxides can be found in forms of filter devices for industrial stacks (denitrogenization – DENOX plants) or active filter systems for e.g. tunnel exhausts. A further solution according to [2] could be the photochemical conversion of (nitric oxides) NO_x to low concentrated nitric acid by semiconductor metal oxides due to heterogeneous photocatalytic oxidation (PCO).

When earlier work mainly dealt with the treatment of waste water, PCO recently has received considerable attention regarding the removal of pollutants in air. For about 10 years efforts have been made, first in Japan, in a large scale application of this photocatalytic reaction for air-purifying purposes [3]. For the degradation of exhaust gases originated from traffic a sheet-like application close to the source would be desirable. Large illuminated surfaces in the road environment are for example road noise barriers including the road or sidewalk surfaces itself. Therefore noise barrier elements and paving stones are interesting substrates to study.

In [1] a comparative study on the NO_x degradation of active concrete surfaces is addressed. Thereby a representative profile of the economically available paving block products of the European market is considered. The presented paper is a continuation of this research using the results derived with one of these paving blocks as basis for further analysis. Furthermore the previously developed test procedure and setup are applied and therefore briefly described in the following.

The reaction rate is an important parameter to evaluate and model the efficiency of PCO. For fluidized bed reactors and other types of photoreactors the PCO of NO_x in presence of UV-light is well described in literature. However, for large scaled concrete applications there is no sufficient data available.

This paper addresses the measurements using a test setup capable of analyzing photocatalytic degradation of NO on concrete paving block samples. Using varying volumetric flow scenarios as well as different pollutant concentrations with otherwise constant test conditions a reaction model is derived describing the sample in terms of a reaction rate constant (k) and an adsorption equilibrium constant (K_d). Using these parameters, air-purifying concrete paving blocks can be explicitly described.

In addition to the flow kinetics of the system external factors can notably influence the performance of PCO. The number of influencing factors is large. However, only minor variation of UV-A intensity and relative humidity can considerably change the efficiency of the PCO. Therefore their influence on the reaction is investigated and a respective modification of the reaction rate computation is proposed.

2. REACTION MODEL

2.1 Model development

In this section the reaction process in the reactor is modeled. First, one should observe that the NO had to diffuse to the concrete surface, where subsequently the conversion to NO_x takes place. So the process contains two transfer steps, the mass transfer from gas to wall and the conversion at the concrete surface. In line with findings by [4] and [5], here it will be demonstrated that the conversion is the rate limiting step.

The NO mass flux from gas to surface is governed by:

$$\dot{m} = \frac{ShD}{D_h}(C_g - C_w) = \frac{ShD}{2h}(C_g - C_w) \tag{1}$$

with D_h, as hydraulic diameter, and C_g and C_w are the NO concentrations (in mg NO per m^3 air) in air (mean mixed or bulk) and on the surface. The relation between C_g and C_{con} is as follows:

$$C_g = \frac{M_{NO}\rho_{air}}{M_{air}} C_{con} \tag{2}$$

Considering that the molecular mass of the deployed synthetic air (M_{air}) is 28.8 g/mole (80% M_{N2} and 20% M_{O2}), that of NO (M_{NO}) is 30.0 g/mole, and that ρ_{air} is about 1 kg/m^3, it follows that C_g (in kg/m^3) is about C_{con} (in mole/mole), or equivalently, C_g (in mg/m^3) is about C_{con} (in ppmv = 10^{-6} mole/mole).

Sh is the Sherwood number, amounting to about 5 for slits with one inert and one exchanging side [6], and D the diffusion coefficient of NO in air, which amounts to about 1.5 10^{-5} m^2/s ($\sim \upsilon_{air}$).

If it is assumed that the diffusion to the concrete surface is the limiting step (conversion takes place instantaneously and completely), the NO concentration at the surface will be zero. The NO mass balance equation then reads:

$$v_{air} h \frac{dC_g}{dx} = -\dot{m} = -\frac{ShDB}{2h} C_g \tag{3}$$

with as boundary condition:

$$C_g = C_{g,in} \tag{4}$$

Integrating Eq. (3) and application of Eq. (4) yields:

$$\frac{C_{g,out}}{C_{g,in}} = e^{-\frac{ShDL}{2v_{air}h^2}} \tag{5}$$

with $C_{g,out} = C_g(x = L)$, L being the length (200 mm). Substituting all variables, including $v_{air} = 0.17$ m/s and h = 3 mm, into Eq. (5) yields $C_{g,out}/C_{g,in} \approx 0.04$. In other words, in the case that the diffusion to the wall would be rate limiting step, the exit concentration would be close to 4% of the inlet concentration, i.e. 96% of the NO would be converted. The present measurements and previous research ([1]) learned this is not the case, so that the conversion rate at the surface cannot be ignored (cp. Tables 1 and 2). In the following, it is now assumed *a priori* that the conversion is the rate limiting step, so that C_w now equals C_g, which will be verified *a posteriori*.

For the prevailing photocatalytic gas-solid surface reaction, only adsorbed NO can be oxidized. In the past therefore the Langmuir-Hinshelwood rate model has been widely used, e.g. by [4], [5] as well as [7], and which will also be applied here. Following this model, the disappearance rate of reactant reads:

$$r_{NO} = \frac{kK_d C_g}{1 + K_d C_g} \tag{6}$$

with k as reaction rate constant (kg/m^{3}s) and K_d as the adsorption equilibrium constant (m^3/kg). The NO balance equation now reads:

$$v_{air} \frac{dC_g}{dx} = -r = -\frac{kK_d C_g}{1 + K_d C_g} \tag{7}$$

Integration and using the boundary condition, Eq. (4), yields:

$$\frac{1}{k}+\frac{1}{kK_d}\frac{\mathrm{Ln}\left(\frac{C_{g,in}}{C_{g,out}}\right)}{(C_{g,in}-C_{g,out})}=\frac{L}{v_{air}(C_{g,in}-C_{g,out})}=\frac{V_{reactor}}{Q(C_{g,in}-C_{g,out})} \tag{8}$$

As $V_{reactor}$ = LBh and Q = v_{air}Bh, again, $C_{g,out} = C_g(x = L)$.

In Table 1 this $C_{g,out}$ of the experiments with the paving stone is summarized. The inlet concentration $C_{g,in}$ had values of 0.1, 0.3, 0.5 and 1 mg/m^3 (or ppmv), and the flow rate Q was 1, 3 and 5 l/min.

Table 1: NO outlet concentrations of the reactor considering varying inlet concentrations and flow rates for the photo-catalysis of the paving stone example

C_{in}	C_{out}			NO_x removal rate [%]		
[ppmv]	Volumetric flow rate Q [l/min]			Volumetric flow rate Q [l/min]		
	1	3	5	1	3	5
0.1	0.011	0.032	0.041	89.0	68.4	59.4
0.3	0.039	0.157	0.197	87.1	47.6	34.3
0.5	0.210	0.309	0.356	58.0	38.3	28.9
1.0	0.334	0.729	0.779	66.6	27.1	22.1

2.2 Validation of the model

In Figure 1, $y = V_{reactor}/Q(C_{g,in}–C_{g,out})$ is set out versus $x = \mathrm{Ln}(C_{g,in}/C_{g,out})/(C_{g,in}–C_{g,out})$, and the data fit with the line y = (1.19 s)x+2.98 m^{3}s/mg. The intersection with the ordinate corresponds to 1/k, so that k = 0.37 mg/m^{3}s, and the slope to 1/kK$_d$, so that K$_d$ = 2.51 m^3/mg.

In [8] obtained k = 6.84 mg/m^{3}s and K$_d$ = 1.13 m^3/mg was obtained for the NO degradation by woven glass fabrics, their inlet NO concentration being in the range 40 to 80 ppmv. Concerning the photo catalytic ammonia degradation by cotton woven fabrics, [5] obtained k = 0.10 mg/m^{3}s and 0.24 mg/m^{3}s, and K$_d$ = 0.035 m^3/mg and 0.112 m^3/mg, whereby the NH_3 inlet concentration ranged from 14 to 64 mg/m^3.

With the obtained values of k and K$_d$ the conversion rate and diffusion rate can be compared. Dividing the conversion/transfer rates as governed by Eq. (7) and (3) yields kK_d2h^2/ShD, and substituting the prevailing values reveals that this ratio is about 0.2, i.e. the diffusion rate is about five times the conversion rate. Note that the employed kK$_d$ is an upper limit for $kK_d/(1+K_dC_g)$, so that the actual ratio will even be smaller. From this small conversion/transfer rate ratio one can conclude that indeed the degradation rate is much slower than the diffusion rate, and hence it is the limiting rate. This is also confirmed by [2] who found conversion rates proportionally increasing with the specific surface area of the applied titanium dioxide.

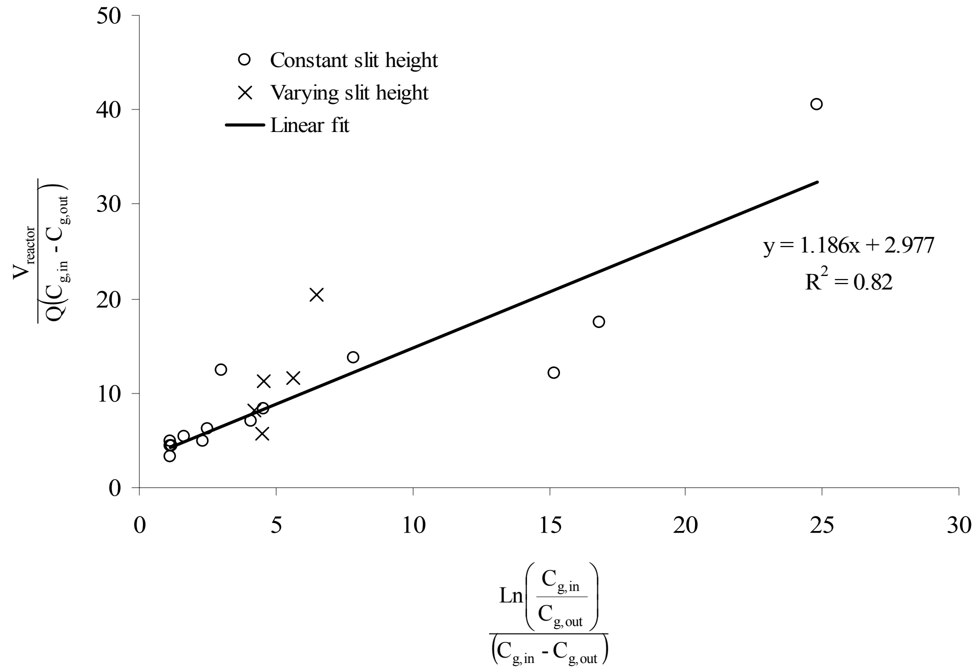

Figure 1: Regression results of data presented in Table 1 and Table 2 for the photocatalysis of the paving stone example

In the addressed research this fact was furthermore investigated by executing experiments with slit heights of 2 and 4 mm, $C_{g,in}$ taken as 0.3 mg/m^3 (0.3 ppmv), and the flow rate Q was 1, 3 and 5 l/min. In Table 2, and also in Figure 1, this data is included. With except for the smallest flow rate (Q = 1 l/min), the degradation rates match well with the values listed in Table 1, and the computed $V_{reactor}/Q(C_{g,in}–C_{g,out})$ and $Ln(C_{g,in}/C_{g,out})/(C_{g,in}–C_{g,out})$ are also compatible with the previous ones set out in Figure 1 and the fitted trend line.

Table 2: NO outlet concentrations and removal rates of the reactor considering constant inlet concentration C_{in} = 0.3 ppmv but varying flow rates and slit heights

Slit height	C_{out}			NO_x removal rate [%]		
[mm]	Volumetric flow rate Q [l/min]			Volumetric flow rate Q [l/min]		
	1	3	5	1	3	5
2	0.093	0.162	-	68.8	46.1	-
3	0.039	0.157	0.197	87.1	47.6	34.3
4	0.065	0.157	0.183	78.3	47.6	39.1

The above literature review shows that the Langmuir-Hinshelwood model has been frequently applied to characterize photocatalytic gas-solid surface processes using various substrate materials. However, to the authors' knowledge, the kinetics of photocatalytic acting concrete has not been analyzed so far.

Other relevant data on photocatalysis on concrete was found in [9]. Here, amongst other things, data is presented on the NO_x removal of a paving stone type (NOXER) which is exposed to varying NO concentrations. With the help of background information regarding the setup and conduction of measurement an analysis according to the Langmuir-Hinshelwood model was derived. The information given on the flow properties were sufficient for adequate application of the model.

Table 3: NO removal and NO_x removal rate for a concrete paving block taken from literature [9]

NO concentration	NO removal	NO_x removal rate
[ppm]	[mmol/$m^2$12h]	[%]
0.05	0.2	89.6
0.1	0.4	88.9
0.2	0.8	90.6
0.5	2.0	88.4
1.0	3.7	82.3
2.0	6.1	68.0
5.0	10.	44.3

Using the data on the NO_x removal rate given in Table 3 a linear fit is derived as given in Figure 2. As can be seen the resulting data points fit remarkably well into the proposed model.

Based on these values, again conversion rate and adsorption equilibrium constant can be derived. For the given data, k amounts to 3.54 mg/m^3s and K_d to 0.538 m^3/mg, respectively. Compared to the own experiments, the conversion rate is notedly higher and relatively smaller than the diffusion transfer rate. On the conversion side this can be explained with different amounts and types of catalyst (anatase) whereas the diffusion could be influenced by different surface morphology of the paving stones. The ratio of conversion/diffusion rates therefore amounts to 0.45 for the NOXER case, i.e. the conversion rate is still more than twice the diffusion rate.

3. MODELING OF EXTERNAL INFLUENCES

In the former paragraph a general model for the reaction kinetics of heterogeneous photocatalytic oxidation on concrete substrates has been derived. This model contains the reaction kinetics and flow related parameters like reactor dimension and pollutant concentration. The difficulty of predicting the performance of a photocatalytic cementitious system including all pertinent factors lies in the large number of variables involved. However, for a comprehensive modeling at least two more external influences on the degradation efficiency have to be included into the model. These are the irradiance and the concentration of water, expressed by the relative humidity.

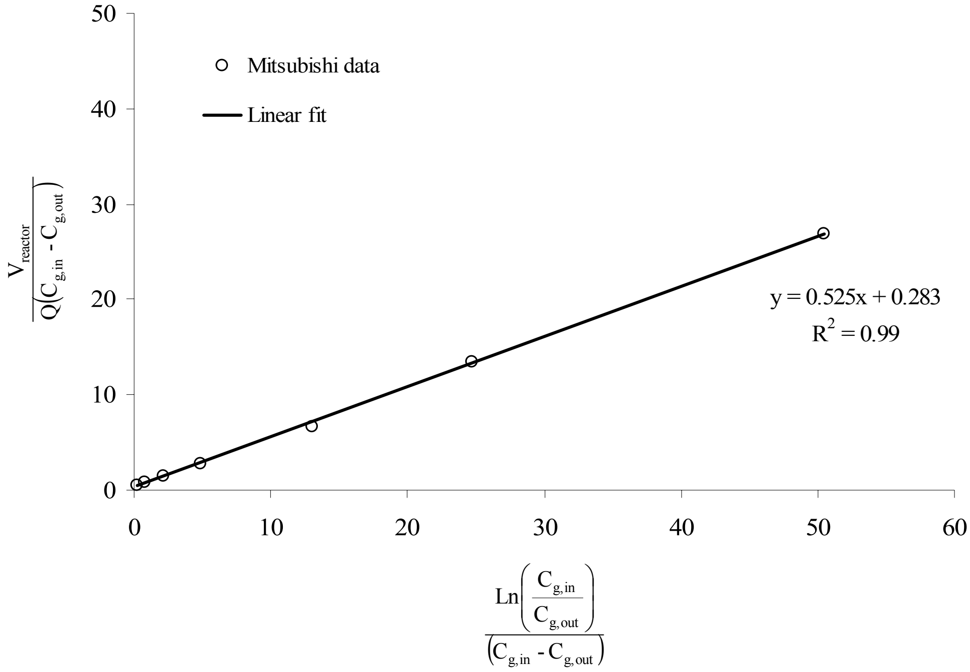

Figure 2: Regression results of data presented in Table 3 for the photocatalysis of a NOXER paving block (data taken from [9])

3.1 Irradiance

The degradation process of NO molecules is caused by the photocatalytic activity of the catalyst surface. This photocatalytic behavior results from the optoelectronic properties of this semiconductor. For the deployed catalyst (titanium dioxide in the anatase modification), the UV-A light shows the most suitable range regarding the wavelength (λ) to start the photocatalytic oxidization. However, not only the wavelength is influencing the efficiency of the system, but also the light intensity or irradiance (E) has an effect on the degradation rate.

According to [10], the increase in the photocatalytic activity caused by increased irradiance can be divided into two regimes: i) for $E \leq 250$ W/m² the degradation increases proportional to E and ii) for $E > 250$ W/m² the photocatalytic activity grows as the square root of E. This linear behaviour in the range of low irradiance ($E < 15$ W/m²) could not be confirmed by own measurements [11].

Figure 3 (left) shows the dependence of the NO removal on the irradiance for low values of irradiance, based on own measurements on a paving block containing TiO_2. A power function describes the relation between the irradiance and achieved degradation rate for very low values of irradiance ($E < 15$ W/m²). Depending on the steps of measurement the derived relation indeed results in an almost linear term for the irradiance interval 20 W/m² < E < 250 W/m².

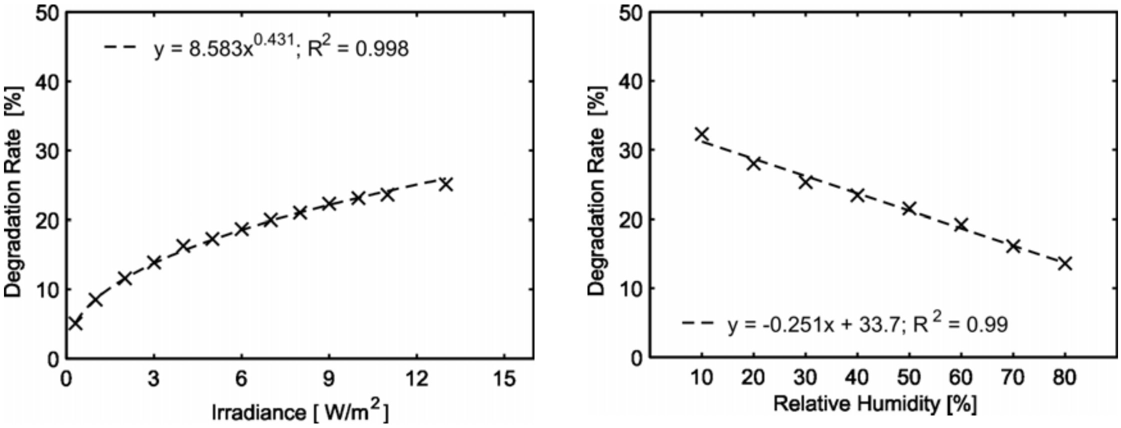

Figure 3: Influence of the (left) UV-A irradiance and (right) relative humidity on the degradation of a active concrete surface

Now it is assumed that the irradiance only has an influence on the reaction rate constant k. In order to incorporate the dependency of the radiative flux, a mathematical expression of the reaction constant k in function of the irradiance E is proposed [12]. Therewith, the reaction rate constant k would read:

$$k = \alpha_1\left(-1+\sqrt{1+\alpha_2 E}\right) \tag{9}$$

With α_1 and α_2 being factors to be fitted from the experiment. This expression would take account for the different, linear and non-linear dependency. When UV-radiation is absent, i.e. E = 0, the reaction rate becomes zero. For small E, Eq. (9) tends $\alpha_1\alpha_2 E/2$, and for large E it tends to $\alpha_1\sqrt{\alpha_2 E}$.

3.2 Relative humidity

The influence of the relative humidity depends to a large extent on the type of material used. According to [3], the hydrophilic effect at the surface is gaining over the oxidizing effect when high values of relative humidity are applied. The water molecules are adsorbed at the surface and prevent therefore the pollutants to adsorb to the surface and react with the TiO_2. Figure 3 (right) gives an overview over the achieved degradation rates depending on the relative humidity. It is evident from Figure 3 (right) that with increasing relative humidity the total efficiency of the system regarding the degradation of NO is decreasing linearly.

The introduction of this dependency into the reaction mechanism seems to be more difficult compared to the influence of irradiance. It is assumed that the relative humidity influences on the adsorption equilibrium constant (K_d) only. From the explanations above we learn, that NO and water compete for free sides at the catalyst surface. Therefore, water vapour can be considered as an additional reactant. For reaction rates on mixtures of volatile organic compounds (VOCs), [4] suggests an extended Langmuir–Hinshelwood model. For the present case this extended expression could consider the influence of humidity. The reaction rate for the reactant NO, r_{NO}, would then read as:

$$r_{NO} = \frac{K_{d,NO}C_{g,NO}}{1+K_{d,NO}C_{g,NO}+K_{d,H2O}C_{g,H2O}}\alpha_1\left(-1+\sqrt{1+\alpha_2 E}\right) \tag{10}$$

The water vapour concentration at 20 °C (experimental condition) and RH = 100% is 17.31 g/m^3, so that $K_{d,H2O}C_{g,H2O} = \alpha_3$ RH with $\alpha_3 = 17.31$ g/m^3 $K_{d,H2O}$. Furthermore, Eq. (10) can be rewritten as:

$$r_{NO} = \frac{K_d C_{g,NO}}{1 + K_d C_{g,NO}} \alpha_1 \left(-1 + \sqrt{1 + \alpha_2 E}\right) \tag{11}$$

with K_d as effective adsorption equilibrium constant in the presence of water vapour:

$$K_d = \frac{K_{d,NO}}{1 + K_{d,H2O} C_{g,H2O}} = \frac{K_{d,NO}}{1 + \alpha_3 RH} \tag{12}$$

Eqs. (11) can be substituted into Eq. (7), which can be integrated, and with Eq. (4), again Eq. (8) is obtained, in which k is now a function of E and K_d of RH. In other words, Eq. (8) can not only be used to study the effects of C_{in} and Q, but also E and RH. From experimental data, α_1, α_2 (both governing k), α_3 (governing $K_{d,H2O}$) and $K_{d,NO}$ can be fitted, which characterize the product.

4. CONCLUSION

Heterogeneous photocatalytic oxidation is a promising air-purifying technology. Besides this, the self-cleaning aspect coming along with PCO should not be ignored either. Concerning this matter, promising results have also been achieved.

The air-purification results obtained with the photocatalysis reactor show that a successful decomposition of NO_x along concrete paving stone surfaces is feasible by using PCO in the presence of UV light. For this research both experimental and modeling work has been conducted. With the derivation of a reaction model, based on Langmuir-Hinshelwood kinetics, now the treatment performance of certain air-purifying concrete products for decomposition of gaseous pollutants (NO) can be predicted. Furthermore, now the unique characterization of photocatalytic concrete products is possible by the derivation of its conversion and adsorption rate constants. The derived model also confirms that in the considered reactor the conversion of NO_x is the rate-determining step in the photocatalytic oxidation of NO_x. Furthermore, for the first time a mathematical expression is proposed, describing the performance of photo-active concrete products. This expression contains both, the kinetic boundary conditions as well as the process conditions. The latter influences and expressions are not validated by experiments yet, but are the subject of ongoing research.

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