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PRE-TURBO SCR – INFLUENCE OF PRESSURE ON NO$_X$ REDUCTION

Positioning the SCR system upstream of the turbocharger is currently being discussed for the SCR of nitrogen oxides in marine engines because it is hot enough at this position to prevent deposits in the SCR catalytic converter. However, this arrangement could also be interesting for applications in passenger cars because the increased pressure level upstream of the turbocharger should lead to a significant reduction of the required catalytic converter volume. With the help of model gas experiments at the Paul Scherrer Institut (PSI), the volume of the SCR catalytic converter was shown to actually be reduced by increasing the pressure, but the effect was smaller than expected.
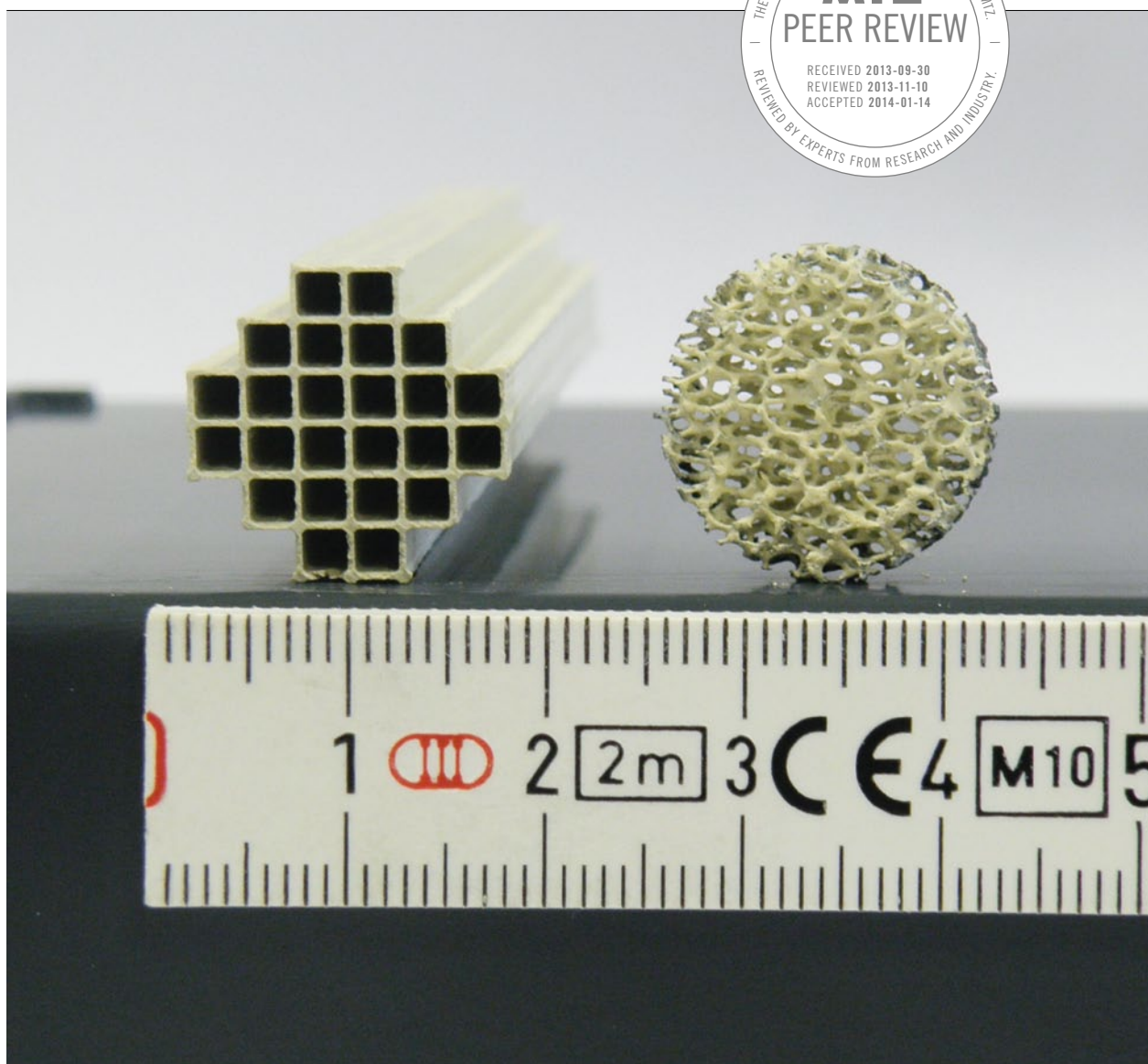
1 MOTIVATION

The emissions legislation for offshore shipping will become much stricter in the future. Thus, the maximum sulfur content in the fuel will be reduced from the current 1 to 0.1 % (or its equivalent in SO_2) in certain zones (Emission Controlled Areas) starting in 2015. Furthermore, the content of nitrogen oxides in exhaust gas is expected to be limited in these areas starting in 2021 [1]. This content will be reduced via selective catalytic reduction (SCR) with a urea solution. High-sulfur fuel oil (heavy oil) will still be used, but the sulfur dioxide produced in the combustion must be removed to ensure that the amount of SO_2 emitted into the atmosphere is equivalent to a sulfur content of 0.1 % in the fuel.

Because SCR processes that use vanadium catalysts must be operated at temperatures between 260 and 330 °C, the SCR system can only be installed upstream of a wet scrubber. At the high sulfur levels of usually 1 to 3.5 % in heavy fuel oil, the temperature must exceed 330 °C dependent on the sulfur content because the ammonia and sulfur dioxide react to sticky ammonium hydrogen sulfate at lower temperatures, which can clog the catalytic converter [2]. However, at very low sulfur contents of 0.1 %, the temperature can be as low as 260 °C.

For two-stage turbocharging, the temperature level of 330 to 430 °C between the turbines is ideal for the SCR process with respect to the sulfur problem. However, the pressures between the turbines in this design are between 3 and 5 bar, which prompted this study of the behaviour of vanadium-based SCR catalysts with urea under increased pressures. In the literature there are only two references which mention a clearly positive influence of pressure on the SCR reaction [3, 4]. Other studies report about less clear results or even no pressure influence was found [5, 6]. In a first step, the effect of pressure on the reduction of NO_x should accordingly be re-investigated in systematic model gas experiments without further affecting the system by the heavy fuel oil.

Under idealised conditions one might assume in a first approximation that the required catalytic converter volume should correspondingly decrease when the pressure increases and the associated volume flows proportionally decrease, for example, twice the pressure should result in half the catalyst volume. The system cannot be reliably designed based on this assumption due to several reasons:
: the exhaust gas is not a perfect gas
: the flow conditions may change
: the gas diffusion in the gas phase, the boundary layer and the pores changes
: the adsorption equilibria for ammonia, NO_x, water and SO_x are shifted
: the number of active sites on the catalyst surface is limited.
So even at full conversion the catalytic converter volume can only be reduced within certain limits.

Based on these limitations, this study aimed to experimentally determine the relationship between pressure increase and cata-

lytic converter volume and the minimum volume of the catalytic converter at higher pressures that conserves the NO_x reduction efficiencies observed at atmospheric pressure. In addition, the effect of foam structures as catalyst supports on the reduction of the catalyst volume under elevated pressures was also investigated compared to conventional honeycomb structures because foam structures have higher mass and heat transfer coefficients [7].

2 EXPERIMENTAL SETUP

The experiments were conducted in a model gas test rig in the laboratory, ❶. The model gas composed of N_2, O_2, NO, NH_3 and H_2O was mixed via electronic mass flow controllers, whereby water was generated in a pulsation-free process via the oxidation of hydrogen with oxygen over a Pt catalyst. The steel reactor (stainless steel St 1.4435, ID = 21 mm) with the sample was divided into a preheating zone and a heated reaction zone. All incoming and outgoing lines to the reactor, the gas pump and the gas measuring cell were temperature-controlled at 170 to 180 °C. At the reactor outlet, the pressure was set by a manually adjustable pressure valve (Swagelok No. SS RL3S6MM 0.7 to 15 bar). A partial gas stream of approximately 200 l_N/h at STP was supplied with a heated gas pump from the reactor outlet into the heated gas-measuring cell of an FTIR spectrophotometer (Thermo Nicolet Nexus) to analyse the reaction gases.

The test samples for the base experiments consisted of two extruded vanadium SCR catalysts with 1.7 % V_2O_5 and cell densities of 225 cpsi and 87 cpsi, respectively, and two SCR-coated metallic foams (2.1 % V_2O_5) with a mean pore size of 2500 μm. The metallic foams were available as 4 mm slices with a diameter of 18 mm and were combined into stacks of four to eight slices depending on the required catalyst converter volume. In the following it is only reported on the results of the foam sample F_2500-A with a catalyst loading of 186 g/l.

3 EXPERIMENTAL MATRIX AND EVALUATION

So-called slip-DeNO$_x$ curves were recorded between 400 and 200 °C in 50 °C steps to measure the catalytic behaviour. These curves were particularly suitable to assess the NO_x reduction performance of catalyst structures [8]. To do so, the ammonia dosage
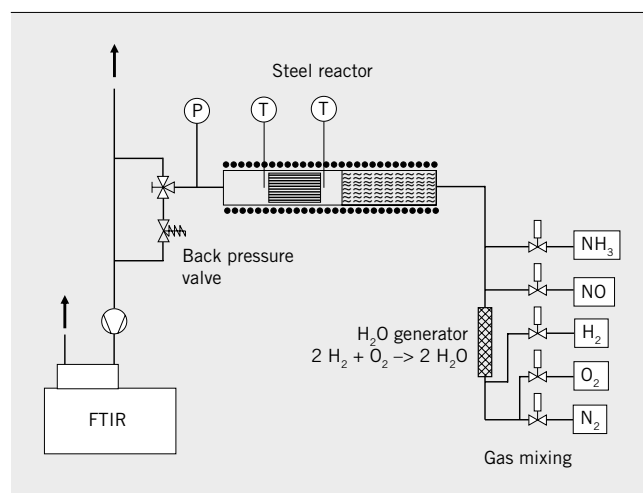
❶ Scheme of the model gas test rig for the investigation of SCR under pressure

was step-wise increased at a given temperature and constant NO dosage, and the NO$_x$ reduction efficiency (DeNO$_x$ [%] = (NO$_{x,in}$ − NO$_{x,out}$)/NO$_{x,in}$ · 100) and ammonia emissions (slip) were measured after equilibration. The achievable DeNO$_x$ at a practice-relevant ammonia slip of 10 ppm is of particular interest. The catalyst loading expressed as a gas hourly space velocity (GHSV) was set high enough to ensure a maximum DeNO$_x$ of 70 % at 350 °C at 10 ppm of ammonia slip because the pressure effect cannot be investigated at full conversion. The intrinsic activity of the catalysts was calculated approximately as the volumetric activity constant, k [s^{-1}], Eq. 1:

EQ. 1	$k = -V^*/W \cdot \ln(1-x)$

V* is the volume flow at T$_{reactor}$ and p$_{reactor}$, W is the converter volume and X the maximum achievable NO$_x$ conversion when ammonia is dosed in excess (= maximum DeNO$_x$).

4 RESULTS

In a first measurement series using the 225 cpsi extrudate, the slip-DeNO$_x$ curves were recorded with a constant catalytic converter volume at a GHSV of 60,000 h^{-1}, a NO concentration of 1000 ppm and reactor pressures of 1, 2 and 4 bar. While the NO$_x$ reduction efficiencies reached a moderate 55 to almost 70 % DeNO$_x$ at atmospheric pressure and a NH$_3$ slip of 10 ppm between 300 and 450 °C, they rose to values between 86 and 95 % at 2 bar. At 4 bar, virtually complete DeNO$_x$ was achieved in this temperature range.

When the pressure is increased, the partial pressures of the reactants will increase correspondingly. This increase can lead to a deterioration of the activity because the number of free active sites decreases intrinsically or due to their occupation by competing adsorption. Therefore, the concentrations of NO and NH$_3$ were reduced at higher pressures in a second measurement series such that the partial pressures of the reactants remained constant for all experiments. The volumes of catalyst were reduced in parallel according to the pressure increase so that the space velocity under operating conditions (SV), and hence the residence time, remained constant in the catalytic converter. At minimum, similar slip-DeNO$_x$ curves and NO$_x$ reduction efficiencies should be achieved independent of the pressure at these conditions.

Indeed, similar high maximum NO$_x$ reduction efficiencies were reached at 200 °C irrespective of the pressure. Furthermore, the DeNO$_x$ values at 10 ppm NH$_3$ slip were relatively close to each other within the measurement accuracy, ❷. This means, the catalyst activity was so low that diffusion limitation in the gas phase did not occur. Because the mean free path of the gas molecules, and thus the diffusion rates of NO and NH$_3$, negatively correlates with the pressure, this limited the SCR reaction. This effect became particularly pronounced at higher temperatures, where the NO$_x$ reduction was already influenced by gas phase limitations at 1 bar. Thus, at a NH$_3$ slip of 10 ppm between 350 and 450 °C, a DeNO$_x$ of approximately 70 % was reached at 1 bar. This value reduced to approximately 50 % at 2 bar and 35 % at 4 bar.

The DeNO$_x$ values do not directly indicate the kind of relationship between pressure increase and catalyst activity. To determine this relationship, the volumetric activity constants needed to be calculated from the maximum DeNO$_x$ and the space velocity and depicted in an Arrhenius plot. At 200 °C, the activity of the catalyst was so small that diffusion limitations could not be observed, and the activity constants were independent of the pressure. However, the activity of the catalyst at 250 °C increased to levels that resulted in diffusion limitation in the gas phase already at 1 bar, ❸. This effect was even more pronounced as the pressure increased; the intermediate temperature range at 2 and 4 bar was only approximately 75 and 50 % of the activity at 1 bar, respectively.

In a third series of measurements, smaller catalytic converters were manufactured according to the calculations, and the slip-DeNO$_x$ curves were measured at 2 or 4 bar and 1000 ppm NO and compared to the curves from the 1 bar experiment at 1000 ppm NO to verify the theoretical considerations. Although the DeNO$_x$
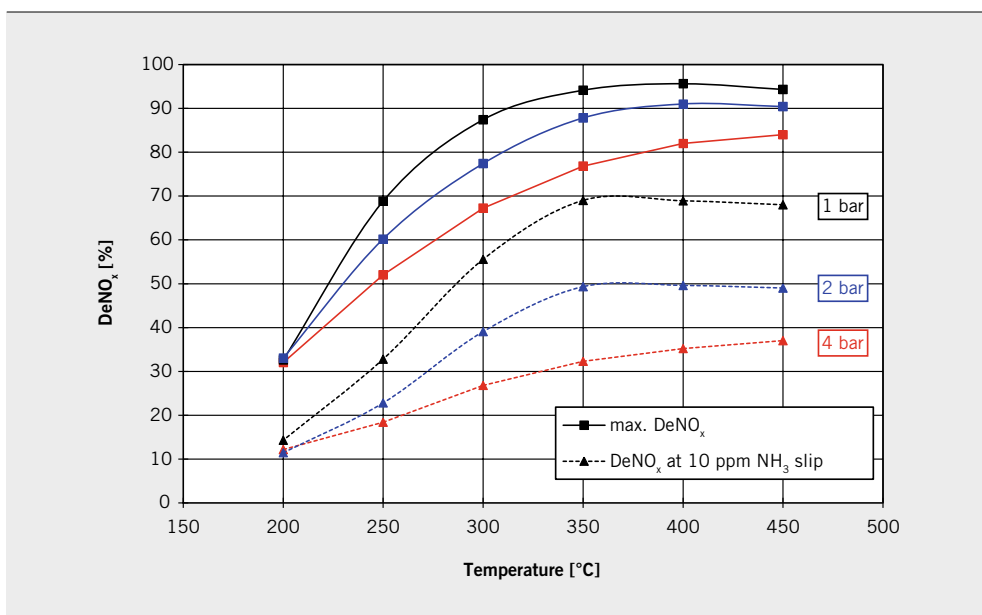
❷ 225 cpsi extrudate: DeNO$_x$ at constant NO partial pressure and the same residence time, independent on the pressure

❸ Volumetric activity constants of the 225 cpsi extrudate from SCR experiments under pressure with variable catalytic converter volume and constant NO partial pressure
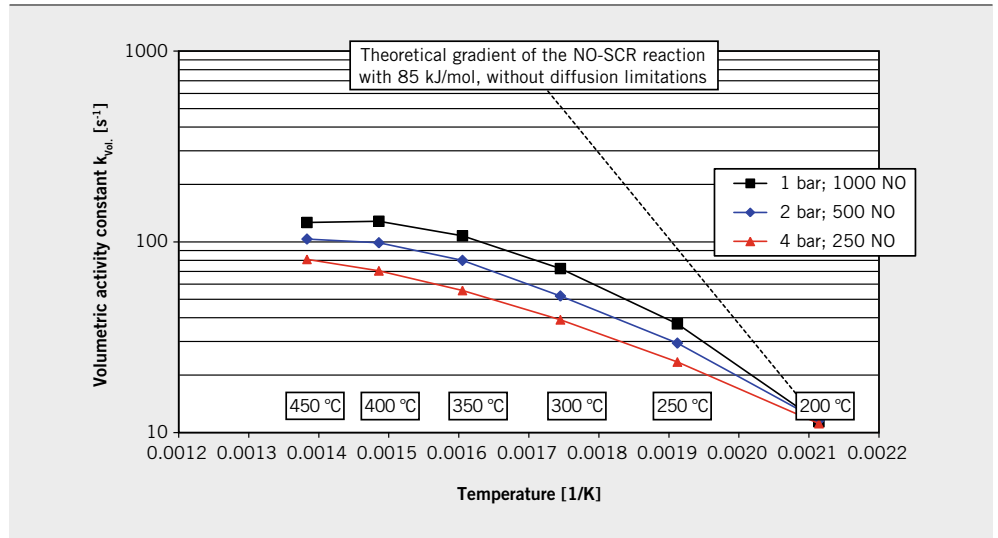
values at 10 ppm NH_3 slip and the maximum achievable $DeNO_x$ values at excess ammonia concentrations were virtually identical between 300 and 450 °C, a direct comparison of the slip-$DeNO_x$ curves shows that the curves were slightly less steep at 2 bar and significantly less steep at 4 bar. The flat slope of the curves was caused by the previously described much slower diffusion of both reactants in the gas phase to the catalyst surface, ❹.

Compared to the 225 cpsi extrudate, diffusion limitation occurred much earlier for the 87 cpsi extrudate. This difference was evidenced by an early ammonia slip, which required that the catalyst be operated at a lower load than indicated by its activity. This change resulted in a small savings in volume for a SCR under pressure. Specifically, the volume at 1 bar was reduced to 80 and 70 % at 2 and 4 bar, respectively.

In contrast to the 87 cpsi extrudate, the foam structure of the F_2500-A material showed much steeper slip-$DeNO_x$ curves that

were reflected in a significantly less pronounced pressure dependency of the slip-$DeNO_x$ curves and the activity constants. Accordingly, the expectable relative catalytic converter volumes at 2 and 4 bar were approximately 65 % and 40 % of the volume at 1 bar, respectively.

Due to the small catalyst loading, the foam structure showed only half of the volumetric activity of the 87 cpsi extrudate at 200 °C and 1 bar. As the temperature was increased, the activity of the catalyst increased to the point that more NO_x could be converted on the foam structure than with the 87 cpsi structure due to the shorter diffusion pathways from the gas phase to the active surface. The volumetric activity of the foam structure was already higher at 300 °C than that of the 87 cpsi structure. At 450 °C, it was almost twice as high. Because of the shorter diffusion pathways in the gas phase, the influence of the pressure on the volumetric activity was smaller.

❹ Slip-$DeNO_x$ curves of 225 cpsi extrudates at 1 bar, 2 bar and 4 bar. The volumes of the extrudates were adjusted such that at 2 bar and 4 bar the same $DeNO_x$ was measured at 10 ppm NH_3 slip as at 1 bar.
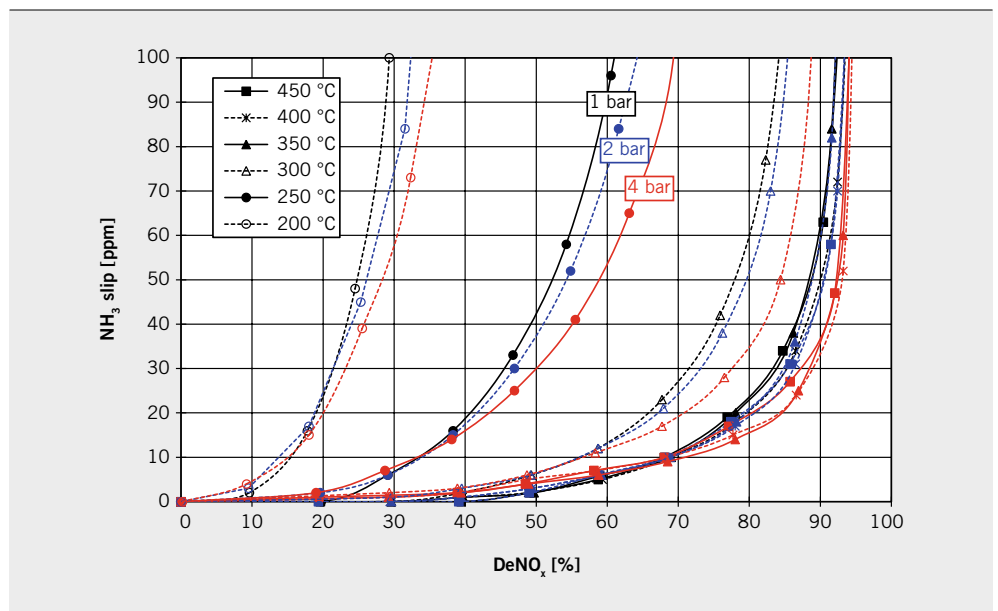
$T_{KAT.}$ [°C]	2 BAR			4 BAR		
	87 CPSI [%]	225 CPSI [%]	F_2500-A 186 G/L [%]	87 CPSI [%]	225 CPSI [%]	F_2500-A 186 G/L [%]
450	77	65	62	61	46	41
400	82	65	64	70	48	42
350	80	68	67	70	52	42
300	80	71	67	68	54	44
250	76	71	62	63	51	38
200	74	70	59	56	46	38

❺ Relative catalytic converter volume for pressure increases to 2 bar and 4 bar with DeNO$_x$ values equal to those at 10 ppm NH$_3$ slip and 1 bar

5 INTERPRETATION OF THE RESULTS

The measurements show that the catalytic converter volume can be reduced as expected if the pressure is increased by applying the SCR upstream of the turbo charger, but the potential is limited. A summary of the relative catalyst volumes that yield the same DeNO$_x$ values at 10 ppm NH$_3$ slip as those observed at 1 bar can be found in ❺ and ❻. The higher pressure reduces the gas volume, which causes a corresponding smaller residence time in the same catalytic converter volume.

The possible volume reduction for SCR under pressure is limited for the large-pore 87 cpsi extrudate (cell width circa 2.4 mm). The catalytic converter volume at 2 bar and 4 bar can be reduced to approximately 80%, and 70% of the volume at 1 bar, respectively. Without diffusion limitations, 50 and 25% volume reductions would be theoretically possible at 2 and 4 bar, respectively. In addition to the reduced volumetric activity, the lowered diffusion rates of NO and NH$_3$ from the gas phase to the surface resulted in much flatter slip-DeNO$_x$ curves, so that traces of NH$_3$ could already be found downstream of the converter for smaller NO$_x$ reduction levels.

The reduced diffusion rates had a lesser effect for the 225 cpsi extrudate, which as attributed to much shorter average diffusion pathways. In particular, the flattening of the slip-DeNO$_x$ curves

was less pronounced with increasing pressure, for example, the dosed NH$_3$ was more likely to react on the surface instead of being emitted as slip. With this cell geometry, the catalytic converter volume at 2 and 4 bar could be reduced to 65 up to 70% and almost 50% of the volume at 1 bar, respectively. The relative volume reductions of the foam structures with a pore size of 2500 μm were comparable with that of the 225 cpsi extrudate.

Most of the catalytic converter volumes reported thus far are relative values and describe how a given system behaves at 1, 2 or 4 bar. A direct comparison that considers the different basic activities of the catalysts is difficult because of the different temperature dependencies of the catalysts. A temperature between 350 and 450 °C is most suitable to this comparison because the catalysts showed a rather flat temperature profile.

Using the volume of the 87 cpsi extrudate at 1 bar as a reference (= 100%), the catalytic converter volumes could be reduced by 50% by only increasing the cell density to 225 cpsi or by applying the 2500 μm foam structures, ❼. This reduction exceeds that observed for an 87 cpsi extrudate under a pressure of 4 bar. When the 225 cpsi extrudate or the foam structure was pressurised, the volume could be reduced to approximately 35% at 2 bar and 25% at 4 bar.

The benefit of SCR under pressure is reduced further when large-pore structures (87 cpsi or even 35 cpsi) are necessary because of a high dust load in the exhaust gas. This limitation indicates that increasing the cell density cannot significantly reduce the volume in applications that are strongly susceptible to clogging. However, this reduction can be achieved by substrates that enable an increase in the mass transfer without compromising the cell width, such as in foam structures. However, the susceptibility to clogging of these structures still requires investigation.

The impact of the pressure pulsations of the engine exhaust on the SCR upstream of the turbocharger with respect to NO$_x$ reduction, mechanical durability and charging technology cannot be simulated in the model gas test rig but should be assessed before the implementation of SCR under pressure. In a two-stage turbocharger application, the placement of the SCR system downstream of the high-pressure turbocharger would be advantageous because these effects are reduced at this location.
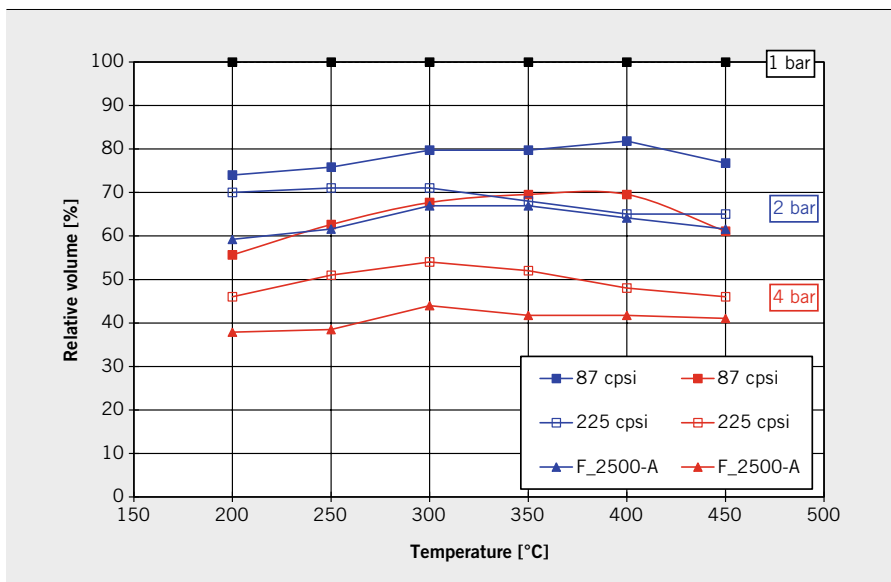
❻ Relative catalytic converter volume for pressure increases to 2 bar and 4 bar with DeNO$_x$ values equal to those at 10 ppm NH$_3$ slip and 1 bar
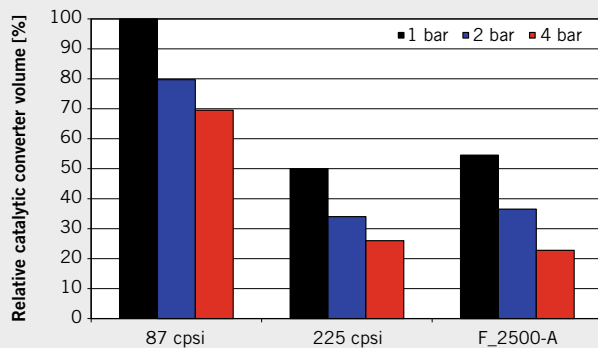
❼ Estimate of the relative catalytic converter volumes for 70 % DeNO$_x$ at 10 ppm NH$_3$ slip and 350 °C (100 % = 87 cpsi at 1 bar)

6 SUMMARY

The effect of increased pressure levels, as they occur in pre-turbocharger position in Diesel engines, on the SCR process were investigated with model gas experiments in the laboratory. The measurements showed that the catalytic converter volume can actually be reduced but the possible volume reduction is not proportional to the pressure increase due to the influence of gas diffusion. Fine cell structures were advantageous, because they showed a high volumetric activity due to their large catalytic surface and their activity was less influenced by pressure. Foam structures turned out to be particularly suitable, since they allow for high mass transfer due to their irregular structure. However, if structures with smooth channels and low cell density have to be used due to a high dust load of the exhaust gas, the benefit of SCR under pressure becomes much smaller.

REFERENCES
[1] Marine Environment Protection Committee (MEPC), 65th session, 13 to 17 May 2013
[2] Christensen, H.; Pedersen, M. F.: Continuous Development of Tier III SCR for Large Two-Stroke Diesel Engines. Paper No. 178, 27th CIMAC World Congress, Shanghai, 2013
[3] Visciglio, V.; Blanchard, G.; Surantyn, R.: A new generation of Rhône-Poulenc DeNO$_x$ catalyst: DN115. In: Catalysis Letters 40 (1996), pp. 39-41
[4] Fujibayashi, T.; Baba, S.; Tanaka, H.: Development of Marine SCR System for Large Two-Stroke Diesel Engines Complying with IMO NO$_x$ Tier III. Paper No. 29, 27th CIMAC World Congress, Shanghai, 2013
[5] Bank, R.; Buchholz, B.; Harndorf, H.; Rabe, R.; Etzien, U.: High-Pressure SCR at Large Diesel Engines for Reliable NO$_x$-Reduction and Compliance with IMO Tier III Standards. Paper No. 188, 27th CIMAC World Congress, Shanghai, 2013
[6] Bank, R.; Buchholz, B.; Harndorf, H.; Rabe, R.; Etzien, U.: Analyse des Korrosionsverhaltens von SCR-Katalysatoren unter den Betriebsbedingungen IMO Tier III-konformer Großdieselmotoren. 2. Rostocker Großmotorentagung, 2012
[7] Giani, L.; Groppi, G.; Tronconi, T.: Mass-Transfer Characterization of Metallic Foams as Supports for Structured Catalysts. In: Industrial & Engineering Chemistry Research 44 (2005), No. 14, pp. 4993-5002
[8] Koebel, M.; Elsener, M.; Madia, G.: NO$_x$-Verminderung in Dieselabgasen mit Harnstoff-SCR bei tiefen Temperaturen. In: MTZ 62 (2001), No. 2, pp. 166-175