

Evaluation and Prediction of Deposit Severity in SCR Systems

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ABSTRACT

In this work we extended the findings from a previous study by the authors on the mechanisms and influence factors of deposit formation in urea-based selective catalytic reduction systems (SCR) [1]. A broader range of operating conditions was investigated in detail. In order to quantify the boundary conditions of deposition, a representative set of deposits was studied during formation and decomposition. A box of heat resisting glass was equipped with a surrogate mixing element to monitor solidification timescales, temperatures and deposit growth. A chemical analysis of the deposits was performed using thermogravimetry. The depletion timescales of individual deposit components were systematically investigated. A moderate temperature increase to 350 °C was deemed sufficient to trigger fast decomposition of deposits formed below 250 °C. Above, the amount of temperature-stable components increased noticeably, and temperatures in excess of 600 °C were expected to be required for fast decomposition. Starting from 270 °C deposits were formed within less than 160 s and accumulated rapidly. Based on the combined data, an existent model for the prediction of deposit formation based on CFD simulations of the thermodynamic properties of the wall film [1] was extended to account for the deposit severity. The model accurately predicted the risk of deposit formation. The impact of the applied mixing element, injector and injection rate were represented very well.

CITATION: Smith, H., Lauer, T., Schimik, V., and Gabel, K., "Evaluation and Prediction of Deposit Severity in SCR Systems," *SAE Int. J. Engines* 9(3):2016, doi:10.4271/2016-01-0970.

INTRODUCTION

Stringent emission standards, such as Euro 6, have forced manufacturers of both light and heavy duty vehicles to implement exhaust aftertreatment systems. Among these, selective catalytic reduction (SCR) has been established as an effective measure to reduce nitrogen oxides (NO_x). Automotive SCR systems use a 32.5 wt.% urea water solution (UWS), also known as AdBlue or diesel exhaust fluid (DEF) to produce the ammonia required for the conversion process. The carrier substance is atomised into the hot exhaust upstream the SCR catalyst and decomposes after the water content has been evaporated. At temperatures as low as 133 °C urea melts and decomposes into ammonia (NH_3) and isocyanic acid (HNCO) in a thermolysis reaction. Isocyanic acid is fairly stable in the gas phase but readily reacts with water vapour to form ammonia and carbon dioxide on typical SCR catalysts [2].

However, during decomposition urea may react with gaseous HNCO to form biuret and a number of other undesired components, such as cyanuric acid, ammelide, ammeline and melamine [3]. Common deposition locations include injector tip and dome, mixing element, exhaust pipe as well as catalyst inlet cone and frontal surface [4, 5, 6, 7, 8, 9, 10, 11].

Excessive deposit accumulation poses a serious threat to reliable system operation by storing considerable amounts of reducing agent, reducing catalyst activity and increasing engine backpressure. On the one hand, investigations have focussed on single correlations, such as deposit formation as a function of temperature or system design. On the other hand, basic research has been conducted to shed light on the deposit formation and decomposition chemistry. The literature review given in this paper therefore focuses on the major impact factors on deposit formation. A short summary of the involved chemistry is given as well as a short review of available modelling approaches.

Mixing elements are employed as primary impingement target in state-of-the-art SCR systems in order to improve ammonia homogenisation and to reduce the deposit formation risk. However, deposit formation may not always be prevented during SCR system operation in case of insufficient UWS preparation. Yet, whether or not a deposit poses a threat to reliable system operation depends on its composition. Therefore, in the experimental part of this work deposit formation was studied on a surrogate mixing element under a broad range of operating conditions. Temperature measurements were conducted to identify deposition temperatures. Video technology was applied to assess solidification timescales and deposit growth. Thermogravimetry

was used to investigate the composition of a representative set of deposits. Furthermore, a systematic study was conducted on the decomposition timescales of individual deposit components.

CFD models used for the prediction of ammonia homogenisation have reached a high level of accuracy and their application has become industry standard [12, 13, 14, 15, 16, 17, 18, 19]. However, models are usually limited to the physical processes and can only cover timescales in the range of seconds to minutes with an acceptable numerical effort. In contrast, the timescales of the deposit formation are typically in the range of minutes to hours. Progress has also been made in modelling approaches for the complex deposit formation and decomposition chemistry. Despite this, their application is limited to reactor experiments, such as the thermogravimetric pyrolysis of urea. In order to cope with these shortcomings, a method was developed to predict the deposit formation risk based on the physical properties of the wall film [1]. It was sufficient to cover the timescales of wall film pathway evolution to allow the interpretation of the crucial boundary conditions that facilitated or impeded deposition. The model shall now be extended to account for deposit severity. Furthermore, a method is proposed to reduce the timescales of solid cooling while maintaining the prediction accuracy. Eventually, the impact of injection rate, UWS spray characteristics and mixing element design were assessed, based on a series-like exhaust system. In order to test the ability of the model to accurately predict the risk of deposit formation the simulation results were verified based on measurement data.

LITERATURE REVIEW

At temperatures below approx. 300 °C only a fraction of the calculated theoretical amounts of NH_3 and HNCO may actually reach the catalyst [4]. Significant amounts of urea may be stored in the system upstream the SCR catalyst in the form of UWS or deposits instead of participating in the NO_x reduction process. Numerous impact factors have been reported in the literature and can be categorised as follows [7, 8]: (1) thermal and flow-related factors, such as the temperature level and relevant deposit formation chemistry, (2) geometry-related factors, such as the mixing element design, (3) engine-related factors, such as the operating conditions, (4) injector-related factors, such as spray characteristics and (5) control-related factors, such as the injection pulse width and frequency.

Strots et al. [10] confirmed that deposit formation could be significantly reduced and the tolerable injection rate increased by raising the temperature level of the exhaust system. Zheng et al. [7] observed that SCR systems were more resistant against deposit formation if an s-bend injection was installed instead of a 45 ° injection. The application of a mixing element further reduced the amount of formed deposits. Munnannur et al. [8] and Way et al. [9] successfully minimised deposit formation by redesigning the injector

dome. Moreover, they revealed that deposit composition correlated at least to some extent with the location of their formation. Cyanuric acid was the major component of deposits obtained from the injector dome, whereas deposits removed from the mixing element and pipe walls were identified as mixtures of mostly urea and biuret [8]. Besides, the temperature stability of deposits was even further increased if they could not completely be removed from the system during single exposure to high temperatures [9].

The strong correlation between the temperature level, injection rate and deposit formation is apparent. Equally, doser integration and mixing section design exhibit high optimisation potentials. However, the formulation of a correlation between formation temperature and deposit composition remains a major challenge and detailed investigations of the corresponding timescales are rare. Therefore, our study provides a comprehensive outline of the deposit formation and decomposition process. It was the objective to assess the severity of deposits formed under a broad range of operating conditions and to determine the timescales necessary for their decomposition within acceptable timescales.

The chemistry of urea decomposition has been investigated under laboratory conditions in numerous works [3, 5, 20, 21, 22, 23, 24], using various techniques such as thermogravimetric analysis (TGA) or high performance liquid chromatography (HPLC). Urea melts and decomposes at 133 °C. However, according to Schaber et al. [3], noticeable decomposition was not observed prior to 150 °C. Biuret formation was initiated around 160 °C and paralleled by small amounts of cyanuric acid as well as ammelide formation from 175 °C. Above 193 °C beginning biuret decomposition coincided with increased production of cyanuric acid, ammelide and ammeline. Decomposition of cyanuric acid was initiated at temperatures exceeding 250 °C and paralleled by gradual conversion into ammelide, ammeline and melamine above 300 °C. Decomposition of the temperature-stable components ammelide and ammeline commenced with sublimation around 410 °C and 435 °C, but required temperatures in excess of 600 °C and 700 °C. Melamine appeared to be somewhat of an intermediate during decomposition of other components as its appearance in urea decomposition residuals correlated with the onset of its decomposition. Schaber et al. [3] presented an elaborate outline of the decomposition process. However, comparison against other data from the literature [5, 20, 21, 22, 23, 24] yields that the amount and type of secondary products formed during decomposition, and thus the temperatures required to achieve complete depletion, may vary significantly depending on the experimental setup. Ebrahimian et al. [25] proposed a urea decomposition model which was able to qualitatively reproduce experimental results of Schaber et al. [3] and Lundström et al. [26], but remained dependent on the initial sample mass. An improved kinetical scheme was proposed by Brack et al. [27] and was able to account for impact factors such as heating rate, initial sample weight and crucible geometry on the thermogravimetric

decomposition of urea. While the qualitative decomposition behaviour was represented well, improvements were still to be made with respect to prediction accuracy and the consideration of other secondary products such as ammeline and melamine. Yet, the work of Brack et al. [27] represented a major step towards the portability of such kinetic models to realistic exhaust system geometries. The application of CFD has become industry standard for the prediction of ammonia homogenisation in SCR systems. Several attempts have been made to predict deposit formation based on CFD simulations of the wall film formation [28, 29, 30] and in combination with rudimentary reaction kinetics [30]. However, major efforts are still necessary to combine detailed reaction kinetics with established CFD methods in order to capture the involved chemophysical processes and timescales with acceptable numerical effort.

MATERIALS AND METHODS

Test Bench Setups

In order to observe the processes involved in impingement and deposit formation, basic investigations were conducted using a volume with optical access. The volume was equipped with a surrogate mixing element and a 16 ° 3 hole series injector with an SMD of 100 µm, Figure 1, as previously described by the authors [1]. Thermocouples were applied to one blade of the mixing element to obtain information about impingement and deposition temperatures.

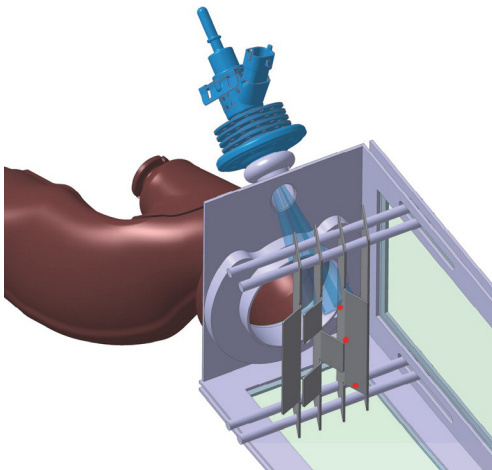


Figure 1. Volume with optical access, surrogate mixing element, injector and injector beams (simplified, locations of thermocouples highlighted in red: area of impingement (1, top), UWS trickling path (2, middle), accumulation area (3, bottom), top and left side of the volume hidden).

In order to assess the influence of the mixing element and the injector on the formation of deposits in a series-like environment, systematic investigations were conducted with four different setups. A close-coupled type exhaust aftertreatment system was equipped with two different oval-shaped swirl mixers and two injectors, Figure 2 (a). Mixer 1 was characterised by short rear blade elements with an inclination angle of approx. 50 °, Figure 2

(b). Mixer 2 was characterised by long rear blade elements with an inclination angle of approx. 70 °, Figure 2 (c). Both exhaust systems were truncated at the downstream end of their mixing elements. A box with optical access was attached in order to allow visual access to the rear side of the mixers. Endoscopy mounts were installed to realise illumination and to provide visual access to the upstream side of the mixers. A 42 ° hollow cone injector with an SMD of 51 µm and a 26 ° 6 hole injector with an SMD of 97 µm were applied and denoted injector 1 and injector 2, respectively. The drop size distributions provided by the manufacturers were validated against own measurements and an excellent correlation was found.

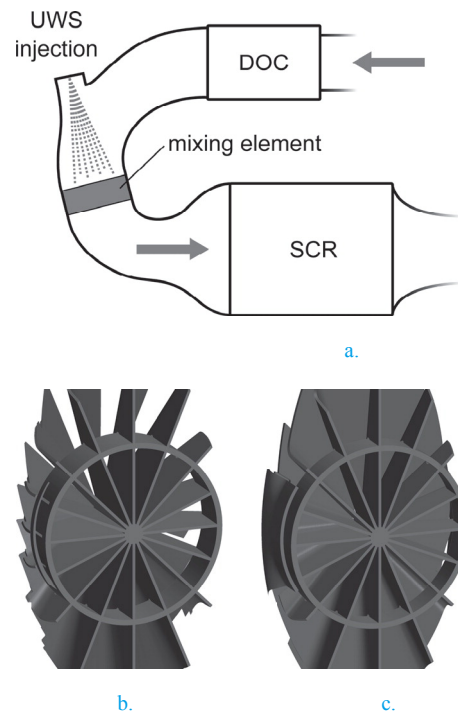


Figure 2. Schematic of the series-like exhaust system (a) and frontal views of mixer 1 (b) and mixer 2 (c).

Experiments were carried out on an engine test bench using a turbocharged 4 cylinder 2.1 l series diesel engine equipped with a DOC and DPF. A customary Canon 650D DSLR, equipped with a Tamron 28 ... 300 mm zoom lens, was used to provide video recordings of the experiments and to assess impingement regimes, deposition timescales as well as locations.

Deposit Formation Experiments

Experiments with the surrogate mixing element were conducted at exhaust mass flows $\dot{m}_E$ of 100 kg/h and 200 kg/h. Exhaust temperatures T_E downstream of the DPF ranged between 200 °C and 335 °C. Injection rates $\dot{m}_{UWS}$ were varied between 3.3 mg/s and 120 mg/s and were adjusted in such a way that deposit formation occurred on the blades of the mixing element. Individual operating conditions will be labelled according to the pattern OP $T_E / \dot{m}_E / \dot{m}_{UWS}$.

Major wall film pathways and common deposition locations were determined during a preliminary study. Thermocouples were then mounted on the reverse sides of the mixing element blade exposed to wall wetting in order not to alter liquid film pathways. Temperature measurements were conducted in the area of impingement (1), along the trickling path of the UWS (2) and at the wall film accumulation area (3), compare [Figure 1](#). The temperature at the impingement area was averaged over a 30 s period just before SOI and was used as a reference for the temperature level of the mixing element. It was denoted $T_{M,SOI}$ and ranged between 185 °C and 310 °C. The steady state injection temperature was averaged over a 300 s period just before end of injection (EOI) and denoted $T_{M,EOI}$. Deposit formation was typically observed between the thermocouples (2) and (3). The exact location was determined based on the video recordings. The temperature at the deposition location was linearly interpolated between the respective thermocouples.

Residual deposits and UWS were removed from the surrogate mixing element and surrounding box prior to each experiment. It was ensured that a steady state temperature was reached before SOI and during the experiments. Temperature measurements were corrected for minor exhaust temperature fluctuations. The time between SOI and the formation of a deposit nucleus was denoted solidification timescale t_s . In case the Leidenfrost effect was observed at the beginning of the experiment, the point of initial wall wetting was taken as a reference instead of SOI. The actual Leidenfrost temperature, or Leidenfrost point, was assumed as the temperature at the point of inflection of the measured temperature curve after which a distinct (second) temperature drop was observed. The values were determined according to the method applied by Fest-Santini [31]. Typically, a temporal offset was apparent between the formation of a deposit nucleus at t_s and noticeable accumulation. Hence, the solidification temperature T_s at which the UWS was converted into a deposit was averaged over a period of 240 s. If the process was exceptionally slow, the averaging period was extended to 1200 s. Deposit accumulation was assessed optically 60 min after SOI by comparison against reference measurements. Deposits were classified based on a scale with six levels, where 1 corresponded to slow growth resulting in a small deposit, [Figure 3 \(a\)](#), and 6 corresponded to intensive growth resulting in deposits with a thickness exceeding half the distance between two blades (approx. 7 mm), [Figure 3 \(b\)](#). Only major deposits, which were formed alongside the liquid film pathways, i.e. at or in between the thermocouple locations, were used for the evaluation. Minor solidification at wall film pathway flanks was not taken into account. The dimensionless deposit growth number was denoted dg .

Net injection duration was 65 min, after which injection was discontinued and the engine was shut down immediately. Deposits were removed from the blades of the mixer and stored in air-tight containers to prevent the absorption of ambient humidity.

Experiments with the series-like exhaust systems were conducted with two different injection rates (35 mg/s and 60 mg/s) and for all four variants. Exhaust mass flow and temperature were kept

constant at 170 kg/h and 275 °C. UWS injection was only triggered when steady state operating conditions had been attained and was maintained for 90 min.

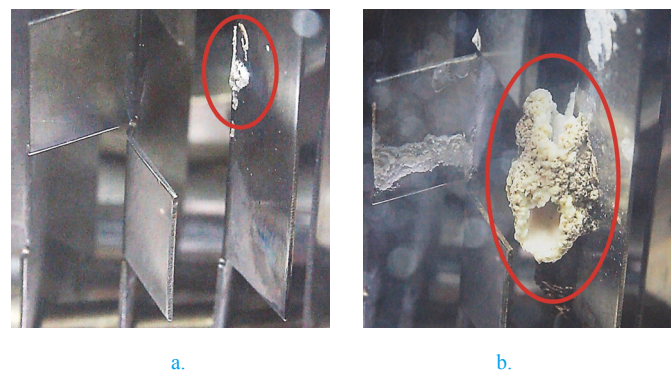


Figure 3. Exemplary deposit accumulation on a typical mixing element blade within 60 min: slow (a, OP200/200/3.3), and intensive (b, OP315/205/75) deposit growth, corresponding deposits circled in red.

Deposit Decomposition and Content Analysis

Urea, biuret, cyanuric acid, ammelide, ammeline and melamine were obtained from Sigma-Aldrich Handels GmbH, Vienna, Austria, and used without further purification. Biuret, ammelide, ammeline and melamine were provided in the form of powders. Urea, cyanuric acid and deposits had to be grinded and mixed in order to yield homogeneous samples in powdery form. Analyses were performed on a Netzsch TG 209 C thermogravimetric analyser. Pure nitrogen was used as purge gas with a constant flow rate of 50 ml/min. An Al_2O_3 crucible was used for all experiments. During the measurement campaigns the sample weight was maintained within the range of $\pm 5\%$ of the average value in order to minimise an impact on the results.

For the analysis of the deposit content, the decomposition behaviour of the samples was compared against that of the reference substances, [Figure 8](#). Typically, 3.9 mg of sample was heated from room temperature to 800 °C at 10 °C/min. Based on the TGA measurements, a number of critical temperatures were identified, [Table 1](#). A mass loss of $\geq 2\%$ was used to identify the start of decomposition. In case of urea, biuret, cyanuric acid, ammelide and melamine, the initial sample weight was used as a reference. In case of ammeline, the residual mass at 250 °C, prior to the beginning of the main decomposition stage, was taken as a basis. A mass loss of $\geq 8\%/^{\circ}C$ was assumed to identify decomposition at noticeable rates. Sample depletion was assumed when the residual weight dropped to $\leq 1\%$ of the original mass. In order to obtain information about the deposit content, a representative set of samples, which covered the entire solidification temperature range, was analysed, [Figure 6](#) and [Table 2](#). An impact of the temperature interpolation method was eliminated by choosing only such deposits that were formed on the reverse sides of the respective thermocouple locations.

Table 1. Critical temperatures of the pure reference substances.

substance	unit	start of decomposition	noticeable decomposition	sample depletion
urea	[°C]	151	174	377
biuret	[°C]	195	203	400
cyanuric acid	[°C]	278	326	372
ammelide	[°C]	348	382	664
ammeline	[°C]	348	410	702
melamine	[°C]	250	287	337

For the analysis of the decomposition timescales, a selection of the reference substances was pyrolysed at varying temperature levels. Typically, 2.6 mg of sample was heated to the desired temperature with a heating rate of 100 °C/min. The target temperature was then maintained for 60 min. Sample depletion was assumed when the residual weight dropped to $\leq 1\%$ of the original mass and the corresponding time was noted, Table 3. The heating period was excluded from the decomposition time. In case depletion was not achieved within less than 60 min, the residual weight was listed.

Numerical Modelling of UWS Preparation

Simulations of the UWS preparation process were carried out with the commercial CFD code STAR-CD 4.16 [32]. A validated CFD model was used as suggested by Fischer [12, 13] and extended in a previous work by the authors [14]. Meshes for the four exhaust systems were generated based on their original geometry and included 3.4 Mio (mixer 1) and 2.8 Mio cells (mixer 2). Polyhedral meshes were used with a maximum base size of 3 mm. Refinements were applied in crucial areas, such as the mixing elements. In case of mixer 1 the complexity of individual geometric features was responsible for the considerable increase of the mesh size. A RANS approach was applied using a Reynolds Stress Turbulence Model (RSM) in order to account for the anisotropy of the velocity fluctuations [12, 13]. In addition, the turbulent Schmidt number Sc_t was reduced to 0.15 to compensate the underestimation of turbulent ammonia homogenisation which was found to be inherent to RANS based models [12, 13, 14, 15, 16]. Solid walls and the mixing elements were modelled using conjugate heat transfer (CHT) in order to ensure realistic temperature distributions and a correct thermal response to wall film evaporation. Catalyst substrates were represented as porous media. Porosity coefficients for the main flow direction were calibrated against measurement data in order to model backpressure and adjusted for the lateral directions in order to mimic flow straightening by the catalyst channels. The injected spray was initialised based on measured droplet size distributions and modelled by an Euler-Lagrange approach. Spray cone angles and orientation as well as the injection velocities were set up according to manufacturer specifications. The location of the injector holes was taken from the respective injectors applied during the measurement campaign. Droplet wall interaction was modelled using the multiregime Bai-Gosman model [32, 33] which was adapted to UWS by Fischer [12, 13] and extended in a previous work of the authors [14]. The splash boundary was set to $A_w = 600$ to ensure correct description of secondary droplet formation [14]. The deposition limit was modelled using a

constant temperature offset $\Delta T_{DL} = 207$ °C to the concentration-dependent UWS saturation temperature [14]. Additionally, a transition regime with a width of $T_{DL,u} - T_{DL,l} = 40$ °C was implemented which blended between wetting and non-wetting droplet wall interaction regimes. UWS was modelled as a two-component fluid considering boiling and evaporation. The temperature-dependent saturation pressure curves were used to determine the saturation temperature based on the actual urea concentration, according to Raoult's and Dalton's law. Urea decomposition was represented as a single step, involving melting, evaporation and thermolysis, by lumping together the respective enthalpies. A two-dimensional, finite volume approach was applied to describe the liquid film. The Nukiyama pool boiling model was used to account for the heat transfer between liquid film and solid walls. Active scalars were used in order to model the vapour content and their transport within the background fluid. A detailed summary and discussion of the models is given in the works of Fischer [12, 13].

A test case based on the described model was set up in order to evaluate the impact of the thermal mass on the cooling behaviour of the walls. Stainless steel with a reference density $\rho_{s,ref}$ of 7900 kg m³ was assumed for the solid material. The model consisted of a rectangular flat plate and adjacent fluid domain. UWS was injected at a rate of 35 mg/s and with an inclination angle of 45 ° to the plate surface. A 6 hole spray was assumed according to the characteristics of injector 2, compare section *Test Bench Setup*.

DEPOSIT FORMATION ON A MIXING ELEMENT

Boundary Conditions of Deposit Solidification

The boundary conditions of deposit solidification were investigated on a surrogate mixing element using the box with optical access. In order to identify and compare the different interaction regimes between liquid phase and system walls, the measured deposition temperatures T_s as well as the steady state injection temperatures $T_{M,EOI}$ were combined into an interaction map, Figure 4. Complementing data obtained during a previous investigation on droplet wall interaction, as described by the authors in [14], was added to the chart. On the abscissa the temperature level of the mixing element before SOI $T_{M,SOI}$ is shown, which shall be representative for the enthalpy level. On the ordinate the steady state temperature, which appeared during the observed phenomena, is shown. As indicated by the diagonal, it cannot exceed $T_{M,SOI}$. For low exhaust enthalpies, the minimum temperature was determined by the droplet temperature upon injection, ranging from 50 °C to 80 °C (data not shown). For high exhaust enthalpies, it was limited by the occurrence of the Leidenfrost effect at maximum injection rate (120 mg/s). The following scenarios were observed: intermittent wall wetting (1), Leidenfrost effect (2), Leidenfrost transition (3), Leidenfrost point (4), deposit formation (5), and permanent wall wetting (6), Figure 4. Approximate boundaries between the regimes were added but shall not be interpreted as sharp thresholds. In fact, the regimes blended into each other.

