

## Improved system performance for automotive exhaust cleaning

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#### List of abbreviations

Abbreviation	Description
AdAmmine	Trade name for Strontium chloride octa ammine
AdBlue	Trade name for 32.5% wt/wt urea solution in water
ASDS	Ammonia storage and dosing system
ASDS-2012-LD	ASDS version 2012 for light duty
CARB	California air resources board
СО	Carbon monoxide
$\mathrm{CO}_2$	Carbon dioxide
CVD-AFM	Control-volume dosing ammonia flow manifold
De-NO <sub>x</sub>	Same as SCR
ECU	Engine control unit
FLA	Fill level algorithm
MFC	Mass flow controller
MU	Main unit
NEDC	New European driving cycle
NH <sub>3</sub>	Ammonia
OBD	On board diagnostics
SCR	Selective catalytic reduction of nitrous oxides
SU	Startup unit

 TABLE 1

 LIST OF ABBREVIATIONS USED THROUGHOUT THIS REPORT

### List of symbols

Symbol	Description
m <sub>sat</sub>	Mass of $\rm NH_3$ saturated AdAmmine
M <sub>sat</sub>	Molar mass of saturated AdAmmine ( $Sr(NH_3)_8Cl_2$ )
m <sub>unsat</sub>	M ass of $NH_3$ depleted AdAmmine
M <sub>unsat</sub>	Molar mass of depleted AdAmmine (Sr(NH <sub>3</sub> )Cl <sub>2</sub> )
no	Total number of moles of AdAmmine (sat. and depl.)
n <sub>sat</sub>	Moles of NH3 saturated AdAmmine
n <sub>sat,0</sub>	Initial number of moles of sat. AdAmmine
n <sub>unsat</sub>	Moles of NH3 depleted AdAmmine
n <sub>unsat,o</sub>	Initial number of moles of depl. AdAmmine
Р	Actual pressure of NH3
p <sub>eq</sub>	Equilibrium pressure of NH3 above AdAmmine
Т	Actual temperature
Teq	Equilibrium temperature of AdAmmine
Vo	Total volume
$V_{\rm f}$	Gas free-volume
Vs	Solid volume
Х	Saturation degree of $NH_3$ in AdAmmine
Xo	Initial saturation degree of AdAmmine
ρο	Initial density of AdAmmine
ρsat	Bulk density of $\rm NH_3$ saturated AdAmmine
ρunsat	Bulk density of NH3 depleted AdAmmine

 TABLE 2

 LIST OF SYMBOLS AND THEIR MEANING USED THROUGHOUT THIS REPORT

## 1. Resume på dansk

Det er en stigende udfordring at sikre ren luft i byområder, hvor en kraftigt forøget trafikmængde, der især består af en stigning i antallet af dieseldrevne køretøjer, har ledt til en generel forringelse af luftkvaliteten. Hvor almindelige benzindrevne biler er udstyret med en 3-vejs katalysator, der sikrer at udstødningsgasser såsom CO, NO<sub>x</sub>, og uafbrændte kulbrinter fjernes, samt at partikeldannelsen (sod) er lav, er situation anderledes for dieselbiler, der af motortekniske årsager ikke kan udstyres med en sådan 3-vejs katalysator. Tværtimod udleder dieselbiler høje mængder af føromtalte, hvoraf specielt NO<sub>x</sub> og sodpartikler er dokumenteret skadelige for helbredet. Eftersom andelen af dieselbiler nærmer sig, og i visse steder i Europa endda overstiger, 50% af den samlede europæiske bilflåde er problemet med NO<sub>x</sub> og sod et stigende problem der ikke lader sig løse uden et teknisk indgreb. Selv i en by som København er kravet om en høj luftkvalitet ikke opfyldt for NO<sub>2</sub>. Dette er den primære grund til at der i Europa, og flere andre steder i verden, er indført lovgivning omkring emissionsgrænserne for nyere dieselbiler.

Med introduktionen af de såkaldte Euro 5 (allerede effektueret) og kommende Euro 6 (nye typer personbiler fra 1. september 2014, nye personbiler og varebiler dog fra 1. september 2015) samt 6+ (6b og c, forventet fra 2017) standarder i Europa og med de tilsvarende CARB standarder i USA har der åbnet sig et marked for ny teknologi til såkaldt 'after-treatment, eller efterbehandling, af udstødningsgasserne fra dieselbiler. Den foretrukne metode der er valgt er en som allerede igennem en lang årrække har fungeret på diverse kuldrevne kraftvarmeværker, nemlig selektiv katalvtisk reduktion af NOx (SCR, eller de-NOx) med ammoniak. Den af Amminex udviklede AdAmmine teknologi, og af Bosch udviklede AdBlue (urinstof) teknologi, er to mulige metoder der på sikker vis kan levere ammoniak til SCR reaktionen. Den væsentligste forskel imellem de to produkter er, at hvor AdBlue er en væskeformig vandig opløsning af urinstof, der først skal forstøves og så undergå en termisk dekomponering samt hydrolyse før det spaltes til ammoniak er AdAmmine i stand til at levere gasformig ammoniak uden sidereaktioner, blot ved termisk aktivering af materialet. Derudover har Adblue alle muligheder for diverse sidereaktioner, hvoraf flere kan lede til aflejringer og tilstopning af SCR systemet, hvilket er et reelt problem på flere bus/lastbilsystemer der bruger AdBlue SCR til at opfylde Euro 5 standarden. Samtidigt har AdAmmine flere funktionelle fordele frem for AdBlue, hvor det blandt andet har potentialet til at blive lettere samt at fylde mindre end et tilsvarende AdBlue system. Slutteligt kan AdAmmine systemet opnå en NOx reduktion der er endnu bedre end Euro 6 kravene.

I bilindustrien er der fire primære drivende kræfter der styrer enhver teknisk udvikling. De er en øget præstation, vægtreduktion, volumenreduktion, samt en generel reduktion af omkostninger. Vægt- og volumenreduktion leder direkte til en forbedret brændstoføkonomi og køreoplevelse, samt giver mere plads på bilen der gør det lettere for bilingeniørerne at finde plads til samtlige komponenter. Sidstnævnte er ofte er en meget kompliceret og besværlig proces, der kan forhindre større ændringer af designs fordi ændring et sted nødvendiggør ændringer et andet sted osv. Disse drivende kræfter er så store, at selv få procent forbedringer af enkeltkomponenter på en bil kan retfærdiggøre store summer af allokerede resurser.

Dette projekt adresserer disse drivende kræfter, eftersom et positivt resultat foruden at forbedre de-NOx ydeevnen, også vil føre til en reduktion i vægt, volumen samt de samlede omkostninger af AdAmmine systemet.

En oplagt mulighed for at opnå alle disse tre mål er hvis ammoniakken lagret i AdAmmine kan udnyttes med en større effektivitet. Ydermere vil en forbedret udnyttelse af den tilgængelige ammoniak bevirke at man undgår et for sent, eller endda for tidligt, skift af beholder, der både er unødigt dyrt og miljømæssigt ufordelagtigt. For at opnå bedre udnyttelse af ammoniakken i en AdAmmine beholder er det nødvendigt at kende den samlede mængde ammoniak tilbage i beholderen, til en hvis præcision. Dette kræver en eller anden metode til at måle fyldningsgraden af beholderen, der er svarende til det der allerede findes for væsker i tanke (eks. flydemåler). Projekt er støttet af Miljøstyrelsen med i et budget på i alt Kr. 1.756.236 over en periode på 11/2 år med start d. 1. december 2011. Det primære mål med projektet er at demonstrere mindst 5% forbedret ydelse af et ammoniak assisteret SCR system, defineret ud fra systemets vægt eller størrelse og/eller en forøget NOx reduktionsevne. Dette mål opnås ved at udvikle og implementere en algoritme der med stor nøjagtig kan bestemme ammoniak-fyldningsgraden i en AdAmmine beholder ombord på et køretøj (herefter: ammoniakmåler). Som reference bruges den eksisterende ammoniakmåler, der ved opstartstider for både main unit (MU) og startup unit (SU) i bedste fald kan bestemme den faktiske fyldningsgrad ned til +/- 15 % præcision og i værste fald blot kan bruges til at bestemme om AdAmmine beholderne er tomme eller fulde.

For at kunne opfylde lovkrav til OBD (fra On-Board Diagnostics, der er en slags automatisk fejlsøgning der skal beskytte bilen/passagerer i mod skader ved anvendelse af fejlbehæftede komponenter), kræves det at den totale ammoniakmængde i AdAmmine systemet er kendt, således at chaufføren kan advares i tide før systemet løber tør for ammoniak. Dette betyder, at enhver usikkerhed på bestemmelsen af den tilgængelige ammoniak i AdAmmine ved en ammoniakmåler kræver, at en ekstra ammoniakmængde medbringes for at forhindre at føreren i bilen oplever, at systemet ikke når at advare ham/hende om, at ammoniakmængden i systemet er for lav. I tilfældet 15% unøjagtighed kræves derfor 15% mere ammoniak. Kan denne usikkerhed nedbringes betyder det en direkte besparelse på den totale systemvægt/volumen samt en forbedret NO<sub>x</sub> omdannelse pr masse, hvilket er en vigtig drivende kraft i forhold til at gøre systemet endnu mere konkurrencedygtigt.

Igennem denne rapport vil en række af de observationer vi har gjort i løbet af projektet blive dokumenteret. Resultaterne er så lovende, at vi i skrivende stund er i gang med at implementere en samlet strategi for en ammoniakmåler på vores ASDS-2012 LD prototype system. Vi arbejder fortsat med at forbedre metoden og algoritmerne bag den. Forneden er der vist en opsummering af hovedmålene opnået med projektet:

- 1. En forøget nøjagtighed af ammoniakmåleren fra at måle +/- 15% på den absolutte mængde NH<sub>3</sub> til at måle +/- 5% på den absolutte mængde NH<sub>3</sub>. Dvs. en samlet forbedring af metoden på 66% i forhold til udgangspunktet, samt en reduktion i den nødvendige mængde af ammoniak med 10%, hvilket mindsker systemets nødvendige kapacitet og som overstiger hovedmålet med projektet (5% mindre NH<sub>3</sub>).
- 2. En potentiel reduktion i energiforbruget med op til 60% efter indførslen af en ammoniakmåler. Dette er en vigtig parameter til at forberede konkurrenceevnen og systemets samlede miljøaftryk, eftersom det direkte kan føres til en reduktion af CO<sub>2</sub> udledningen.
- 3. En samlet strategi for en ammoniakmåler for AdAmmine systemet, der opfylder lovkrav til OBD.

## 2. Introduction

Securing high air quality in urban areas is an increasingly challenging task. This is partly due to overall increased traffic, but especially the increasing amount of diesel cars compared to petrol cars is leading to an increase in air pollution. Petrol cars are fitted with a 3-way catalyst that removes carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), as well as un-burnt carbonhydrates. Furthermore, petrol engines are low in soot particulate emissions. For diesel cars the situation is different as the 3-way catalyst does not work there and diesel cars therefore have high emissions of especially particles and NO<sub>x</sub> gasses. Both particles and NO<sub>x</sub> gasses are documented hazardous. As diesel cars are approaching and some places even exceeding 50% of the European car fleet the problems with particles and NO<sub>x</sub> is increasing to unacceptable levels. Even Copenhagen cannot fulfill the goals for air quality.

As a result legislation is introduced putting limits to the emissions from diesel cars mainly in Europe and USA. Thus, the market for de-NOx technologies for diesel powered vehicles is strongly driven by US and EU legislation governing emissions of NOx. In Euro 6, the NOx-emission has to be reduced to 80-125 mg/km, depending on the type of vehicle. The Euro 6-standard will come into effect on September 1st 2014. The even more strict Euro6+ (6b and 6c) is expected to come into effect in 2017. The Tier2-Bin5 which is already implemented in North America corresponds to 43.5 mg/km. For meeting either norm, dedicated exhaust treatment is needed. By 2014 car makers are obliged to introduce NO<sub>x</sub> emission reducing technologies for in order to sell cars in Europe. Selective catalytic reduction (SCR) combined with an ammonia source has been chosen as the preferred solution by most car makers. The Amminex developed AdAmmine and Bosch developed AdBlue (urea) are the two possible technologies for providing ammonia. The unique difference between the two products is that the AdAmmine system delivers pure ammonia gas that can be directly dosed in the exhaust and perform the SCR, whereas the AdBlue is an aqueous solution of urea that first has to undergo injection before a complex thermal decomposition and hydrolyses yields the desired ammonia gas. Apart from many functional advantages of AdAmmine compared to AdBlue, the AdAmmine system has the potential to become lighter, cheaper and occupy less volume than a comparable AdBlue system. Furthermore, the Amminex system has been shown to be able to provide NOx reductions better than the Euro 6 requirements.

In the car industry four main drivers are present in almost any technical development: improved performance, reduction of weight, reduction of volume and reduction of costs. Reduction of weight translates directly into better fuel economy and better handling of the car. Reduction in volume gives more space and more freedom to the designers. Reduction of costs gives better earnings. These drivers are so strong that large amounts of development resources are spent on improving even a few percent on individual parts of the car.

The present project addresses exactly these drivers as positive outcome of the project will result in improving de-NOx performance, while reducing weight, volume and costs of the AdAmmine system. One obvious possibility to obtain all of the three optimization goals is if the ammonia stored in the AdAmmine can be utilized with a larger efficiency Furthermore, a better utilization of the available ammonia will help prevent a too late or even premature change of cartridge that is both expensive and environmentally stressful. In order to obtain a better utilization it is first necessary to know to a certain precision, the actual content of ammonia left inside the AdAmmine cartridge. This

requires some device, or method capable of measuring the level, equivalently to that which can be done for liquids contained in a tank.

Measuring liquids inside a tank is a rather well known task, that range from the very simple mechanical floater that upon the rise or fall of the liquid level activates a micro switch, and thereby sends a measurable signal that can be translated into a known level, to the more complex methods that involve analyzing a signal due to reflection of ultrasonic or even microwaves. It is, however, a much more complex task to measure the level of a chemically bound substance inside an enclosed tank, where it is not possible, or wishful, to extract material for chemical analysis, such as is the case for ammonia bound in AdAmmine filled cartridges. This gives the Amminex system an extra challenge when compared to the competing AdBlue (trade name for 32.5% wt/wt urea in water) system, which utilizes the thermal decomposition of urea in order to form the reactant ammonia. Amminex has developed an independent method to estimate the level of ammonia on-line that relies on the simultaneous measurement of flow and pressure, both of which are otherwise readily available for control of dosing to the SCR system. The method is described in detail in a patent application ("Method of determining the filling level of a solid ammonia storage medium in an ammonia storage container", patent pending), and is in short an algorithmic approach wherein the data (flow/pressure) logged is processed by the engine control unit (ECU) through a level sensing algorithm, leading to the estimation of the fill level (relative amount of ammonia left). In more detail, the method utilizes that during desorption of ammonia from the AdAmmine, a porous solid matrix is left behind, which contains a considerable pore-structure (Hummelshøj et al., 2006). The pore-volume (gas free-volume) therefore increases as the filling level decrease. At the same time a change in desorption kinetics occurs as the activated AdAmmine also changes. By accounting for both effects, a simplified model can be set up that can be solved following an algorithm, which is simple enough that it may be implemented on an ECU.

In addition to the patent pending method, known as <u>Fill L</u>evel <u>Algorithm 1</u> (or FLA 1) a second method called FLA 2 was developed during the course of this project. The method is specifically designed for the ASDS dosing hardware (CVD-AFM: Control Volume Dosing - Ammonia Flow Manifold). This method, as with FLA 1 determines the gas free-volume and correlates it to the filling level of the cartridge on which the measurement is made. The method does not require the measurement of the flow-rate, but requires a CVD-AFM specifically, and involves solving a set of differential equations to determine in addition to the gas free-volume, a mass-transfer coefficient and desorption rate. The new fill level algorithm allows optimizing the heating strategy, which in turn reduces power consumption of the whole ASDS.

When determining the filling level, a predetermined universal, but cartridge geometry dependent, relation  $V_f(X)$  between the gas free-volume ( $V_f$ ) and the filling level X is used to calculate a value of the filling level X<sub>est</sub>, based on the fill level algorithm determined gas free-volume  $V_f$ . This means that for the same cartridge geometry the same Vf(X) applies even for a multitude of cartridges. Establishing this relation  $V_f(X)$  as precisely as possible is of key importance, as it directly determines the estimation of the fill level and affects prediction accuracy. Any offset between the established  $V_f(X)$  and the 'actual'  $V_f(X)$  for a specific cartridge, which may be slightly different due to variations in the cartridge production, will translate into an erroneously determined fill level from the algorithm output  $V_f$ , as the predetermined  $V_f(X)$  is not the true. Nevertheless, the process of establishing the predetermined  $V_f(X)$  is not unlike that which is done when calibrating equipment that measures one specific physical attribute and correlates it to another, e.g. volts to pressure. The predetermined  $V_f(X)$  is therefore also called a 'calibration curve'.

# 3. Main project goals and findings

This project has been supported by Miljøstyrelsen for a total budget of 1.756.236 kr over approximately 1½ years starting on the 1<sup>st</sup> of December 2011. The primary goal of the present project is to demonstrate at least a 5% improved performance of an ammonia assisted SCR system either on size or NO<sub>x</sub> reduction capability by developing and implementing an accurate level sensing algorithm to optimize the use of the ammonia on a vehicle. The benchmark is a level sensing method based on start-up times for both Main Unit (MU) and Startup Unit (SU). The uncertainty of this method depends on the actual fill level, and is, at best, between +/- 15%. To fulfill the legislative requirements for OBD (on-board diagnostics) we must give the expected total ammonia mass in the Ammonia Storage and Dosing System (ASDS), to allow for driver warning before the system becomes depleted. Hence, any uncertainty on the level sensing directly translates into a demand for added ammonia. In principle, this means that the system must contain a spare of 15% additional ammonia (we do not account for the negative uncertainty, as it is irrelevant), which increases weight and size. If the 15% can be decreased, it will mean a smaller size and, additionally, more NO<sub>x</sub> conversion pr unit mass.

Below, a summary of the main results we have obtained in this work is given. Throughout the report results will be shown that demonstrate these findings. The results are so promising that we are currently implementing a complete level sensing strategy on our ASDS-2012 prototype system, and we are continuously working to improve the algorithms behind the method.

With the work done in this project we have:

- 1. Increased the accuracy of the level sensing from +/- 15% on the absolute amount of NH3 to +/- 5% on the absolute amount of NH<sub>3</sub>. Thereby the total improvement in accuracy is approx. 66% in comparison to the starting point. This furthermore decreases the mass of NH<sub>3</sub> needed by 10% that reduces the size and increases NO<sub>X</sub> conversion pr unit mass (Main goal 5%)
- 2. Decreased the potential power consumption by up to at least 60% (additional benefit) This is a crucial parameter in improving the competiveness and the ecological fingerprint of our system, as it directly decreases the total CO<sub>2</sub> penalty.
- 3. Developed a complete level sensing strategy for the ASDS for on-board diagnostics (OBD)

#### 3.1 The duality of level sensing: power and weight reduction

The ASDS consists of two principal units: the main-unit (MU) and the startup-unit (SU) which are filled with AdAmmine. In addition to the units a dosing device (CVD-AFM) delivers the user fed setpoint  $NH_3$ . The MU contains the bulk  $NH_3$ , while the SU only has a limited capacity of  $NH_3$ , as its main purpose is to allow for fast system functionality and low energy cost. To optimize power consumption, the SU is the primary unit to dose from, as the MU takes significant time to heat up, which means a larger energy requirement before it is even ready to dose. Nevertheless, the limited capacity of the SU requires that it must be refilled from time to time before it runs out of  $NH_3$  which means it will be unable to reduce  $NO_X$ . In the ASDS this is done by heating the MU to a pressure above the SU, which causes  $NH_3$  to be redistributed (absorbed) into the SU thereby refilling it. As driving cycles are per definition not known a-priori (you do not program your car with your intended course before departing!), some driving cycles will end abruptly, and, without the MU reaching a pressure higher than the SU. Nevertheless, some NH3 will still be transferred from MU to SU during the cool-down period as the SU looses more energy to the surroundings than the MU, but the amount will be low. Without a fill level algorithm on the SU, the fill level is only known in the two extremes: i.e. when it is empty and needs to be refilled since it is unable to maintain pressure, or when it has been completely refilled as the pressure never drops towards equilibrium again. Refilling the last few grams of NH3 is by far the most time consuming task, and not necessary from the perspective of the system functionality. Therefore, it is also the task that requires most energy pr. gram NH3 refilled. By knowing the fill level of the SU at all times, we may know when the unit has been refilled and when we do not require the energy-heavy MU to be forced into operation again, until the next time refilling is required. Hence, knowledge of the fill level is not only important for reduction in the total system weight, but also in reducing the energy cost.

### 4. Dependency of model parameters and filling level X for 'ideal' cartridges

As mentioned previously, the gas free-volume depends on the filling level X of the AdAmmine. An analytical expression can be derived by setting up a volume balance for the system, since the total volume of the cartridge is made up of gas free-volume (V<sub>f</sub>) and solid volume (Vs) that consists of both saturated and unsaturated AdAmmine:

$$V_0 = V_f + V_s \tag{1}$$

In the ideal cartridge, the first simple assumption is to assume the total cartridge volume is initially filled up by saturated AdAmmine. Secondly, the solid volume consists of both saturated and unsaturated AdAmmine:

$$V_0 = V_f + \frac{m_{sat}}{\rho_{sat}} + \frac{m_{unsat}}{\rho_{unsat}}$$
(2)

The masses of saturated and unsaturated AdAmmine may also be expressed by the amount of moles and hence the saturation degree (or filling level), X since:

$$X = \frac{n_{sat}}{n_{unsat} + n_{sat}} = \frac{n_{sat}}{n_0} \Longrightarrow m_{sat} = n_{sat} M_{sat} = M_{sat} n_0 X \text{ and}$$

$$m_{unsat} = n_{unsat} M_{unsat} = M_{unsat} n_0 (1 - X)$$
(3)

Which upon insertion into eq. (2) gives:

 $n_0$ 

$$V_0 = V_f + n_0 \left(\frac{M_{sat}X}{\rho_{sat}} + \frac{M_{unsat}(1-X)}{\rho_{unsat}}\right)$$

(4)

Since the initial amount of AdAmmine is given from the initial mass of AdAmmine (or vice verse), while in the first assumption the cartridge volume was made up of pure saturated AdAmmine, eq. (4) becomes:

$$V_{0} = V_{f} + \frac{V_{0}\rho_{sat}}{M_{sat}} \left( \frac{M_{sat}X}{\rho_{sat}} + \frac{M_{unsat}(1-X)}{\rho_{unsat}} \right) = V_{f} + V_{0} \left( X + \frac{M_{unsat}\rho_{sat}}{M_{sat}\rho_{unsat}} (1-X) \right)$$
(5)

Eq. (5) can be solved for  $V_f$  to give the relation between  $V_f$  and X:

$$V_f = \left(\frac{M_{unsat}\rho_{sat}}{M_{sat}\rho_{unsat}} - 1\right) V_0 X - V_0 \left(\frac{M_{unsat}\rho_{sat}}{M_{sat}\rho_{unsat}} - 1\right)$$
(6)

It can be seen from eq. (6) that  $V_f$  should change linearly with X and should scale with the size of the cartridge  $V_0$ .

### 5. Dependency of model parameters and filling level X for 'real' cartridges

On a real cartridge, however, the total volume is not initially made up of only saturated AdAmmine. Instead the initial amount of AdAmmine is again made out of saturated and unsaturated parts:

$$n_0 = n_{sat,0} + n_{unsat,0}$$

The initial density  $\rho_0$  is known from production of the cartridge:

$$\rho_0 = \frac{m_{sat,0} + m_{unsat,0}}{V_0} = \frac{n_{sat,0}M_{sat} + n_{unsat,0}M_{unsat}}{V_0}$$
(8)

The initial saturation  $X_0$  is also known from production:

$$X_0 = \frac{n_{sat,0}}{n_0} \tag{9}$$

(7)

Hence eq. (7) becomes:

$$n_{0} = \frac{\overline{\rho_{0}V_{0} - n_{0}X_{0}M_{sat}}}{M_{unsat}} + n_{0}X_{0}$$
(10)

Which can be solved to give  $n_0$  as a function of the initial saturation and density, as well as cartridge volume:

$$n_{0} = \frac{\rho_{0}V_{0}}{M_{unsat}\left(1 - X_{0}\right) - M_{sat}X_{0}}$$
(11)

Inserting eq. (11) in eq. (4) gives:

$$V_{0} = V_{f} + \frac{\rho_{0}V_{0}}{M_{unsat}(1 - X_{0}) - M_{sat}X_{0}} \left(\frac{X}{\rho_{sat}M_{sat}} + \frac{(1 - X)}{\rho_{unsat}M_{unsat}}\right)$$
(12)

Which may be solved for  $V_f$  as previously to give:

$$V_{f} = \frac{-V_{0} \left(M_{sat} \rho_{unsat} - M_{unsat} \rho_{sat}\right) \rho_{0}}{\rho_{sat} \rho_{unsat} \left(M_{sat} X_{0} + M_{unsat} \left(1 - X_{0}\right)\right)} X + \frac{V_{0} \rho_{sat} \left(M_{sat} \rho_{unsat} X_{0} - M_{unsat} \left(\rho_{0} - \rho_{unsat} \left(1 - X_{0}\right)\right)\right)}{\rho_{sat} \rho_{unsat} \left(M_{sat} X_{0} + M_{unsat} \left(1 - X_{0}\right)\right)}$$

$$(13)$$

Eq. (13) reduces to eq. (6) if  $X_0 = 1$  and  $\rho_0 = \rho_{sat}$ , and again shows that  $V_f$  scales with the cartridge size  $V_0$ . More importantly, however, it shows that while  $V_f$  depends linearly on X, with coefficients that depend on the materials properties of AdAmmine, it *also* depends on production parameters  $\rho_0$  and  $X_0$ . For prototype production of cartridges it is to be expected that  $\rho_0$  and  $X_0$  varies from cartridge to cartridge, and as a natural consequence the correlation  $V_f(X)$  is not unique since it does not only depend on the material properties and cartridge size. Only when a series production is established, we can expect  $\rho_0$  and  $X_0$  to be constant from cartridge to cartridge, and therefore the correlation  $V_f(X)$  to be unique for a given cartridge type. In practice, however, an empirically

established expression for  $V_f(X)$  will be used that is based on the measurement of  $V_f(X)$  for a multitude of cartridges of the same type to reduce the scattering of data as much as possible.

# 6. Fill level algorithms 1 and 2

#### 6.1 The fill level algorithm 1 (FLA 1)

In fill level algorithm 1 (hereafter called FLA 1), the pressure change due to dosing is logged, and processed by fitting a model equation of the dynamic pressure response at a given flow rate to the experimental data. The two model parameters are the gas free-volume ( $V_f$ ) and the desorption rate ( $m_{kin}$ ). As mentioned previously, the gas free-volume changes with the filling level as an increasing porosity builds up when gas is desorbed from the solid matrix. Therefore, by plotting the calculated gas free-volume to the actual filling level, a correlation can be obtained, which is universal to the specific type of cartridge as it depends only on the cartridge geometry and the various physical parameters of the saturated and unsaturated AdAmmine.

#### 6.1.1 FLA 1 limitations

The theoretical framework is given in the patent application, and will therefore not be discussed further here. Nevertheless the premises of FLA 1 are interesting as they set a limitation to the cartridge size and -equally interesting - dosing hardware for which FLA 1 is useful. The assumptions for FLA 1 are listed below and are:

- 1. Low influence of thermal inertia
- 2. Pseudo equilibrium in the sample interval  $t \in [t_1, t_2]$ :  $\begin{cases} P_{eq} = \max(P) \\ T = T_{eq} \end{cases}$
- 3. Fill level does not change over the sample time

Assumption 3 is almost always fulfilled as the capacity of both MU and SU are significant in comparison to what can be dosed for even very large sample intervals. Assumptions 1 and 2, however, are not since thermal fluctuations are bound to happen as the controller tries to maintain set-point pressure. The frequency of these oscillations depends on the heat capacity of the system: for a high heat capacity, the system will respond slowly in terms of changing temperature, whereas for a low heat capacity changes will occur much faster. Hence, for large cartridges (i.e. MU) where the heat capacity is significant assumption 1 and 2 is more likely to hold than for smaller cartridges (i.e. SU) where the smaller heat capacity also makes the system more likely to change its temperature over the sample interval. Furthermore, as the method is statistical by fitting data to a model, it is known that less data will give a less accurate representation with higher uncertainty. Nevertheless, as discussed above, too long sample intervals will defy assumptions 1 and 2, so this means an upper limit exists, which - depending on cartridge size - is somewhere between a few seconds and 1 minute. This shows that for SU sized cartridges the FLA 1 is not likely to yield any useful information, whereas for MU sized cartridges the FLA 1 should perform well.

#### 6.1.2 Effect of refilling SU on fill level estimation of MU

An SU refilling will act as a second 'drain' term, additional to the flow out of the cartridge in the equations for FLA 1. This drain will be SU fill level dependent, and it will be impossible to distinguish between a lower desorption rate from the MU and a constant desorption *coupled with* absorption in SU. Figure 1 shows results of a simulated cartridge behavior using Amminex model v3 on which level sensing by FLA 1 was carried out on an MU while the SU is refilling.



FIGURE 1: RESULTS OF FILL LEVEL ESTIMATION USING FLA 1 ON DATA GENERATED BY SIMULATION AT DIFFERENT SU FILL LEVELS SHOWN AS A CONTOUR PLOT (A), WHILE THE LINES (DOTTED, AND BROKEN) DEPICTED ON (A) ARE REPLOTTED ON (B) SHOWING THE DIFFERENT FUNCTIONALITY OF 'VF' WHEN THE SU IS REFILLING COMPARED WITH A HIGH RATE, COMPARED TO WHEN TO WHEN IT IS NOT (CORRESPONDING TO LOW AND HIGH SU FILL LEVELS, RESPECTIVELY.)

Clearly, the SU fill level plays a major role in determining the fill level of the MU. In fact, for SU fill levels below 90 %, the linearity otherwise observed at higher SU fill level (Figure 1(a-b) dotted line) becomes very poor (Figure 1(a-b), broken line). This means that for doing MU fill level detection, the SU has to be either full, or disengaged in some other way, for example by using a shut-off valve to actively cut off the SU from the MU during collection of input data for the FLA 1.

Simulated data were used instead of experimental data for the simple reason that these are more readily available (free, and much less time consuming) while at the same time being fairly quantitative, though this was not the primary concern. Rather it was the objective of this study to gain qualitative insight into how MU fill level detection was influenced by an SU refilling.

#### 6.1.3 Effect of ambient temperature

During the cartridge lifetime (here defined as the time until the cartridge has to be refilled, and assumed to be approximately 1 service interval), the ambient temperature when driving may vary markedly as seasons change. It is therefore a natural concern to have whether or not FLA 1 will perform equally well for low and high ambient temperature conditions. In the FLA 1 model, the temperature is assumed to be equal to the equilibrium temperature at the given cartridge pressure. A very low ambient temperature may change the overall temperature gradient inside the cartridge, which may also affect average temperature of the salt. Nevertheless, as the cartridges are externally heated, as well as insulated, the expected influence of the ambient temperature is low.

Simulations were carried out using Amminex model v3 in which the ambient temperature was changed from  $-15^{\circ}$ C to  $55^{\circ}$ C. Fill level algorithm 1 was then run over the generated level events. Figure 2 shows the calculated gas free-volume for a multitude of filling levels (10 to 100%) and ambient temperatures ( $-15^{\circ}$ C to  $55^{\circ}$ C).



FIGURE 2: INFLUENCE OF AMBIENT TEMPERATURE ON THE FLA 1 FOR MU TYPE CARTRIDGES (A: CONTOUR PLOT, B: 2D SCATTER PLOT). THE INSULATION OF THE MU PREVENTS A GREAT DEAL OF THE EFFECT ON THE CALCULATION OF THE FREE VOLUME 'VF', WHERE THE INFLUENCE IS MAINLY SEEN ABOVE 35 DEG C. THE VALUES SHOWN ARE CALCULATED AS THE MEAN OVER 10 CONSECUTIVE LEVEL EVENTS. THE EFFECT ON 'VF' IN THE REGION MOSTLY AFFECTED DEPENDS ON THE FILL LEVEL, AND IS BETWEEN 7-18%.

From Figure 2 (a-b) it can be concluded that the calculated gas free-volume does not depend significantly on the ambient temperature. There is a slight trend tending towards a smaller 'Vf' with decreasing temperature (a), but as it can be seen from (b) this variation is small. Whereas it was to be expected that the MU would not experience a high variation with ambient temperature due to its insulation, the SU, however, being non-insulated, might experience a higher influence of the ambient temperature.

#### 6.2 The fill level algorithm 2 (FLA 2)

Fill level algorithm 2 was developed specifically for a CVD-AFM type dosing hardware. It utilizes the dynamic of the pressure response when filling the CVD-AFM volume from an AdAmmine containing cartridge, to estimate the gas free-volume (as for the FLA 1) which again allows determination of the filling level X. The method is currently being evaluated for purposes of patent application, and will therefore not be described in detail here. The main principle is similar to FLA1 to some extent in that we measure the dynamic response of the pressure when stimulated mechanically by opening a valve, and apply an algorithm (model) that allows us to determine the gas free-volume, which relates directly to the fill level of the unit. The time which the measurement takes is significantly shorter (within 1 second) than FLA1 and without the NH3 cost of the FLA1. However, the method performs only well for smaller cartridges, such as the startup-unit (SU), because of the large difference in volume between CVD and SU

### 7. Results of FLA 1

### 7.1 FLA 1 for 3 MU cartridges using an MFC as dosing hardware on an NEDC driving cycle

Using an MFC is the best way to fulfill the assumption of pseudo equilibrium, since dosing occurs continuously without the many disturbances to pressure, which may be found in a CVD-AFM that may result in causing the solid-gas pseudo equilibrium assumption to fail. Consequently testing FLA 1 on MUs with an MFC is the best way of verifying the concept of the FLA 1. Figure 3 shows the input data used in determining the gas free-volume from FLA 1.



FIGURE 3: INPUT DATA (PRESSURE, RED CURVE AND FLOW, BLACK CURVE) TO THE FLA 1 HIGHLIGHTED WITH A LIGHT BLUE OVERLAY. A 50 SECOND MOVING INTERVAL IS SWEPT ACROSS THE HIGHLIGHTED DATA FROM START TO FINISH, AND THE AVERAGE OF THE DETERMINED GAS FREE-VOLUME IS OUTPUTTED.

The output of the FLA 1 is generated by running the algorithm over the entire highlighted data in a 50 second sweeping interval, and taking the average of all calculated gas free-volumes. Figure 4 shows the result of running FLA 1 over the data for different filling levels (measured by weighing), and for 3 cartridges of the same type (MU-02500).



FIGURE 4: AVERAGED OUTPUT OF THE FLA 1 RUN OVER AN NEDC AT SEVERAL FILLING LEVELS FOR 3 DIFFERENT, BUT SAME TYPE, CARTRIDGES (MU-02500). WITH THE EXCEPTION OF COMPLETELY FULL CARTRIDGES, THE REST OF THE DATA NEATLY FALLS ONTO A STRAIGHT LINE, SHOWING LITTLE CARTRIDGE-TO-CARTRIDGE DEVIATION. MEASUREMENTS WERE CARRIED OUT AT 200C.

The results clearly demonstrate that FLA 1 provides a model response 'V<sub>f</sub>' that is linear with the filling level X, as predicted by eq. (13), and furthermore that the cartridge-to-cartridge reproducibility is high, as witnessed by the low scattering of the model output for the 3 cartridges shown on Figure 4.

### 7.2 FLA 1 on MU cartridges using stepped flow-dosing with an MFC as dosing hardware

The randomness of a real world driving cycle introduces some noise into the estimation of the gas free-volume. To improve this, stepped flow dosing is proposed. During the stepped flow the dosing is effectively halted, and a flow-profile that introduces a step from 0 to a fixed maximum (e.g. 10 mg/s) flow-rate for a certain time (e.g. 30 seconds) then returns to 0 again is demanded of the dosing unit. This predetermined flow-profile thereby increases reproducibility and comparability of the pressure-response curves needed as input for FLA 1. Figure 5 shows an example of how the pressure responds to a step-change in flow-rate. First, the pressure (red curve) begins to drop as the flow is stepped from 0 to 10 mg/s. Then, as the flow steps from 10 mg/s down to 0 again, the pressure begins to rise.



FIGURE 5: PRESSURE RESPONSE (RED CURVE) TO STEP CHANGE IN FLOW-RATE (BLUE CURVE). THE PRESSURE IMMEDIATELY DECREASES AS GAS IS DRAWN OUT OF THE ADAMMINE CARTRIDGE, BUT BEGINS TO INCREASE AGAIN AS A COMBINATION OF BOTH DESORPTION (SHORT TIME SCALE) AND TEMPERATURE INCREASE (LONG TIME SCALE). THE SAMPLE RATE HERE WAS 2 HZ.

The rate of the pressure-increase on the short time-scale is determined by the desorption rate since the previous pressure drop causes ammonia to desorb, which cools the reaction front and creates a temperature gradient creating the driving force for a heat flux towards the reaction surface and causes additional desorption. On the longer time-scale, thermal fluctuations induced by the controller, as it regulates the pressure, can cause the pressure to either increase or decrease, depending on which part of the oscillation cycle the stepped flow-change was introduced.

The results of running FLA 1 over stepped flow-changes such as the one shown on Figure 5 can be seen in Figure 6. As for the NEDC generated data, the model output, the gas free-volume, increases linearly with decreasing fill level, as also expected theoretically from eq. (13).



FIGURE 6: FLA 1 MODEL FIT TO DATA GENERATED BY STEP-CHANGING THE FLOW-RATE FROM 0 TO 10 MG/S FOR 30 SECONDS, AFTER WHICH THE FLOW-RATE WAS SET TO ZERO. AS FOR THE NEDC GENERATED INPUTS THE TREND IS LINEAR, WITH THE EXCEPTION OF THE 100% FILL LEVEL, WHICH SEEMS CONSEQUENTLY TO YIELD MARKEDLY SMALLER MODEL OUTPUT.

Not all step sizes and lengths give equally good results. In fact, too long or too short sustained flow gives poor model fits. The reason is a violation of the pseudo equilibrium assumption for the longer sustained flow-rates, and too poor statistics for the shorter ones. Figure 7 shows that the optimal flow-rate for the step changes has been found to be approximately 10 mg/s for 30 seconds for the 3.6 L MU cartridges. Other values may be found for different size cartridges.



FIGURE 7: LINEARY OF MODEL DETERMINED GAS FREE-VOLUME WITH FILL LEVEL, AS A FUNCTION OF THE TIME INTERVAL OF THE SUSTAINED FLOW (10 MG/S) DURING FLOW STEPPING (ALSO CALLED 'PULSE DOSING TIME'). FOR SHORT TIME INTERVALS, THE MODEL OUTPUT IS NOT LINEAR WITH THE FILL LEVEL. IT APPEARS THAT AN OPTIMAL VALUE OF APPROXIMATELY 30 SECONDS SUSTAINED FLOW EXIST FOR THIS PARTICULAR CARTRIDGE SIZE.

#### 7.3 FLA 1 on MU cartridges using CVD-AFM as dosing hardware

Unlike the mass-flow controller, which delivers a continuous and regulated stream of ammonia when requested, the CVD-AFM delivers short bursts of ammonia, in between trying to regulate its internal volume at a set-point pressure, by opening its inlet valve to the AdAmmine cartridge. The concept provides high accuracy dosing, but at the loss of a continuous flow.

As this may be thought to influence the FLA 1 output, since the assumptions may fall, the use of a CVD-AFM was also tested for MU sized cartridges (MU-02506) of approx. 3.6 L. Figure 8 shows the result of the FLA 1 model output (gas free-volume) by running the FLA 1 over NEDC generated input (flow and pressure). It is clear that the results are scattered and no clear trend can be seen.



FIGURE 8: FLA 1 OUTPUT ON NEDC GENERATED DATA FOR 6 MU-02506 CARTRIDGES USING A CVD-AFM AS DOSING HARDWARE. NO CLEAR TREND FOR VF(X) CAN BE SEEN AND THE RESULTS APPEAR HIGHLY SCATTERED.

### 7.4 FLA 1 on MU cartridges using stepped flow-dosing with a CVD-AFM as dosing hardware

Figure 9 shows the pressure fluctuations during dosing and clearly demonstrates how the pressure response becomes highly disturbed from the many refilling events of the CVD-AFM volume, which can be seen as a way of creating 'noise' on the pressure signal. The noise cannot easily be filtered out, unless a controlled and fixed flow profile is used.



FIGURE 9: PRESSURE RESPONSE INSIDE A MU CARTRIDGE DURING DOSING WITH A CVD-AFM. THE SUDDEN DROPS IN PRESSURE CORRESPOND TO FILLING THE CVD-AFM VOLUME. DOSING AMMONIA OUT IS NOT SEEN, AS THE INLET VALVE (SITUATED BETWEEN THE ADAMMINE CARTRIDGE AND THE CVD-AFM) IS KEPT CLOSED WHEN DOSING FROM THE CVD-AFM.

By using a controlled stepped flow-dosing profile it is possible to smooth out the noise, at least to some degree. Figure 10 shows the pressure response due to dosing of 10 mg/s for 30 seconds. The measured pressure inside the MU (red curve) is as expected highly disturbed. Considering the pressure evolution during a flow step with an MFC as the benchmark (c.f. Figure 5), several filters have been tried out. Using a moving average is clearly not a good representation of how the pressure response would have looked had an MFC been used to generate the step. Instead, it appears that using the maximum pressure and neglecting the pressure surges that occur when the CVD-AFM refills, gives the best continuous pressure decrease and the least 'noisy' signal.



FIGURE 10: PRESSURE RESPONSE WITH A CVD-AFM THAT OCCURS WHEN A STEP IN THE FLOW IS INTRODUCED GOING FROM 0 TO 10 MG/S, KEEPING THAT FLOW FOR 30 SECONDS, AND THEN STOPPING THE FLOW AGAIN GOING BACK TO 0. THE PRESSURE IS MEASURED INSIDE THE MU. THE PRESSURE IS HIGHLY DISTURBED FROM THE CONTINUOUS REFILLING OF THE MU (LIGHT BLUE LINE). RUNNING DIFFERENT FILTERS (BLUE, RED AND BLACK LINES) OVER THE DATA CAN BE SEEN TO YIELD DIFFERENT OUTCOME. THE MOST COMPARABLE TO THE PRESSURE RESPONSE THAT OCCURS WHEN USING AN MFC IS THAT WHICH IS OBTAINED WHEN THE MAXIMUM OF THE PRESSURE IS USED, BY NEGLECTING THE SURGE IN THE PRESSURE AS THE CVD-AFM REFILLS AND INTERPOLATING THE MISSING VALUES.

The input data generated using steps of 10 mg/s for 30 seconds with a CVD-AFM dosing unit was run through FLA 1. Figure 11 shows the results of running the different data filters over the input pressure response. It is clear, that using the maximum pressures by finding the peaks and interpolating the pressure in between yield the best linearity of  $V_f(X)$  (blue line). In comparison, and as expected, the raw data is simply too 'noisy' and disturbs the model result of  $V_f(X)$ .



FIGURE 11: FLA 1 MODEL OUTPUT PARAMETER (GAS FREE-VOLUME) AT VARIOUS FILLING LEVELS AND WITH DIFFERENT FILTERS (LIGHT BLUE: RAW DATA, RED: MOVING AVERAGE SINGLE PASS, BLACK: MOVING AVERAGE DOUBLE PASS, AND BLUE: MAXIMUM PRESSURE WITH INTERPOLATED PRESSURE IN BETWEEN) FOR STEP DOSING USING A CVD-AFM. THE DIFFERENT SYMBOLS AT EACH FILLING LEVEL REPRESENT DIFFERENT STEPS IN THE FLOW (ON AVERAGE 10 STEPS WERE PERFORMED AT EACH FILL LEVEL). CLEARLY, THE BEST LINEARITY IS OBTAINED WHEN APPLYING THE 'MAXIMUM VALUES INTERPOLATION' FILTER (BLUE LINE). NOT SURPRISINGLY, THE RAW DATA (LIGHT BLUE) AND THE MOVING AVERAGE FILTERS (RED AND BLACK LINES) FAIL TO REDUCE THE SCATTERING.

There are no guarantees, however, that using the maximum pressure spikes will completely eliminate all scattering. Regardless of what data filter is used, the assumption of pseudo equilibrium will fall with a CVD-AFM. Even with the best filter ('maximum value interpolation' filter, Figure 11, blue curve), the model output of 10 steps still appears scattered, in particular at low filling levels. In fact, the measured maxima may be somewhat random in nature as they not only depend on the actual pressure inside the MU, but also on the control of the CVD-AFM, as it tries to keep its pressure at its set-point. This becomes evident when looking at the result of running the FLA 1 over data generated on several MU cartridges. Figure 12 shows that the cartridge-to-cartridge reproducibly is poor, even when using the best filter as shown on Figure 11. Unfortunately, the behavior is inherent to the CVD-AFM and it is unlikely that FLA 1 will provide usable results for cartridges when the dosing concept is similar to that of the CVD-AFM.



FIGURE 12: CARTRIDGE TO CARTRIDGE REPRODUCIBILITY FOR STEP DOSING (10 MG/S FOR 30 SECONDS) USING A CVD-AFM AS DOSING UNIT, WHERE THE INPUT DATA RECORDED HAS BEEN TREATED WITH THE 'MAXIMUM VALUES INTERPOLATION' FILTER AS DESCRIBED ELSEWHERE. THE RESULTS ARE DISCOURAGING AS THE DATA IS SCATTERED FROM CARTRIDGE TO CARTRIDGE. THE REASON MAY BE AN INHERENT PROBLEM OF THE CVD-AFM WHICH CAUSES DISTURBANCE OF THE EQUILIBRIUM THUS INVALIDATING THE PSEUDO-EQUILIBRIUM ASSUMPTION, REGARDLESS OF WHAT DATA FILTER IS USED.

### 8. Results of FLA 2

#### 8.1 FLA 2 on a 250 mL SU

Where the CVD-AFM was inhibiting the proper interpretation of results of obtained using FLA 1, the FLA 2 is specifically designed for exactly the CVD-AFM. Figure 13 shows the result of running FLA 2 over input data. The scattering of data appears low, while the linearity of the  $V_f(X)$  correlation is high.



FIGURE 13: RESULTS OF RUNNING THE FLA 2 OVER INPUT DATA (PRESSURE EVOLUTION WHEN FILLING THE CVD-AFM) GENERATED ON A 250 ML SU. MULTIPLE 'EVENTS' HAVE BEEN SHOWN (VARIOUS SYMBOLS). THE SCATTERING IS LOW, AND THE LINEARITY IS HIGH FOR VF(X).

#### 8.2 Cartridge to cartridge reproducibility

Figure 14 compares multiple cartridges analyzed with FLA 2. Considering that each of the SU prototypes is handmade, it is surprising to see that the cartridge-to-cartridge reproducibility is as high as is the case.



FIGURE 14: CARTRIDGE TO CARTRIDGE REPRODUCIBILITY OF FLA 2 OUTPUT (GAS FREE-VOLUME) FOR 3 CARTRIDGES OF THE SAME TYPE (250 ML). SURPRISINGLY, VF(X) APPEARS TO BE APPROXIMATELY IDENTICAL FOR ALL 3 CARTRIDGES. THIS IS SOMEWHAT IMPRESSIVE, WHEN CONSIDERING THAT THE SU PROTOTYPES ARE ALL HANDMADE.

#### 8.3 Accuracy of the FLA 2 on multiple SU

Determination of the fill level takes place by first establishing a universal, but cartridge design dependent (geometry, size, content), functionality  $V_f(X)$ . Using the data on Figure 14, the relation  $V_f(X)$  could be established by fitting the linear function  $V_f(X)=aX+b$ . Then, the prediction accuracy was estimated by calculating X from the estimated  $V_f$ , using this 'calibration curve'. Figure 15 shows the estimated fill level as a function of the actual fill level. The prediction line (solid black line) can be used to illustrate the deviation from perfect prediction. The two additional lines (broken black lines) illustrate the limit of 10% error on determining the mass relative to the total initial mass. The points on the figure are the calculated fill levels from the calibration curve using the gas free-volume determined by FLA 2. Good accuracy can be observed down to the minimum fill level of ~35%, well within the +/- 10% error margin.

Below 35% the algorithm has not been tested thoroughly. This means that below 35% the accuracy of the total system fill level becomes influenced by the mass of the STU at that point. For example, in a system of 3.2 kg NH<sub>3</sub> contained in two MUs with one 115 g STU, the STU makes up for less than 3.6% of the total NH<sub>3</sub> capacity. As the MUs then become depleted, the influence of not accurately knowing the STU fill level below 35% then becomes higher. However, when specifying the system capacity we do not include the NH<sub>3</sub> stored in the STU. This is because the MUs are the main storage tanks, which are also changed at each service interval (and replaced by new) whereas the STU will not be changed on the vehicle for its lifetime (unless it fails and has to be replaced). Hence, the accuracy on determining the total system capacity is given by the accuracy of determining the MU

fill level, which, by following the method given in section 10, provides a conservative estimate of the remaining  $NH_3$  accurate to within +/- 5%.

There is no requirement on the accuracy of the level sensing given by OBD requirements. In fact, the only requirement is that the driver be warned at certain points (i.e. at least 2400 km remaining, at least 800 km remaining etc.). This means, the warning should be set *before* these limits are reached. However, OEMs do not want to warn the driver prematurely. Hence, the requirement on accuracy comes from OEMs. Nevertheless, knowing the actual fill level of the STU is vital for power reduction and for the fill level strategy detailed in section 9, however the lower limit may be avoided by commencing refilling



FIGURE 15: ACCURACY OF THE FLA 2 ON 3 CARTRIDGES (SU-04201, APPROX. 250 ML VOLUME). THE DATA POINTS SHOW THE RESULT OF CALCULATING THE FILL LEVEL THROUGH THE FLA 2 DETERMINED GAS FREE-VOLUME WITH THE PREDETERMINED VF(X). THE SOLID LINE SHOW THE PERFECT PREDICTION, AND THE TWO BROKEN LINES SHOW THE ERROR MARGIN WHEN THE ESTIMATION HAS TO BE WITHIN 10% RELATIVE ERROR ON THE INITIAL AMMONIA MASS. MOST POINTS ARE EVEN WITHIN +/- 5% ACCURACY.

# 9. Energy savings with the FLA 2

With an accurate fill level detection on the SU, we are able to control the refilling through the thermal activation of the MU, to limit the number of times it is on and thereby reduce the total energy cost of the ASDS. To allow the demonstration of this we have set up a mathematical model, in which the saved energy has been calculated based on an entire service interval driving cycle (10.000 km) as it is near impossible to show in the laboratory due to massive time-consumption this would require. The 'service interval driving cycle' is a realistic 10.000 km driving scenario obtained from a Tier 1 supplier who has constructed this scenario based on direct OEM .With the benchmark fill level strategy short driving may result in the SU fill level not being known, with the MU being forced into operation at each driving cycle that requires significant amounts of energy. Figure 16 shows a comparison of the energy per mass of  $NH_3$  dosed saved in comparison to the existing level strategy. The 'lower' limits (X axis), denote the lowest fill level allowed before activating refilling (i.e. actively heating the MU).



FIGURE 16: THE ESTIMATED SAVED ENERGY (1-ENERGY REQ. WITH LEVEL SENSOR/ENERGY REQ. WITHOUT LEVEL SENSOR) FROM A 10.000 KM DRIVING SCENARIO AFTER IMPLEMENTING A LEVEL SENSOR. THE CALCULATIONS WERE PERFORMED USING THE MODEL DESCRIBED IN APPENDIX A AS RUNNING SUCH A LONG DRIVING SCENARIO IN THE LABORATORY IS NEAR IMPOSSIBLE IN TERMS OF TIME CONSUMPTION.

From Figure 16 we estimate a potential saving of up to 63% of the total energy consumption upon the full implementation of the FLA 2. This energy saving will translate into reduced fuel penalty and directly adds value *on top of* the already reduced size requirement due to the higher precision of the level sensor.

## 10.Amminex level sensing strategy

Based on the preceeding results, a level sensing method is proposed that is highly accurate (within 5% of the total NH<sub>3</sub>), and in addition, fulfills the requirements of the OBD. It is based on a simple mass-balance, by keeping track of the NH<sub>3</sub> that has been dosed out of the system. We have developed highly accurate leak detection algorithms capable of detecting micron sized holes on the pressure-side. Furthermore, we check the integrity of the dosing unit by verifying that it does not leak, and that the pressure sensor inside it is measuring correctly. Additionally, we can check the accuracy of the dosing unit through fill level algorithms on the SU (FLA 2), or by other means e.g. by placing a secondary pressure sensor to verify the primary pressure sensor in the dosing unit, by having two volumes in series etc that both measure the same dosed etc. Finally, we can detect whether or not a cartridge contains NH3 since the pressure response is unique to AdAmmine and if it has been changed to a cartridge of a different capacity. All combined, we can, within the accuracy of the dosing unit, determine the total capacity of the system. The method may not be as direct as having a floater inside a liquid tank, but it is both tamper proof and OBD'able.

With the suggested fill level strategy we can create a level sensor that is verified and accurate within 5% of the total mass. Hence, we can decrease the mass needed by 10% and thereby the main goal of increasing performance in terms of improving NO<sub>x</sub> reduction capabilities and/or reducing the system size by 5%, has been fulfilled.

# 11. Conclusions

From the experimental data it is clear that while FLA 1 performs well with an MFC dosing unit for MU sized cartridges, it fails to yield useable results when the MFC is replaced by a CVD-AFM dosing unit. The reason is a combination of 'noise' introduced on the input pressure-signal from the CVD-AFM dosing dynamics, and a continuous disturbance of the pseudo equilibrium which exists between gas and solid, thereby invalidating the primary assumptions of FLA 1. FLA 2 performs well for SU of size 250 mL and 500 mL. For the 250 mL cartridge, accuracy on the ammonia mass relative to the initial full mass was within +/- 10% over the measured range of filling levels. Theoretical analysis show that by increasing the cartridge size, the noise on the pressure signal will completely distort the calculation of the gas free-volume required for determination of the fill level. Indeed, for a 3.6 L cartridge the FLA 2 does not perform well with the current CVD-AFM hardware. Increasing the CVD-AFM volume, or increasing the pressure of the MU before performing the fill level event (or any combination of these) can theoretically increase the precision of the FLA 2 on such large cartridges.

We proposed a complete level sensing strategy that is composed of four main modules: direct integration of the dosed  $NH_3$  signal within +/- 5% accuracy), leak detection on the pressure side (SU and MU and inlet tubing) and dosing unit integrity checks (valve leak and p-sensor), cartridge change detection to verify the initial total NH3 system capacity and finally verification of the flow integration by an independent fill level determination through FLA 2 on the SU that takes place when SU is dosing without MU.

Finally we have been able to demonstrate that:

- 1. The accuracy of the level sensing has been increased to within that of the dosing unit (5%) that directly decreases the mass of  $NH_3$  needed by 10%, which in turn reduces the size and increases NOx conversion pr unit mass (Main goal 5%)
- 2. The potential power consumption can be reduced by at least 60% (additional benefit)

#### Improved system performance for automotive exchaust cleaning

The purpose of the project has been to develop a solution, that estimates the content of ammonia in the AdAmmine cartridges, in order to improve the system efficiency and the NOx reduction.

Formålet med projektet har været at udvikle en løsning, der med større præcision kan bestemme indholdet af ammoniak i AdAmmine beholderne, så systemet til NOx reduktion fungerer mere effektivt.



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